Reactive Molecular Dynamics Simulation of Transformer Oil Pyrolysis Based on ReaxFF Reactive Force Field

Xuelei WANG1*, Wei XU1, Wen-bing ZHU1 and Qing-min LI1

1State Grid Electric Power Company Shandong Electric Power Research Institute, Jinan, China
2State Key Lab of Alternate Electrical Power System with Renewable Energy Sources, North China Electric Power University, Beijing 102206, China

E-mail address: jiafeimao11111@163.com

Abstract. Fast pyrolysis of transformer oil occurs at local high temperature caused by internal fault in power transformers and this may lead to transformer insulation deterioration. Because numerous subjects such as electrical, material and chemistry are involved and further research of microcosmic reaction mechanism is limited. In this paper ReaxFF reactive force field in which atom connectivity is presented by bond order is introduced to carry out reactive molecular dynamics simulation for transformer oil molecular models and their pyrolysis mechanism at high temperature are investigated. Alkanes C16H34, cycloalkanes C16H30 and aromatic hydrocarbons C16H18 with the same C atoms number 16 are taken as transformer oil examples and initiation pyrolysis mechanism, molecular interaction and products distribution during the whole process for different types of molecules at high temperature are simulated based on ReaxFF reactive force field reactive molecular dynamics. The results indicate that the pyrolysis of these three molecules is similar, the unimolecular dissociation is the main pathway at the early stage of pyrolysis while at the later period it is intermolecular radicals interaction dominated; the final products are mainly small hydrocarbons and radicals, such as C2H4, C3H6, CH4, H2, C2H6, C3H8, while most of the large hydrocarbons and radicals whose C atoms more than 6 mainly serve as intermediate products and decompose into small hydrocarbons and radicals with reactions going on. The difference is that the saturation of generated small molecule hydrocarbon increases for C16H34, C16H30 and C16H18.

1. Introduction
Oil is the main insulation material for oil-immersed transformers [1]. When the transformer undergoes some partial defects, such as a local overheating defect, it will generate heat high enough to endanger the stability of the oil. If not dispatched in time, the heat is able to rise the local temperature to a high level in the transformer and cause oil fast pyrolysis. The transformer oil cracking is a very complicated process of chemical change, involving electrical, material, chemical, and many other disciplines. The existing macroscopic experimental study on insulation defects is not sufficient to explain the in-depth mechanism of the pyrolysis process of oil insulation from the microscopic mechanism point of view.

For the past few years, with the quantum mechanics theory gradually improving, continuous development and update of the force field and the popularity of the computing speed and capacity promotion of the computers, the theory and methods of molecular simulation was developing rapidly [2-4]. Simulation of the molecular structures and behaviors based on molecular model on the atomic
level, it can not only precisely calculate the micro parameters of the insulation material, but also help analyzing the microscopic mechanism of all kinds of complicated phenomenon, so as to explain the relationship between microstructure and macro properties for isolating material [5-7].

At present, there are some researches on the analysis of the micro mechanism of oil. Ding junxia [8], Wang quande [9] and other scholars have taken C7H16 and C12H26 respectively as the example to analyse detailedly for the dynamic cracking process of main components of engine fuel based on the reaction molecular dynamics method of ReaxFF field. These successful applications laid the foundation for the study of the pyrolysis mechanism of transformer oil by using the ReaxFF field reaction molecular dynamics simulation method.

In this paper, ReaxFF reaction field is introduced, and C16 hydrocarbon is taken as an example to simulate the pyrolysis process of transformer oil.

2. Brief overview of reaxff MD simulations

In the ReaxFF reaction field model, the concept of atomic type in the classical force field no longer exists, and there is no connectivity between the atoms in the system. Instead, the connectivity at the current moment is determined by calculating the Bond Order (BO) between any two atoms. Therefore, the core of ReaxFF reaction field is the expression of bond level BO. Based on the definition of bond level, the interaction between atoms is defined as the function of bond level, which can be divided into bond, Angle, dihedral Angle, conjugate, coulomb, van der Waals and adjustment terms through complex function calculation. The expression of interaction energy is shown in equation (1).

$$E_{\text{system}} = E_{\text{bond}} + E_{\text{over}} + E_{\text{under}} + E_{\text{val}} + E_{\text{pen}}$$

$$+ E_{\text{conj}} + E_{\text{tors}} + E_{\text{vdWaals}} + E_{\text{Coulomb}}$$

(1)

In formula (1), $E_{\text{bond}}$ denotes the bond energy, $E_{\text{over}}$ and $E_{\text{under}}$ denote the atom over- and under-coordination penalty term, $E_{\text{val}}$ denotes valence angle terms, $E_{\text{pen}}$ denotes penalty energy, $E_{\text{tors}}$ denotes torsion angle energy, $E_{\text{conj}}$ denotes the contribution of conjugation effects to molecular energy, $E_{\text{vdWaals}}$ denotes non-bonded van der Waals Interactions, and $E_{\text{Coulomb}}$ denotes Coulomb interactions.

