Using molecular dynamics simulation, we present a comprehensive study of the volatile thermal degradation of high-density polyethylene (HDPE) across a temperature range of 300 K to 1823 K. We find that degradation at temperatures higher than $\sim$ 1373 K generates significant quantities of reducing gases such as $\text{CH}_n$ and hydrogen molecules which are beneficial to the steelmaking industry. Our results provide a new understanding of HDPE’s phase transformation from solid to gas that occurs during superheating at steelmaking’s electric arc furnace environment offering a new method for eliminating end-of-life HDPE from landfill.

Keywords: High-density polyethylene, High temperature degradation, Molecular dynamics

INTRODUCTION

The massive increase in the volume of end-of-life polymeric products is driving intense research efforts towards more innovative recycling techniques [1–3]. For instance, one emerging opportunity is to use waste polymers to generate fuel sources and reducing agents for steelmaking industry through high temperature degradation process [4,5]. In addition to reducing the volume of the landfilled waste polymers, this approach has the economic benefit of partially substituting expensive conventional fossil fuels. As an advancement in this field, we have recently achieved enhanced volume and improved stability for slag when we used a blend of high-density polyethylene (HDPE) and natural coke in a steelmaking electric arc furnace [5]. The improved slag quality was attributed to the kinetic advantage of using HDPE as it produces higher hydrogen output during high temperature degradation which enhanced slag foaming.

Although, thermal degradation of HDPE has been studied both experimentally [6-8] and theoretically [9], these investigations were limited to temperatures below 973 K. Therefore, the atomistic description of the high temperature ($\sim$ 1800 K) degradation of HDPE during rapid heating has not been fully investigated yet. The main reason for this is the challenge posed by the prohibitively high temperatures and large scale settings [10] that inhibits probing of all thermo-chemical reactions individually [11]. Furthermore, theoretical mechanistic [12] and empirical [13] models that have previously been developed to predict the final products of gasification and pyrolysis of polymers have not considered temperatures higher than $\sim$ 1273 K [14]. Therefore atomistic molecular dynamics (MD) simulation appears to be an insightful tool for studying high temperature degradation of the polymeric structures and the formation of the final products. In this work, we use comprehensive MD simulation to study thermal degradation of HDPE at temperatures as high as 1823 K.

SIMULATION SETTINGS

We used the molecular dynamics package Large scale Atomic/Molecular Massively Parallel Simulator (LAMMPS) [15] to simulate the high temperature degradation of HDPE. A cubic cell containing a single chain HDPE with 80 C atoms and 162 H atoms was used as the initial geometry. This approach allows studying HDPE’s decomposition in reductive environment similar to the one of the electric arc furnace (EAF). Using a relatively large molecular chain also allows detailed evaluation of the chemical reactions associated with the molecular transformation process. We then applied periodic boundary condition (PBC) to the system in X, Y and Z directions. PBC allows the molecules near the either boundaries to interact with the molecules of the opposite sides and thus facilitates realistic simulation without
being computationally too demanding. All interactions between the C and H atoms including Coulomb forces were governed by a Reax potential [16,17]. Reax Potential is a general bond order based force field that provides precise descriptions of the bond breaking and bond forming process in hydrocarbons. Reax potential accounts for nonbonding interactions such as van der Waals and Coulomb forces by considering interactions between every pair of atoms, irrespective of connectivity. The initial random velocities for individual atoms were assigned to give a Maxwell–Boltzmann distribution corresponding to the target temperature. The equations of motion were integrated using the velocity Verlet algorithm with a time step of 0.03 fs.

We used the following algorithms to reach equilibrium state at any given temperature: (1) NVE integration where number of moles (N), volume (V) and energy (E) are kept constant [18]. Within NVE ensemble the temperature is raised by adding non-translational kinetic energy i.e. heat to the equilibrated configuration in a manner that conserves atoms aggregate momentum; (2) Langevin thermostat to recalculate the position of the atoms at each time step [19]; (3) Berendsen barostat to stabilize the pressure fluctuations in the system with the target pressure of 1 atm [20]. To see if the simulation had reached equilibrium, we monitored the energy, temperature and pressure fluctuations at regular intervals during the simulation. By \( t = 1.5 \text{ ns} \) the system reached stable condition where the fluctuations of energy, temperature and pressure became minimal.

