

Application of molecular simulation in transformer oil–paper insulation

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Abstract: Molecular simulation technology is a new technology emerging with the rapid development of computer technology. It has the advantages of clear microscopic models, in-depth and precise calculation etc., it has been widely used in the oil–paper insulation system of transformer in recent years. Based on the application of molecular simulation technology in the oil–paper insulation system of transformers in this study, the current research status and progress of molecular simulation in these area are elaborated in detail from the aspects of transformer insulating oil and insulating paper according to the domestic and foreign literature, and the application of molecular simulation technology in plant insulating oil and nano-modified insulating oil is emphatically analysed. The complementing research method of molecular simulation and experiment is pointed out, which provides certain reference for solving many problems existing in the field of oil–paper insulation system of transformers.

1 Introduction

With the increase of the voltage level, it is necessary to improve the performance of the insulation material of the electrical equipment. As important insulation material of power transformers, the performance of oil–paper composite insulation media directly determines the service life of transformers, and affects the safe operation of the entire power grid. The insulation performance of oil–paper insulation system gradually declines due to the influence of heat, electricity, machinery and other factors, during the long-term operation of transformers, which causes a major hidden danger to the safe operation of the entire power grid [1]. Thermal ageing is one of the main ageing forms of the oil–paper insulation system of transformers. During the thermal ageing process of oil–paper insulation system, a series of harmful substances such as water and acid will be generated, which will further accelerate the ageing speed of oil–paper insulation system under the action of electric field. For a long time, domestic and foreign scholars have carried out extensive research on the macroscopic properties of the thermal ageing of oil–paper insulation system. However, due to the intersection of electrical, physical, chemical and other disciplines, as well as being restricted by the traditional experimental methods, the research on the micro-mechanism of macroeconomic phenomena is mainly based on the summarisation and induction of experimental data [2].

In the past 20 years, the rapid progress of science and technology has brought tremendous changes to various scientific researches. Molecular simulation technology as a completely new research methods have also been rapidly developed [3]. Molecular simulation technology has shown great vitality in the chemical, biochemical, energy, pharmaceutical, and other fields, and it has also achieved great success in the field of oil–paper insulation system of transformers. Many phenomena and microphysical processes that cannot be observed in experiments can be obtained by molecular simulation technology at the molecular level. The interaction process of transformer oil–paper is extremely complicated, which make it difficult to be studied and understood deeply under the present experimental conditions. However, the rise of molecular simulation technology makes the interaction process of transformer oil–paper be studied easily. The distribution of moisture between oil and paper is studied using molecular dynamics simulations in [4], the results show that the moisture in

oil–paper system can form stable hydrogen bond with cellulose, so a conclusion was made that the moisture in oil–paper system is mainly bound in cellulose. Molecular simulation helps to study the interaction between oil and paper and their degradation mechanism under special operating conditions at the micro level, which can help to clarify the causes of damage to insulation equipment, and provide a theoretical basis for the proposed effective protection scheme.

In this paper, the application of molecular simulation technology in oil–paper insulation transformer is reviewed in detail, firstly, the current research status and progress of molecular simulation technology in oil–paper insulation system of transformer is elaborated in detail from the aspects of transformer insulating oil and insulating paper according to the domestic and foreign literature. Secondly, the application of molecular simulation in plant insulating oil and nano-modified insulating oil is emphatically analysed. Finally, the research method that combines experiment with molecular simulation is proposed, which provides certain reference for solving many problems existing in the field of oil–paper insulation system of transformers.

2 Molecular simulation method

Molecular simulation methods have four mainly kinds: quantum mechanics method, molecular mechanics method, molecular dynamics method, and molecular Monte Carlo method [5].

2.1 Quantum mechanics method

Quantum mechanics method designs new molecule with specific kinetic energy by calculating the micro-parameters of the molecular structure, such as the relationship between the character and charge density, bond order, orbit, and energy level. This method describes a simple, non-real system that calculates a single small molecule in a vacuum at 0° of absolute temperature. With the development of computer hardware and algorithms, this technology has been applied to macromolecules, including models of oligomers of polymers, and have a good result.