In the molecular dynamics simulation of the reaction, each cycle needs to calculate the interaction between the above atoms and the function of bond level. As the bonds are broken and formed, the list of atomic connectivity is constantly updated.

3. Molecular dynamics simulation of high temperature pyrolysis of transformer oil

3.1. Molecular Model Construction

Transformer oil is a mixture, and it is unrealistic and unnecessary to characterize the molecular structure of all the components in the oil during the simulation. As long as the model constructed in the simulation process fully shows the main physical and chemical properties of transformer oil, it is ok. Different types of transformer oil components have bigger difference, but both paraffin base oil and naphthenic base oil, transformer oil are the primary components of alkanes, cyclanes and aromatic hydrocarbon, considering the molecular number of carbon atoms, generally between 15 ~ 23, for this reason, this article C16, for example, constructing alkane C16H34 respectively, two naphthene C16H30 and three types of double loop aromatics C16H18 molecular model, used to characterize the transformer oil major components of thermal cracking process simulation. The C16 molecular model is shown in figure 1, where gray atomic is carbon and white atomic is hydrogen.
3.2. Pyrolysis simulation details

In this paper, ADF ReaxFF Dynamics module is used to simulate the molecular dynamics of transformer oil cracking. Given the IEC directives specified in [10], the local overheating transformer internal causes the temperature of the metal melt is often as high as above 1000°C, and with reference to the literature [11], [12] to C_7H_16 and C_12H_26 pyrolysis simulation temperature is set as high as 3000k, therefore, in this paper, the temperature range of pyrolysis simulation is set to 2400k to 3000k.

In order to compare the transformer oil with different compositions of the whole process of high temperature cracking and intermolecular interactions, respectively under the temperature from 2400k to 3000k to simulate the C_{16}H_{34}, C_{16}H_{30} and C_{16}H_{18} molecules, each build contains five molecules of the amorphous cell, the density is still set to 0.9g/cm³, simulated 100ps, record all kinds of molecules of the reactants and products in the distribution of the cracking process. The parameters of all pyrolysis simulation are set as follows: the ensemble is NVT (i.e., keep the number of atoms in the simulation system N, volume V and temperature T constant), the force field is ReaxFF6.0, berendsen thermostat temperature control parameter is 0.01ps, the equilibrium time is 1.0ps, and the time step is 0.1fs. All the calculations in this paper adopted the periodic boundary condition, and the Discover Minimization was used to optimize the system energy to achieve the minimum energy before each simulation. In the simulation, the atomic coordinates and velocities as well as the bond levels of each atomic pair were recorded every 100fs to analyze the decomposition products. In addition, BO=0.2 was used as the criterion for the formation of the product, that is, when BO≥0.2, the chemical bond was formed and the product was generated.

4. The simulation results and discussion

In order to compare the whole pyrolysis process of different components of transformer oil and the intermolecular interaction, amorphous cells containing 5 similar molecules were established for C_{16}H_{34}, C_{16}H_{30} and C_{16}H_{18} respectively, and the pyrolysis simulation was conducted for several times at 2400K~3000K. The pyrolysis reaction results at the temperature of 2400K and C_{16}H_{34} at 21ps, 25.7ps, 65ps and 100ps are shown in figure 2-5. In order to clearly see the interactions between different molecules, different molecules are marked with different colors and the molecular line model is adopted. As can be seen from the figure, C_{16}H_{34} pyrolysis only occurs in the C-C chain breaking and dehydrogenation of C_{16}H_{34} single molecule at 21ps, generating macromolecular free radicals and H and other components without intermolecular interaction. At 25.7 ps, substances such as unsaturated hydrocarbon C_2H_4 and small molecule free radical CH_3 were generated, and intermolecular interactions were observed (that is, a molecule was composed of different colors, as shown in the bat
model). At 65ps, the original \( \text{C}_{16}\text{H}_{34} \) was almost completely lysed, and the number and species of small free radicals were significantly increased, and the number of molecules involved in the interaction was also increasing. The intermolecular interaction was very common, and a molecule was even composed of 4-5 colors (as shown in the bat model), indicating that the intermolecular free radical interaction was becoming more and more complex. At 100ps, the products are mainly \( \text{H}_2 \), small molecular hydrocarbons or free radicals, etc., but there may be cases where free radicals synthesize large molecules, as shown in the bat model. The above analysis shows that the early stage of pyrolysis reaction is dominated by monomolecular pyrolysis, and the late stage of pyrolysis is dominated by free radical interaction.