**RESULTS AND DISCUSSION**

**Initial Stages of Degradation**

Using the equilibrated configuration, we applied heating rate of 1.5 kcal/mol/fs to increase the temperature from 300 K to 1823 K to investigate the thermal transformation of HDPE as a function of temperature. The applied temperature range extends across ambient to the temperature of molten iron in an EAF. First we present the calculated density of HDPE chain molecule and the resultant products during heating as plotted in Fig. 1(a).

The density at 300 K for HDPE chain in this simulation is \( \sim 640 \text{ Kg/m}^3 \) which is in agreement with the measured values of bulk HDPE density in pellet form [21]. Then as temperature increased to 673 K (Stage I) the density decreased monotonically. However for temperatures between 437 K and 562 K (Stage II) the rate of density change almost stagnated. The change in the density slopes between Stage I and Stage II is comparable to the solid/liquid HDPE density ratio which indicates solid to liquid phase transition. Experimentally, the melting point of HDPE was reported to be in the range of 493 – 553 K depending on the HDPE’s manufacturing pro-

![Fig. 1](a) The calculated density as function of temperature. (b) The evolution of kinetic energy of HDPE chain and temperature as a function of simulation time.

With increasing temperature, we counted the resultant smaller C and H chains by examining the bond connect-
tivity at various temperatures to monitor the structural changes as a function of temperature. The results are presented in Table 1. We found that the HDPE chain maintained its structural integrity at temperatures up to $\sim 330$ K. For higher temperature the C–C and C–H bonds started to vibrate with higher amplitudes although no bond broke for a while. At 703 K, the main chain began to break down into few fresh HDPE chain molecules through scissions. The prediction of the HDPE chain breakage is consistent with earlier thermogravimetric analysis reporting that the degradation of HDPE begins to take place in the 703 K – 743 K temperature range [23]. Furthermore, isothermal and dynamic decomposition measurement of HDPE also detected that the chemical transformation of HDPE starts at $T = \sim 723$ K [24].

For temperatures above 766 K, the HDPE monomers further fragmented into few hydrocarbon molecules, all containing four or more C atoms. As seen in Table 1, at this temperature range, the dominant outcome of the degradation process was generally heavier molecules; for instance, at $T = 849$ K, there were only two lighter $C_2H_n$ molecules while there were four bigger hydrocarbon chains. This trend is on agreement of experimental pyrolysis of polyethylene, in which at 873 K, HDPE yielded negligible amount of gaseous products [8]. When temperature increased to 1396 K, on the other hand, there was no hydrocarbon molecule containing more than three C atoms whereby the absence of larger molecules indicated the complete transformation into the gaseous phase which is in agreement with the density calculations of Fig. 1(a). One noteworthy point was that all resultant molecules were linear, indicating the absence of toxic polycyclic aromatic hydrocarbons in the final products.

**Diffusion Process**

Fig. 1(b) shows the average kinetic energy as a function of temperature. For temperatures below $\sim 1373$ K, the kinetic energy of the system was composed of the kinetic energy of the randomly scissioned radicals. Since, all the C–C bonds in polyethylene have the same strength (except those in the terminal positions), HDPE chain initially decomposed by a random-chain scission mechanism. As the random scission process continued, the freshly produced radicals further interacted with the remaining HDPE chain molecule and sped up the gasification process. As temperature rose, degradation by radicals became dominant over the scission mechanism. Since degradation by radicals requires higher kinetic energy, the value of kinetic energy of the system rose at accelerated rate at high temperatures above $\sim 1373$ K as demonstrated in Fig. 1(b). This observation proves that temperature plays an important role in the transformation process of HDPE as it provides the kinetic energy to break the bonds C–H bonds which is prerequisite $H_2$ formation at temperatures above 1396 K. This point is even more signified when we consider that the C–C bond formation energy is 348 kJ/mol while C–H bonds have a considerably higher formation energy of 413kJ/mol. The role of such high temperature in $H_2$ generation seems to be critical. For instance, a detailed analytical model of HDPE pyrolysis and the corresponding experiments did not predict any $H_2$ generation at temperatures below $\sim 973$ K [7,25].

