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THERMAL TREATMENT OF VARIOUS SAMPLES OF LOW-MOLECULAR-WEIGHT POLYETHYLENE – A BY-PRODUCT OF POLYETHYLENE PRODUCTION

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Abstract: A comparative thermal analysis was conducted on three industrial samples of low-molecular-weight polyethylene (LMWPE)—a by-product of polyethylene production—with the aim of determining optimal conditions for carbonization and subsequent activation. The study employed TGA/DSC methods (Ar, 10 °C/min) and laboratory-scale carbonization in a flow-through argon reactor, with gas sampling at specific temperature “windows” followed by GC analysis (TCD + FID). The results indicate that melting occurs in the range of approximately 30–150 °C with less than 1% mass loss; thermal degradation begins at 300–400 °C, with major decomposition occurring between 420–520 °C. The residual mass at 1000 °C was approximately 33% (LMWPE-1), 38% (LMWPE-2), and 53% (LMWPE-3), indicating differences in molecular architecture and suggesting LMWPE-3 as the preferred precursor in terms of carbon yield. Gas evolution trends showed a transition from C_3–C_{17} olefins/paraffins (300–520 °C) to dominant H_2 and CH_4 evolution at higher temperatures, accompanied by increased aromaticity of the solid residue. It is recommended to limit the upper carbonization temperature to ~500 °C to avoid melting and coalescence, and to employ the 750–820 °C range as the optimal “window” for high-temperature treatment relevant to subsequent alkaline activation.

Keywords: low-molecular-weight polyethylene (LMWPE), pyrolysis, TGA/DSC, carbonization, gas-phase products, carbon residue, activated carbons.

Introduction. The increasing volume of polymer waste and by-products from the petrochemical industry has intensified the demand for resource-efficient technologies that convert these streams into high value-added products [1–3]. One such by-product is low-molecular-weight polyethylene (LMWPE), a secondary output of polyethylene production. This material is characterized by low ash content, hydrophobicity, and enhanced chemical reactivity. LMWPE is considered a promising precursor for carbon materials used in water and gas purification. However, its thermal behavior is strongly dependent on its origin and molecular architecture, necessitating targeted investigation [4–6].

While the thermal degradation of polyolefins has been extensively studied using model samples of LDPE/HDPE, industrial LMWPE formed under real production conditions remains insufficiently explored. This issue is particularly relevant in the context of Uzbekistan, where LMWPE is consistently generated at major gas-chemical facilities and could serve as a local feedstock for the production of activated carbons [8–10]. The scientific and practical challenge lies in establishing the relationship between composition, thermal behavior, and carbon yield across various batches of LMWPE, thereby enabling the development of optimized carbonization and activation protocols [10–14].

The aim of this study is to comparatively assess the thermal behavior of three industrial LMWPE samples of different origins under pyrolysis in an inert atmosphere and to identify the temperature regimes that ensure the formation of a stable carbon framework with maximum yield. To achieve this, TGA/DSC analyses were conducted, along with laboratory-scale carbonization in a flow-through argon reactor, including the analysis of gas-phase products evolved across selected temperature intervals. Particular attention was paid to identifying the “upper” carbonization temperature that avoids melting and coalescence, as well as the high-temperature “window” relevant for subsequent alkaline activation.

The results obtained provide a methodological foundation for designing an energy-efficient process for converting LMWPE into carbon sorbents aimed at advanced treatment of petroleum refinery wastewater. Simultaneously, they offer practical criteria for feedstock selection based on thermal stability and expected carbon yield, which are essential for industrial-scale implementation and integration into a circular economy framework.

Experimental Section (Materials and Methods)

The objects of this study were three samples of low-molecular-weight polyethylene (LMWPE): LMWPE-1 and LMWPE-2 obtained from the Shurtan Gas Chemical Complex, and LMWPE-3 sourced from Uz-Kor Gas Chemical (Ustyurt Gas Chemical Complex). Prior to the experiments, the raw materials were cleaned of mechanical impurities, thoroughly washed, dried at 100–105 °C to constant weight, and, if necessary, fractionated. The thickness of the sample layer on the holder was limited to 5–10 mm.

Thermal treatment was carried out using a custom laboratory setup (Figure 1), comprising: an argon cylinder (1), pressure regulator (2), flowmeter (3), and an electrically heated reactor (4, 5). The sample was placed on a stainless-steel mesh (7), suspended on a reinforcement rod (6). Temperature was monitored using a thermocouple (10) connected to a KS-2 control unit (11). The evolved gases were transported through a gas line (9) to a gas analyzer (12).

