Mechanistic studies of CO₂ plasma-assisted polyethylene degradation

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Abstract: We report an investigation of CO_2 plasma-initiated degradation of polyethylene plastics in a DBD discharge reactor, coupled to online molecular beam mass spectrometry analysis. Detailed chemical speciation analysis identified the distribution of volatile alkane, alkene, carbonyl, alcohol, and carboxylic acid intermediates, and studies of authentic model compounds provided mechanistic insight into the dominant reaction pathways.

1. Introduction

The upcycling of polymers to fuels and fine chemicals, a key strategy for reducing plastic waste, is challenging due to the high required energy and the low selectivity of polymer C-C bond activation. Low-temperature plasmas can initiate polymer breakdown via reactive radicals, excited neutrals, and charged species, making them potentially more energy-efficient than traditional pyrolysis. However, the detailed plasma-polymer interaction pathways have not been explored fully, and their product distributions cannot be easily predicted.

In this work, we studied the degradation of polyethylene (PE) plastics and the reactions of model PE-derived hydrocarbons in a dielectric barrier discharge (DBD) plasma flow reactor. The experimental results provide i) a time-resolved overview of the depolymerization process and ii) mechanistic insights into the plasma interactions with chemical intermediates that can be translated to the fully complex PE degradation.

2. Methods

We investigated the chemistry of PE conversion in an atmospheric pressure CO_2 plasma, using kHz discharges with average powers of 30 – 200 W, in a tubular DBD reactor, coupled to an online time-of-flight (TOF) mass spectrometer. We surveyed the breakdown of high-density and low-density polyethylene (HDPE and LDPE) to monitor the distribution of volatile product species with ~10 s time resolution. In addition, we performed detailed studied of representative model hydrocarbons, which were identified as intermediates in the survey experiments, by entraining their vapor in the CO_2 flow.

3. Results and Discussion

The survey HDPE and LDPE experiments produced a broad range of volatile compounds, including alkanes, alkenes, carbonyls, alcohols, and carboxylic acids. The reaction progress varied greatly with the plasma power and the pre-treatment protocol; however, the fraction of alkenes and oxygenated compounds generally increased, while that of alkanes decreased as a function of time.

The model compound studies revealed rich sequential kinetics, which depended strongly on the molecular structure of the feedstock compound. Figure 1 shows a representative evolution of the main detected products in the reaction of the smallest model alkane, propane (C_3H_8). Ion signals are plotted as a function of the effective reaction time, defined as the product of plasma power
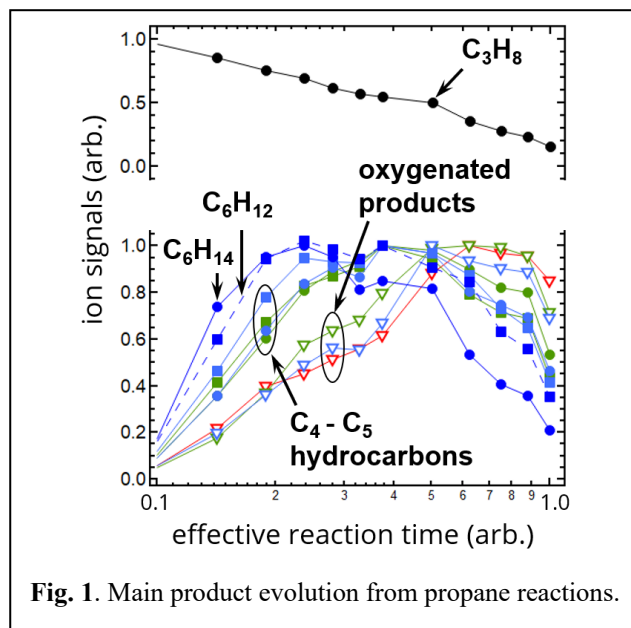

Fig. 1. Main product evolution from propane reactions.

and residence time in the reactor. These results show the prompt formation of C_6 hydrocarbons (from self-reactions of C_3H_7 radicals), followed by $C_4 – C_5$ hydrocarbons (indicative of C-C bond activation), and lastly oxygenated species.

Other model compound experiments included linear and branched alkanes, alkenes, carbonyls, and alcohols in the C_3-C_5 size range. Alkenes and carbonyls exhibited similarly complex chemistry, whereas alcohols were found to be much less reactive, demonstrating a dependence on the initial molecular structure.

4. Conclusion

We have performed extensive investigations of plasma-driven processes integral to depolymerization of PE plastics. The experimental data suggest the sequence of C-H activation, C-C activation, and O incorporation pathways as the basis for a general mechanism of PE-based polymer plasma processing.