Since the rise in temperature was coupled with a sharp decrease in the density, we expect that depopagation reactions further degrade the HDPE chain to form lighter molecules. The depopagation reactions in which small alkenes are generated from the decomposition of larger alkane radicals are well known to be dominant in dilute polymeric systems [26]. In the case of HDPE, the depopagation reaction generates new shorter monomers from the freshly formed radicals. During the depopagation reaction, the termination occurs when a pair of radicals...
Fig. 2. (a) The schematic representation of intact high-density polyethylene chain molecule at room temperature. Larger black spheres represent C atoms while smaller gray spheres represent H atoms. The shade around the atoms represents charge densities (b) The interacting light molecules generated at $T = 1823$ K. Sample $H_2$ and $CH_n$ molecules are marked by circles.

interact to reform a new molecule. This process is illustrated by the set of Equations 1–5. Equation 1 shows free radical formation by breakdown while Equations 2 and 3 show free radical transfer and finally Equation 4 shows the free radical termination by disproportionation while Equation 5 shows the radical termination by combination.

\[ R' \rightarrow R-C'H-CH_{2}-R \rightarrow R' + CH_2=CH-CH_2-R, \]  
\[ R' + R-CH_2-R \rightarrow R-C'H-RH \rightarrow R-C'H=CH_2-R', \]  
\[ R' + R' \rightarrow R-CH=CH_2 + RH, \]  
\[ R' + R' \rightarrow R-R. \]  

As in Table 1, we see that generation of hydrogen molecules was initiated at the temperature of 1396 K which was preceded by the generation of $CH_n$ molecules at 988 K. Furthermore, the number of hydrogen and $CH_n$ molecules increased dramatically when temperature passed above $\sim 1373$ K. This trend is in agreement with earlier experiments where high level of hydrogen release from HDPE at high temperatures was reported [27]. In this stage, the hydrogen generation stemmed from the thermal cracking reactions of ethane and ethylene described in the Equations (6–9):

Initiation

\[ C_2H_6 \rightarrow 2CH_3, \]  

Propagation

\[
\begin{align*}
CH_4 + C_2H_6 & \rightarrow CH_4 + C_2H_5, \\
C_2H_5 & \rightarrow C_2H_4 + H, \\
H + C_2H_6 & \rightarrow H_2 + C_2H_5,
\end{align*}
\]  

Termination

\[ C_2H_5 + C_2H_5 \rightarrow C_2H_6 + C_2H_4, \]  

\[ C_2H_6 + 1600 \text{kcal/kmol} \rightarrow C_2H_2 + H_2. \]  

To cross examine the $H_2$ and $CH_n$ generation at higher temperature, we simulated the HDPE degradation process at 1823 K using ab initio molecular dynamics as implemented in SIESTA code [28]. Ab initio simulation does not depend on predefined force-field and thus its accuracy is completely temperature independent. Fig. 2(a) schematically presents the initial structure of the HDPE chain molecule. After the system was equilibrated, we specified the output molecules by probing the charge densities surrounding every individual atom to establish bond connectivity as demonstrated in Fig. 2(b). We found that total number of 36 light molecules of $H_2$ and $CH_n$ were generated by the end of the run which is in general agreement with the classical molecular dynamics simulation. It appears that the generation of $H_2$ and $CH_n$ is facilitated by the formation of double and triple C–C bonds in $C_2H_n$ and $C_3H_n$ at higher when temperature is sufficiently high.
CONCLUSIONS

In conclusion, we conducted molecular dynamics simulations to understand thermal transformation of HDPE at high temperatures. Our results suggest that at high temperature of steel making, thermal degradation of HDPE at 1823 K results in evolution of important gaseous reductants ($H_2$, $CH_n$). With increasing the temperature from 1396 K to 1823 K, the number of hydrogen and $CH_n$ molecules increased dramatically. These results suggest HDPE as a good reductant candidate to generate significant reducing gases including hydrogen in steelmaking applications.

CONFLICTS OF INTEREST

The authors declare that there is no conflict of interest.

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