Table 1 Compositions (mass fraction) of the naphthenic and paraffinic transformer oil

Transformer oil type	Paraffin	Naphthenic				Aromatic hydrocarbons
		One ring	Bicyclic ring	Three-membered ring	Four-membered ring	
cycloalkyl	11.6	15.5	28.5	23.3	9.7	9.9
paraffin base	28.2	21.1	19.8	11.2	4.5	12.6

2.2 Molecular mechanics method

Molecular mechanics method, also known as force field method, is a non-quantum mechanics technique that solves the problem at the molecular level. The principle is that the internal stress of a molecule reflects to some extent the relative potential energy of the calculated molecular structure. Molecular mechanics method is based on the classical mechanics' calculation method, the calculation will ignore the movement of electrons, and the energy of the system is considered as a function of the type and location of the nucleus, these potential energy function is called force field.

2.3 Molecular dynamics simulation

Molecular dynamics simulation is a method used to calculate the balance and transfer properties of a classical multi-system. It is a good approximation for many materials, and in many ways molecular dynamics simulations are similar to real experiments. It takes a specific particle (such as atom, molecule, or ion) as the basic research object and regards the system as a set of particles with certain characteristics. The classical method of mechanics is used to study the movement law of the microscopic molecule, and the macroscopic characteristics and basic rules of the system are obtained.

2.4 Monte Carlo method

The main difference between the Monte Carlo method and the general calculation method is that it can solve the problem of multi-dimensional or complex factors relatively easily. It uses many methods in statistics, also called statistical experimental methods. Instead of using real experiments to solve the problem like the conventional mathematical statistics, this method grasps some characteristics of the problem, uses mathematical methods to establish the probability model, and then carries out the numerical simulation experiment through the computer according to the process described by this model as the approximate solution to the problem [6].

3 Research progress of molecular simulation in oil and paper insulation

3.1 Molecular simulation applied to transformer oil

In general, transformer insulating oil is the mixed hydrocarbon that consists of paraffin, naphthenic, and aromatic hydrocarbons. At present, the domestic mineral transformer oil mainly includes paraffinic oil and naphthenic oil, the components and proportions are shown in Table 1.

At present, domestic and international scholars have carried out some researches on the micro-mechanism analysis of mineral oil degradation. By using C_7H_{16} and $C_{12}H_{26}$ as examples, the dynamic pyrolysis process of the main components of engine fuel was analysed using reaction molecular dynamics method based on ReaxFF force field in [7, 8]. The distribution of the products at different temperatures was systematically analysed, and the pyrolysis mechanism of C_7H_{16} and $C_{12}H_{26}$ was revealed from the atomic level. These successes lay the foundation for the study of pyrolysis mechanism of transformer oil by Reax FF field reaction molecular dynamics simulation method. Taking C_{16} as an example, three molecular models of paraffin $C_{16}H_{34}$, bicycloalkane $C_{16}H_{30}$, and bicyclic aromatic hydrocarbons $C_{16}H_{18}$ were constructed in [9], then the Reax FF reaction molecular dynamics method was introduced to simulate the pyrolysis reaction at high temperature and with the acidity in oil, so the pyrolysis of mineral oil and the

mechanism of acid in it were revealed at the atomic level in the paper.

Temperature, moisture, acids, and impurities are considered as important factors affecting the thermal ageing of transformers. Relevant scholars have made relevant research in this respect. The diffusion of water and the restraint effect of oil on the insulating oil was studied by means of molecular dynamics using the MS software in [10], the results show that with the increase of simulated temperature, the diffusion of water molecules gradually increases, i.e. the binding effect of oil on water gradually diminishes as the temperature increases. The diffusion behavior of hydronium ions in oil with different moisture contents was studied using molecular dynamics simulations in [11], the simulation results indirectly illustrated the synergistic effect of moisture and acid on transformer insulation ageing. The diffusion coefficient, interaction energy and radial distribution function of furfural molecules and hydronium ions with different moisture content oil molecular model were calculated by molecular dynamics simulation in [12], it is concluded that the increase of water significantly reduces the diffusion ability of furfural and small molecule acids and forms stable hydrogen bonds with furfural and small molecule acids; at the same time, the polar interaction of moisture with furfural and small molecule acids changes the interaction energy of each other.

