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MODELING THE PYROLYSIS OF HIGH-DENSITY POLYETHYLENE USING THE REAXFF FORCE FIELD

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Abstract

The pyrolysis process of high-density polyethylene (HDPE) was investigated using molecular dynamics simulation with the reactive force field ReaxFF. The aim was to determine the qualitative and quantitative composition of the gaseous pyrolysis products and to identify the optimal temperature regimes that maximize the yield of valuable products while minimizing environmental impact. The simulations were carried out using the Materials Studio and LAMMPS software packages. An atomistic model of HDPE with added oxygen molecules was created, followed by geometry optimization, energy minimization, and equilibration in the NVT ensemble at 300 K. Pyrolysis was simulated at temperatures ranging from 600 °C to 2000 °C. The results suggest that 1000 °C is the optimal temperature for the thermal decomposition of HDPE. These findings confirm the effectiveness of ReaxFF in analyzing the chemical processes of pyrolysis and can be used in the development of polymer waste recycling technologies.

Key words: pyrolysis, high-density polyethylene, molecular dynamics, ReaxFF, gaseous products.

The problem of polymer waste disposal, particularly high-density polyethylene (HDPE), is highly relevant due to environmental threats and the continuously increasing use of polymer materials in industry, agriculture, construction, and daily life. Every year, millions of tons of plastic waste are generated worldwide, a significant portion of which is not further recycled. One of the promising methods of recycling is pyrolysis — the thermal decomposition of polymers in an oxygen-free environment [1]. This process enables the production of gaseous, liquid, and solid products [2], which can be used as secondary energy resources or raw materials for the chemical industry.

Modern approaches to studying pyrolysis are based on numerical modeling using molecular dynamics (MD) and reactive force fields such as ReaxFF. This allows for the analysis of molecular behavior at the atomistic level and the prediction of chemical reaction pathways with high accuracy and relatively low computational cost.

Preparation for MD modeling included constructing the initial atomistic configuration, consisting of ten polyethylene chains (C₁₀₀H₂₀₂) and 100 oxygen (O₂) molecules randomly placed in a cubic cell with a set density of 0.99 g/cm³. Random amorphous structures of PE–O₂ are presented in Figure 1. Model creation and preprocessing were carried out in the Materials Studio software environment [3]. To obtain the conformation of physical significance, geometric optimization, energy minimization and structural relaxation was performed for 5 ns using the canonical NVT ensemble at temperature 300 K. To enable large-scale reactive molecular dynamics simulations, the optimized structures were exported from Materials Studio and converted into the LAMMPS [4] data format using the msi2lammps interface. This included the generation of topology, atomic

coordinates, and force field assignments compatible with the ReaxFF potential. Pyrolysis modeling was conducted using LAMMPS with the ReaxFF reactive potential, which accounts for interactions among carbon, hydrogen, and oxygen atoms. The use of a reactive force field made it possible to dynamically track bond formation and breaking events, capturing the chemical evolution of the system in real time. Custom input

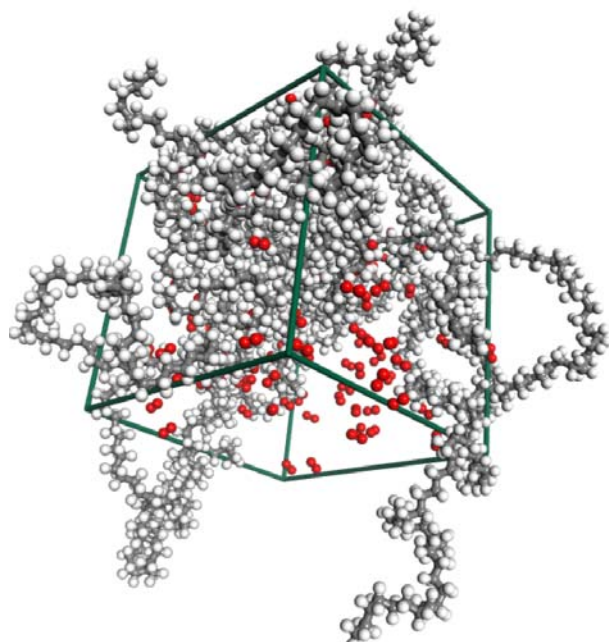


Figure 1. Random amorphous structures of PE–O₂ constructed in Materials Studio

scripts were then prepared to define simulation parameters such as ensemble settings, temperature control, and data output intervals. These scripts also specified the use of the reaxff module to monitor species evolution during the pyrolysis process, providing detailed insights into reaction pathways and product formation dynamics.

