ReaxFF-MD in the field of pyrolysis of insulating oil: a review

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Abstract. This article reviews the application of the Reactive Molecular Dynamics (ReaxFF-MD) method in the field of insulating oil. It introduces the commonly used methods for constructing models of insulating oil and oil-paper, summarizes the pyrolysis mechanisms and influencing factors of insulating oil, analyzes the performance differences and advantages of different types of insulating oil, discusses the interactions and coupling effects in the oil-paper system. The paper points out the current status and existing issues in this field, providing a reference for further theoretical and experimental research.

1. Introduction

The stable operation of power transmission equipment depends on the protection of transformer insulating oil. Insulating oil plays a vital role in insulation, cooling, and arc suppression. There are various types of insulating oils, such as mineral oil, vegetable oil, silicone insulating oil, and synthetic insulating oil, each with unique properties and suitability under specific conditions. With the upgrading of power systems and continuous innovation in transformer technology, the performance requirements of insulating oil are becoming more stringent.

The insulation performance of insulating oil is evaluated based on the standards issued by the International Electrotechnical Commission (IEC) and the American Society for Testing and Materials (ASTM). These standards include breakdown voltage, acidity, dielectric loss factor, and dissolved gas analysis, among others. However, these characterization methods can only explain the macroscopic changes in insulating oil performance, without a reasonable interpretation of the microstructural and compositional changes, thus limiting the research in the field of insulating oil chemistry.

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Since the 1980s, with the rapid development of computer technology, it has been widely used in the chemical and materials fields. Molecular simulation techniques, based on quantum mechanics and molecular dynamics, simulate the motion and structural changes of molecules in space and time, revealing the reasons for material property changes from a microscopic perspective. Molecular simulation can be used to explore chemical reaction processes, cracking pathways, characteristic spectra, chemical bond properties, and more. These calculations can corroborate macroscopic experiments and predict the trends of macroscopic experiments. In the early 21st century, Van Duin et al. proposed the Reactive Molecular Dynamics (ReaxFF-MD) method, which combines the advantages of quantum mechanics and molecular dynamics. This method uses criteria such as bond size to determine whether two atoms are bonded, ensuring both accuracy and computational resource efficiency.

Since the establishment of the first-generation ReaxFF force field in 2001 (only supporting C\(\text{H}\text{O}\) elements), various ReaxFF systems have been developed over the past two decades. The cumulative elements supported by various ReaxFF potential function force field files amount to over 40, and force field files supporting calculations of interactions between multiple elements are continuously being developed. For example, in 2022, Mao et al. developed a ReaxFF potential function force field supporting multiple elements, including C-H-O-S-Mo-Ni-Au-Ti, to investigate the surface reactions of MoS2 and a composite agent exposed to different environments. In the field of voltage and insulating oil, the use of molecular simulation calculations to study reaction processes in different environments has gradually increased. Overall, the applications of molecular dynamics (MD) simulations in the field of insulating oil can be roughly categorized into the following aspects: (1) exploration of the pyrolysis pathways of insulating oil; (2) study of interactions between insulating oil molecules and other molecules; (3) investigation of changes in molecular structure and modification mechanisms after adding nanoparticles to insulating oil.

Based on a correlation analysis using literature by Liu et al. as a foundation (as shown in Figure 1), it is evident that Reactive Molecular Dynamics has become increasingly widespread in the field of insulating oil over the past decade.

This article, grounded in the research on reactive dynamics in the field of insulating oil, compiles a comprehensive review of this domain. By collating the most recent articles, distilling their innovative content, amalgamating commonalities across various articles, and identifying areas necessitating further research, the article aims to offer a more profound understanding of the application of Reactive Molecular Dynamics within the insulating oil field. The main body of the article is bifurcated into two sections: the first part encapsulates existing simulation system models, while the second part furnishes a meticulous analysis of prevailing conclusions and introduces personal insights.
2 Model construction

Before conducting molecular simulations, researchers need to establish a simulation system. In reality, insulating oil is a mixture due to aging behaviors occurring during production and storage processes. However, for the sake of studying the mechanism of insulating oil, most researchers simplify the composition of insulating oil as much as possible.