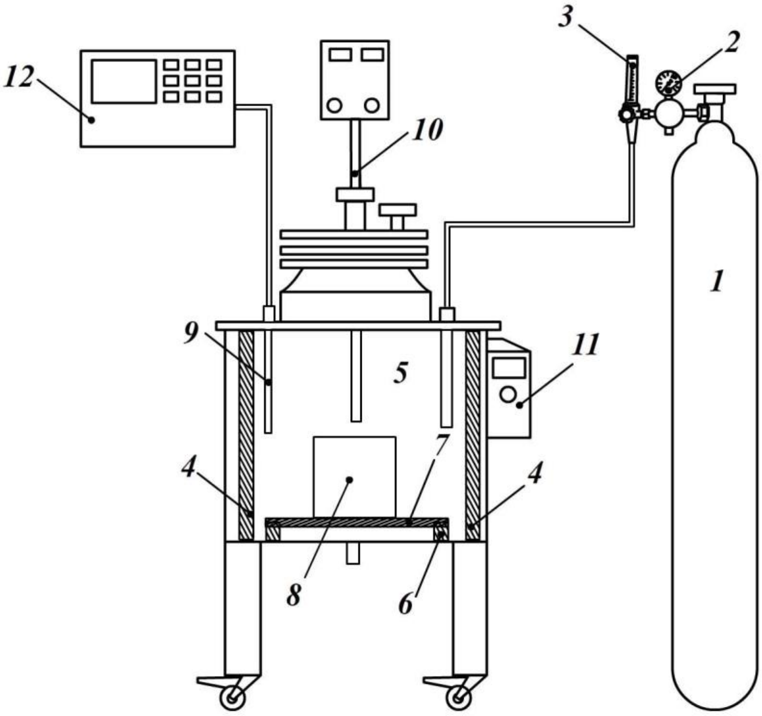

Figure 1. Laboratory setup for the carbonization and thermal activation process

Prior to heating, the system was purged with argon until the oxygen content registered zero on the gas analyzer. A stable flow of inert gas (typically 150–200 mL/min) was then maintained. The programmed heating was conducted at a rate of 10 °C/min following a uniform profile:

- Heating up to 120 °C with a hold time of 20–30 minutes (to remove moisture and trace volatiles);
- Heating up to 300 °C (initial transformations of macromolecular chains);
- Heating up to 500 °C with an isothermal hold of 60 minutes to form the primary carbon framework.

At the end of the hold, the samples were cooled to 80–100 °C under argon flow, removed, and weighed. The carbonizate yield was calculated as the ratio of the mass of the residual carbon to the mass of the dry sample. Each series of experiments was conducted in at least duplicate; the deviation in yield was limited to ≤3% (relative).

The composition of the evolved gases was monitored throughout the experiment: samples were collected through a heated line (~120 °C) into gas-impermeable bags at defined temperature windows ≤150, 150–300, 300–420, 420–520, and >520 °C (with a “blank” argon sample taken before each series). Gas analysis was performed by gas chromatography (TCD + FID), using separate columns for $H_2/CO/CH_4/CO_2$ and for C_1–C_5 hydrocarbons, with multipoint calibration against standard mixtures. Each gas sample was analyzed in duplicate, with acceptable deviations in volumetric component fractions limited to ≤5% (relative).

The obtained data (mass loss, carbonizate yield, and gas composition) were used to compare the thermal behavior of LMWPE-1, LMWPE-2, and LMWPE-3 and to select optimal regimes for subsequent processing.

Results and Discussion. The results of the thermal treatment of three industrial LMWPE samples in an inert atmosphere are presented. To compare the decomposition outcomes and carbon yield, Figure 1 illustrates the dependence of the residual mass on temperature after a 2-hour isothermal hold. The characteristic mass loss intervals and their relationship with the molecular architecture of the feedstock and potential carbonizability are discussed below.

The "residual mass vs. temperature" curves for the three LMWPE samples clearly demonstrate a two-stage thermal decomposition behavior in argon. Mass losses are minimal, not exceeding 1–3%, up to approximately 200 °C; this corresponds to the removal of adsorbed moisture and trace volatile components. Subsequent heating to 300–700 °C is accompanied by a rapid increase in mass loss, corresponding to the chemical degradation of the polyolefin matrix. At temperatures ≥ 700 °C, the rate of mass loss decreases, and the curves approach plateau regions indicative of the stabilization of the coke-like residue.