The calculations were performed at six temperatures: 600 °C, 800 °C, 1000 °C, 1400 °C, 1800 °C, and 2000 °C. Each simulation lasted 250 ps with a time step of 0.5 fs. To maintain a stable temperature in the system, a Nose–Hoover thermostat with a damping constant of 50 fs was used [5]. Data on molecule formation was recorded every 1000 steps and processed to construct time-dependent concentration profiles of the gaseous products.

Based on the simulation results, time and temperature-dependent profiles of the main gaseous products (H₂, CH₄, CO, C₂H₂, C₂H₄) were built. The analysis showed that after the initial phase (up to 60 ps), the molecular system enters a phase of active molecular decomposition. During this period, a sharp increase in

the amount of hydrogen, ethylene, and other compounds is observed, resulting from the breakdown of polymer chains and subsequent reactions. A comparison of the results at different temperatures revealed that the highest hydrogen yield occurs at 1800 °C and 2000 °C, while the optimal compromise between energy consumption and product quality is achieved at 1000 °C.

An increase in temperature beyond this point leads to a decrease in the amount of methane and carbon monoxide, which can be attributed to their further decomposition and participation in secondary reactions. At 2000 °C, the yield of carbon monoxide (CO) drops substantially—by about 79% relative to 1000 °C, while at 1800 °C it decreases by approximately 37% compared to 1000 °C, indicating a clear inverse relationship between temperature and CO production at higher thermal conditions. The amount of methane (CH₄) also shows a slight decrease, suggesting the presence of active secondary reactions. In contrast, no significant temperature-dependent trend was observed in the yield of ethylene (C₂H₄). At 600 °C and 800 °C, no significant degradation of the polyethylene matrix was observed, which is explained by the high thermal stability of HDPE and insufficient energy to activate chemical reactions within the given simulation timescale. These temperatures proved ineffectiveness for generating gaseous products over the 250 ps simulation period.

In result, the application of molecular dynamics modeling with the ReaxFF force field enables a highly detailed study of the pyrolysis processes of high-density polyethylene. It was established that the most optimal temperature regime is 1000 °C, as it provides the most favorable results in terms of product yield - such as H₂, CH₄, C₂H₄, and CO - while maintaining moderate energy consumption and limiting the formation of harmful byproducts compared to other temperature regimes. The obtained results open prospects for the practical use of numerical modeling in the development and optimization of industrial processes for the thermal recycling of polymer waste. Future research will include the analysis of the pyrolysis of other polyethylene and polystyrene products, as well as simulations that consider the presence of other polymers and additives.

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МОДЕЛЮВАННЯ ПІРОЛІЗУ ПОЛІЕТИЛЕНУ ВИСОКОЇ ЩІЛЬНОСТІ З ВИКОРИСТАННЯМ СИЛОВОГО ПОЛЯ REAXFF

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Анотація

Досліджено процес піролізу поліетилену високої щільності (ПВЩ) за допомогою молекулярно-динамічного моделювання з використанням реакційного силового поля ReaxFF. Метою було визначення якісного та кількісного складу газоподібних продуктів піролізу та оптимальних температурних режимів для максимізації виходу цінних продуктів і мінімізації шкідливого впливу на довкілля. Моделювання виконано в програмних комплексах Materials Studio та LAMMPS. Створено атомістичну модель ПВЩ із додаванням молекул кисню, проведено її геометричну оптимізацію, енергетичну мінімізацію та врівноваження в NVT ансамблі при 300 К. Піроліз моделювався при температурах від 600 °С до 2000 °С. Отримані результати дозволяють рекомендувати температуру 1000 °С як оптимальну для термічного розкладу ПВЩ. Результати підтверджують ефективність ReaxFF для аналізу хімічних процесів піролізу та можуть бути використані для розробки технологій утилізації полімерних відходів.

Ключові слова: піроліз, поліетилен високої щільності, молекулярна динаміка, ReaxFF, газоподібні продукти.