Figure 2. The pyrolysis results of \( \text{C}_{16}\text{H}_{34} \) at 21ps.

Figure 3. The pyrolysis results of \( \text{C}_{16}\text{H}_{34} \) at 25.7ps.

Figure 4. The pyrolysis results of \( \text{C}_{16}\text{H}_{34} \) at 65ps.

Figure 5. The pyrolysis results of \( \text{C}_{16}\text{H}_{34} \) at 100ps.

In order to study the whole pyrolysis process of different kinds of molecules in more detail, the distribution of reactants and products in the whole process over time was statistically analyzed. \( \text{C}_{16}\text{H}_{34} \), \( \text{C}_{16}\text{H}_{30} \) and \( \text{C}_{16}\text{H}_{18} \) were all 15 molecules as the initial reactants. Due to different degree of cracking of different molecules, in order to simulate all kinds of molecules in a limited time 100ps of the pyrolysis process, different molecules using different temperature Settings, pyrolysis temperature, respectively, to the above three kinds of molecular is set to 2400k, 2600k and 3000k, the reactants and the major
products over time and the average number of molecules of statistical distribution as shown in figure 6-figure 8.

**Figure 6.** Time evolution of major compounds during the pyrolysis of C\textsubscript{16}H\textsubscript{34}.

**Figure 7.** Time evolution of major compounds during the pyrolysis of C\textsubscript{16}H\textsubscript{30}.

**Figure 8.** Time evolution of major compounds during the pyrolysis of C\textsubscript{16}H\textsubscript{18}.

It can be seen from figure 6-8 that the cleavage of C\textsubscript{16}H\textsubscript{34}, C\textsubscript{16}H\textsubscript{30} and C\textsubscript{16}H\textsubscript{18} is similar at 2400K, 2600K and 3000K, respectively. Response once it begins, cracking of the rapid increase of the number of pieces of initial cracking product mainly H and C6 above macromolecular hydrocarbons, free radicals, etc., as the reaction progresses, C1, C2 and C3 small molecule hydrocarbon, free radicals increased, among them C\textsubscript{2}H\textsubscript{4} is most obvious, and most of the macromolecular hydrocarbons C6 above or free radicals as intermediate consumption in the late reaction, reaction end product mainly for the C\textsubscript{2}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, CH\textsubscript{4} and H\textsubscript{2}, C\textsubscript{3}H\textsubscript{6}, C\textsubscript{3}H\textsubscript{4} small molecule hydrocarbon and free radicals. The difference is that the number of C\textsubscript{3}H\textsubscript{6} and C\textsubscript{2}H\textsubscript{6} in C\textsubscript{16}H\textsubscript{34} pyrolysis is similar, while C\textsubscript{3}H\textsubscript{6} is obviously more than C\textsubscript{2}H\textsubscript{6} in C\textsubscript{16}H\textsubscript{30} pyrolysis. In C\textsubscript{16}H\textsubscript{18} pyrolysis, the generation of H\textsubscript{2} and C\textsubscript{2}H\textsubscript{4} is the most, followed by C\textsubscript{3}H\textsubscript{4}, that is, the generation of small molecular hydrocarbon unsaturation of C\textsubscript{16}H\textsubscript{34}, C\textsubscript{16}H\textsubscript{30} and C\textsubscript{16}H\textsubscript{18} successively increases.

**5. Conclusions**

In this paper, ReaxFF reaction field is introduced, and C16 hydrocarbon is taken as an example to simulate the pyrolysis process of transformer oil with different molecular models. According to the statistical results of the product changes in the high temperature pyrolysis process of multiple molecules, the pyrolysis of different types of molecules is similar, and the pyrolysis in the early stage is mainly monomolecular pyrolysis, while the latter stage is mainly intermolecular free radical interaction. The final products of pyrolysis are mainly small molecular hydrocarbons and free radicals such as C\textsubscript{3}H\textsubscript{4}, C\textsubscript{3}H\textsubscript{6}, CH\textsubscript{4}, H\textsubscript{2}, C\textsubscript{2}H\textsubscript{6} and C\textsubscript{3}H\textsubscript{4}. Most macromolecular hydrocarbons and free radicals
above C6 are mainly intermediate products, which are unstable at high temperature and can be easily decomposed into small molecular hydrocarbons and free radicals with the reaction. The difference is that the unsaturation of \( \text{C}_{16} \text{H}_{24}, \text{C}_{16} \text{H}_{30} \) and \( \text{C}_{16} \text{H}_{18} \) to form small molecular hydrocarbons increases successively. This paper reveals the microcosmic reaction kinetics of high temperature pyrolysis of transformer oil of different molecular types from the atomic level, which can provide further microcosmic theoretical basis for the diagnosis and analysis of high temperature overheating defects inside transformer and the evaluation and prediction of insulation life.

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