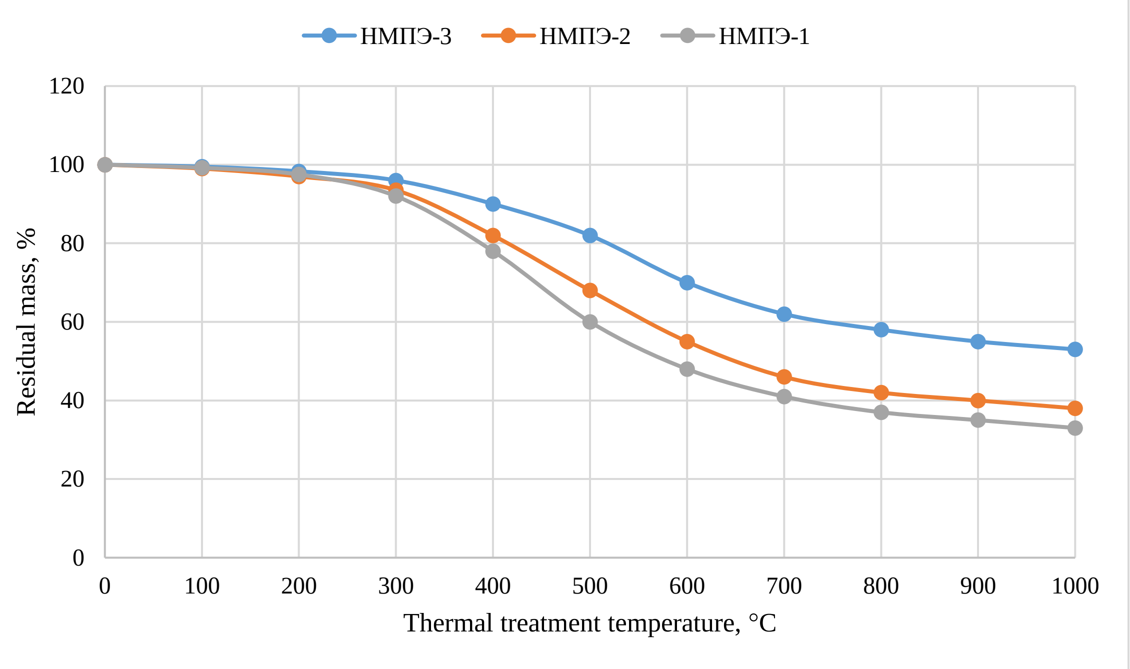

Figure 1. Mass change during thermal treatment of LMWPE samples as a function of temperature over a 2-hour period.

Throughout the entire temperature range, sample LMWPE-3 exhibited the highest thermal stability: at 300 °C, it retained 96% of its initial mass; at 400 °C, 90%; at 500 °C, 82%; at 700 °C, 62%; and at 1000 °C, the residue reached 53%. Corresponding values for LMWPE-2 were lower: 93.5% (300 °C), 82% (400 °C), 68% (500 °C), 46% (700 °C), and 38% (1000 °C). LMWPE-1 demonstrated the lowest stability with 92% (300 °C), 78% (400 °C), 60% (500 °C), 41% (700 °C), and 33% (1000 °C). The characteristic "thresholds" also varied:

the temperature corresponding to 20% mass loss was approximately 520 °C for LMWPE-3, ~440 °C for LMWPE-2, and ~400 °C for LMWPE-1. The interval of maximum mass loss rate occurred between 500 and 600 °C for all samples, with the magnitude of mass loss inversely related to initial thermal stability (LMWPE-1 > LMWPE-2 > LMWPE-3).

These differences in behavior are attributed to the molecular architecture of the feedstock. The higher residual mass of LMWPE-3 throughout the profile indicates a higher average molecular weight and degree of crystallinity, which increase the activation energy barrier for statistical β-scission, promoting early dehydrogenation, cyclization, and condensation of fragments leading to the formation of a thermally stable carbonaceous residue in the 450–650 °C range. In contrast, LMWPE-1 and partially LMWPE-2 contain a greater proportion of low-molecular-weight and branched fragments that are more susceptible to β-scission, yielding volatile C_1–C_{20} products; the fraction of resinous, condensable intermediates is lower, resulting in reduced yield of stable residue.

The observed trends establish technological guidelines. It is advisable to complete the primary carbonization stage near 500 °C: by this temperature, major depolymerization is finished for all samples, while excessive mass loss is avoided, preserving potential for controlled pore development during subsequent chemical activation. Among the precursors studied, LMWPE-3 is preferred for high-yield carbonization (53% residue at 1000 °C). LMWPE-1 and LMWPE-2 remain applicable but require harsher activation conditions or preliminary stabilization to compensate for lower carbon yield and accelerated mass loss between 300–500 °C.

Gas and solid phase analyses reveal a coherent evolution of pyrolysis products under argon with increasing temperature. Up to ~150 °C, trace amounts of moisture and low-boiling additives are released; chromatograms show primarily background argon with minor C_1–C_2 hydrocarbons. This phase corresponds to purely physical processes such as melting of crystallites and desorption of adsorbates, without significant chemical degradation of macromolecular chains.