The mineral oil model primarily consists of alkanes, a small proportion of cycloalkanes, and a very small amount of aromatic hydrocarbons. For example, the mineral oil model established by Haoxi Cong et al. [13] comprises 60.61% C_{20}H_{42}, 29.87% C_{20}H_{38}, and 9.52% C_{20}H_{26}, as shown in Figure 2 (a). Additionally, there is the cycloalkyl mineral oil (Karamay 25 insulating oil) model used by Qin et al. [14, 15] and Zhao et al. [16]. The proportions of individual molecules in this model are 11.6% C_{12}H_{26}, 15.5% C_{14}H_{28}, 28.5% C_{13}H_{24}, 23.3% C_{16}H_{28}, and 9.7% C_{16}H_{26}. This model, shown in Figure 2 (b), has a more complex composition, providing computational accuracy closer to real-world scenarios.

Fig. 2. Construction of simulation calculation model.
The main focus of research on vegetable oil includes FR3 and palm oil, both primarily composed of triglycerides. Triglycerides can be categorized into five classes: stearic acid (C_{57}H_{110}O_{6}), palmitic acid (C_{51}H_{98}O_{6}), oleic acid (C_{57}H_{104}O_{6}), linoleic acid (C_{57}H_{98}O_{6}), and stearic acid linolenic acid (C_{57}H_{92}O_{6}). The structural formula and composition ratios are illustrated in Figure 2 (c) [14, 15, 17]. The structure of natural ester vegetable oil can also be appropriately simplified to consist only of oleic acid [13].

In the field of high-voltage transmission, apart from oil, the remaining substance is primarily insulating paper. Therefore, many scholars, during the study of insulating oil, construct models that include insulating paper. The model for insulating paper construction is mainly cellulose, with many researchers using cellulose disaccharides [13] to achieve satisfactory results. The structural formula is shown in Figure 2 (d). Without considering cellulose crystallization, the degree of polymerization has little impact on molecular conformation or physicochemical properties [18]. Therefore, adjustments to the degree of polymerization can be made based on the research system and available computing power. The degree of polymerization in the literature generally ranges from 2 to 10 [17, 19, 20]. The final oil-paper model is depicted in Figure 2 (e).

3 Study on aging mechanisms of insulating oil

In high-voltage insulation systems, as equipment continues to operate, local defects often occur, such as localized high temperatures. During such instances, where temperatures far exceed the maximum working temperature of insulating oil, the heat in the local system increases, leading to a rapid acceleration of thermal decomposition and gas generation in insulating oil. Macroscopic experiments in this process typically involve dissolution gas experiments, providing limited insights into microscopic mechanisms. Molecular simulations, on the other hand, not only calculate the main pathways of gas generation but also swiftly analyze changes in insulating oil pyrolysis under different conditions.

Researchers such as Huang et al. [21] and Wang et al. [22] conducted high-temperature pyrolysis simulations on mineral oil models at different temperatures. The results indicated that in the initial pyrolysis sequence of mineral oil composition structures, straight-chain alkanes, cycloalkanes, and aromatic hydrocarbons were involved. During pyrolysis, β-position dehydrogenation reactions occur, producing small olefins, and bond cleavage reactions generate alkanes. At higher temperatures, the proportion of unsaturated olefins increases. The pyrolysis mechanism is illustrated in Figure 3 (a) [21]. It is noted that the final pyrolysis products of mineral oil include C_{2}H_{4}, C_{3}H_{6}, CH_{4}, and H_{2}, among others. Wang et al. [23] studied the impact of small acids on mineral oil, revealing an increase in the content of unsaturated hydrocarbons in pyrolysis products.