Between 150–300 °C, initial chemical signs of decomposition appear: low concentrations of olefins (mainly C_2H_4, C_3H_6) and traces of CH_4 emerge in the gas phase, reflecting radical initiation at “weak” sites along the polyolefin chains and 1,5-hydrogen transfer. Gas evolution remains limited, with most volatiles retained in the condensed (liquid) fraction.

In the 300–420 °C interval, β-scission of C–C bonds dominates: the gas mixture is enriched with propylene/propane, butenes/butane, and ethylene, while the condensate accumulates C_5–C_{20} olefins and paraffins. Concurrently, isomerization and limited crosslinking increase chain unsaturation. This stage forms the bulk of the “liquid pyrolyzate,” whereas the fraction of stable solid residue remains small.

The main decomposition stage (420–520 °C) is marked by a sharp increase in total gas release; the proportion of H_2 and CH_4 rises, while significant amounts of C_2–C_4 hydrocarbons (ethylene/ethane, propylene/propane) persist. The emergence of hydrogen and an increasing H_2/CH_4 ratio indicate dehydrogenation and initial dehydrocyclization of olefin fragments. Polycyclic aromatic domains begin to form in the solid phase, serving as precursors to the coke-like residue.

Further heating to 520–700 °C drives secondary condensation and aromatization processes: the gas composition becomes dominated by H_2 and CH_4 with decreasing C_2 fractions, while condensed aromatic domains grow within the solid residue. This is accompanied by densification and partial graphitization of the carbon framework. Between 700–900 °C, the gas phase consists almost exclusively of H_2 and CH_4, reflecting ongoing dehydrogenation of the aromatic phase. The appearance of notable CO and CO_2 is atypical and likely indicates trace oxygen contamination in the system or oxygen-containing impurities in the feedstock.

The structural evolution of the solid product correlates with the residual mass curves: for LMWPE-3 (the most viscous and crystalline feedstock), stable condensed aromatic domains form more rapidly, slowing further degradation and ensuring the highest carbon yield (~53% at 1000 °C). For LMWPE-2 and especially LMWPE-1, a higher content of low-molecular-weight and branched fragments facilitates β-scission and hydrocarbon volatilization, resulting in greater gas-liquid yields and lower residual masses (~38% and 33%, respectively). Elemental analysis of the solid phase with increasing temperature reveals hydrogen depletion (decreasing H/C ratio), increased aromatization, and turbostratic ordering; intrinsic microporosity after pure pyrolysis is limited, so texture development is rationally achieved via subsequent chemical activation.

From an applied perspective, the gas evolution profile suggests an optimized processing strategy: primary carbonization should conclude around 500 °C (completion of main depolymerization with minimal excess char loss), and pore formation should be transferred to the alkaline activation “window” (~750–820 °C). LMWPE-3 is recommended as the base precursor for high-yield carbonization and subsequent activation. LMWPE-1 and LMWPE-2 are suitable but require harsher activation conditions or prior stabilization to compensate for lower carbon yield.

Conclusion. Comprehensive thermal analysis of three low-molecular-weight polyethylene (LMWPE) samples revealed a consistent pattern of their decomposition in an argon atmosphere, alongside significant differences in thermal stability and carbon residue yield. Analysis of the residual mass vs. temperature curves showed that LMWPE-3 provides the highest carbonized yield (~53% at 1000 °C), LMWPE-2 an intermediate yield (~38%), and LMWPE-1 the lowest (~33%). The enhanced mass retention of LMWPE-3 is attributed to its higher molecular order and crystallinity, which slow β-scission and facilitate early aromatic framework formation. The gaseous pyrolysis products evolve from trace C_1–C_2 hydrocarbons at low temperatures, through predominance of C_2–C_4 species at 300–420 °C, to mainly H_2 and CH_4 in the 420–900 °C range, reflecting the transition from depolymerization to dehydrogenation, cyclization, and condensation of aromatic fragments.

The obtained data establish technologically grounded processing conditions. The upper limit for primary carbonization is recommended near 500 °C (heating rate 10

°C/min, argon atmosphere), where the main depolymerization is complete without excessive carbon loss or melt coalescence risk. Development of advanced porosity is best shifted to the subsequent alkaline activation “window” (~750–820 °C). LMWPE-3 is recommended as the base precursor for carbon adsorbent production; LMWPE-1 and LMWPE-2 are suitable but require more severe activation conditions or preliminary stabilization to compensate for their lower carbon yield. These results provide a quantitative basis for designing a balanced and energy-efficient “carbonization–chemical activation” route and for predicting gas composition, which is critical for process safety, gas recovery/utilization, and environmental assessment.

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