In comparison to mineral oil, vegetable oil exhibits superior environmental performance. In recent years, there has been a growing interest in the microscopic degradation mechanisms of vegetable oil. Scholars like Liu et al. [12] simulated the thermal decomposition process of vegetable oil (C_{57}H_{104}O_{6}). They also conducted density functional calculations on the stability of ester bonds and acyl oxygen bonds in vegetable insulating oil, concluding that ester bonds are more prone to breakage, as shown in Figure 3 (b). It is evident that the subsequent pathways of thermal decomposition for vegetable oil are similar to those of mineral oil. Zheng et al. [24] studied the thermal decomposition mechanism of palm oil and investigated the influence of moisture on its pyrolysis. Saturated triglycerides in palm oil are similar to those in Figure 3 (b). However, for unsaturated triglycerides, additional C=C bonds make them more susceptible to decarboxylation reactions, leading to the generation of CO_{2}. Moisture enhances pyrolysis by promoting hydrolysis and facilitating carboxylic acid ionization, increasing hydrogen in the system. This computational result aligns closely with experimental results from TG-FTIR and Py-GC/MS [25].
Compared to single-phase systems like mineral oil and vegetable oil, the oil-paper composite system has been a focal point for numerous researchers. This is due to the mutual influence of degradation between oil and paper in practical scenarios. Scholars such as Zheng et al. [26] and Liu et al. [27] have separately investigated the mechanisms leading to the production of CO2 and methanol during cellulose degradation. Cong et al. [13] explored the impact of vegetable oil and mineral oil on the degradation of insulating paper. The study revealed three degradation pathways: glycosidic bond cleavage, furan ring opening, and dehydroxylation. In comparison to mineral oil, vegetable oil can delay the degradation of insulating paper, attributed to the strong polarity of vegetable insulating oil, allowing it to sequester water molecules generated in the paper [28]. Some researchers [29] also studied the influence of copper on the oil-paper system, indicating that Cu has a significant promoting effect on cracking, which diminishes with an increase in oxygen concentration. In the oil-paper system, researchers have introduced an electric field [30, 31] to study the pyrolysis under electric-thermal coupling conditions. Results suggest that the presence of an electric field facilitates electron displacement polarization, accelerating the decomposition process.

Utilizing molecular simulations to study the pyrolysis process of insulating oil systems can significantly reduce the manpower and resources required for experiments. Moreover, it allows for the microscopic analysis of cracking behavior, facilitating the tracking of the generation process of small molecular substances. This provides theoretical support for the study of gas generation and damage mechanisms in novel high-voltage transmission devices. However, research on the oil-paper system is predominantly focused on thermal stress, with a lack of studies on the effects of electric fields, magnetic fields, and mechanical stress fields. Subsequent research should consider mechanisms under various environmental factors to provide more accurate and reliable support for the application of insulating oil-paper systems.

4. Conclusion

Reactive Molecular Dynamics proves to be an effective method for studying the chemical mechanisms of insulating oil, offering a microscopic perspective on the pyrolysis process and resulting products. This approach provides a foundation for the assessment and improvement of insulating oil performance. The type, composition, structure, and purity of insulating oil influence its pyrolysis behavior and performance. While vegetable oil exhibits...
better environmental sustainability and stability compared to mineral oil, it also has drawbacks such as susceptibility to oxidation, hydrolysis, and biodegradation. The oil-paper system is a crucial component of high-voltage insulation systems, where the interactions and coupling effects between oil and paper impact the pyrolysis and aging of insulating oil. These interactions are also influenced by external environmental factors like temperature, electric fields, magnetic fields, and mechanical stress. Currently, research on Reactive Molecular Dynamics in the field of insulating oil has some limitations, including model simplifications, parameter optimizations, result validations, and the coupling of multiple fields. Further theoretical and experimental studies are necessary to refine and develop this area of research.

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References