3.2 Molecular simulation applied to transformer solid insulation paper

It is also common to use molecular simulation technology in transformer solid insulation papers, there are many types of transformer solid insulation paper, such as insulation paper, heat-stabilised paper, and Nomex paper. Operating experience shows that the life of solid insulation determines the life of the transformer [13]. Solid insulation life refers to the service life of cellulose oil-paper: oil-paper cannot be replaced during the operation until the end of life. The degradation mechanism of cellulose molecules was analysed using a combination of molecular dynamics and quantitative calculation in [14], the simulation results show that under the action of external electric field or thermal field, the β -1-G glycosidic bond in the main chain of cellulose molecule is most vulnerable to rupture and generate a large number of free radicals and small mono-glucose products.

The micro-mechanism of insulation paper thermal ageing degradation has been studied in [15], the results show that the temperature increases will lead to the reduction of mechanical strength of the cellulose system, cellulose chain movement increased, and the role of hydrogen bonds in cellulose weakened. The diffusion characteristics of moisture in insulation were studied in [16], the results show that the diffusion coefficient of water molecules on the surface of insulating paper grain decreases due to the electric field polarisation, and the hydrophilicity of cellulose is enhanced. The effects of oxygen, moisture, and hydronium ions on thermal ageing degradation of insulating paper were analysed by using the characteristic parameters of cellulose chain conformation, flexibility and small molecule diffusion coefficient in [17]. The split process of cellulose monosaccharide cellobiose was simulated at high temperature using the reaction molecular dynamics simulation, indicating that the small molecule fragments of glycolaldehyde, formic acid, CHO_2 radical, carbon dioxide, 1,2 dihydroxyethane, water and so on are the main products of cellulose cracking. Since different stages have different characteristic content, they can be used as a new reference for overheating fault diagnosis [18].

4 Molecular simulation used in plant insulating oil transformers

4.1 Application of molecular simulation in plant insulation oil transformer

Plant insulating oil has high biodegradability, fire resistance, and better electrical properties, which will help prolong the service life of the transformer and make a great contribution to the safe and stable operation of the power grid, it also helps to build a resource-saving and environment-friendly society. It is a new liquid dielectric that may replace mineral insulating oils.

The representative two kinds of commercial liquid plant insulation oil are BIOTEMP oil from ABB Company of the USA and FR3 insulating oil from Cooper Company. They were awarded the American invention patent in 1999 and 2000, respectively, and have been successfully applied to some small distribution transformers. Plant insulating oil has obtained good engineering application in distribution transformers and is gradually being used in large power transformers of transmission voltage level [19].

The application of the molecular simulation in plant insulation oil transformers has also made the corresponding results. The molecular dynamic simulation based on Reax FF field was carried out for palmitate ($C_{51}H_{101}O_6$, $C_{16:0}$) [20] and trilinoleate ($C_{57}H_{92}O_6$, $C_{18:3}$) [21], scholar Zhang *et al.* found that the main product was C_2H_4 under pyrolysis process, and the formation mechanism of cyclopentane was analysed in detail lastly. The reaction molecular dynamics of plant oil molecules under high temperature thermal stress was simulated using the ADF software in [22], Zhang Ying paid more attention in elaborating the initial cracking mechanism of transformer insulating oil molecules, the distribution rules of the main products of pyrolysis, and the generation route of the main products, which provide a reference for the effective establishment of a method for diagnosing overheating of plant oil in transformers.

Unlike mineral oil, the main ingredient of plant insulating oil is ester. The hydrogen bonding of ester and water shows that the plant insulating oil has the effect of binding water molecules, it firstly proposed that the ester exchange reaction and the hydrogen bond which produced in the reaction between the carbonyl oxygen atom in the ester and the water molecule have the combined anti-ageing ability. This conclusion also confirmed by [23], it shows that the insulating paper has a large activation energy in the heat ageing of plant oil, the water molecules have a large interaction force with the plant oil molecules and are easily bound by the plant oil molecules to weaken the cellulose hydrolysis reaction, thus extending the service life of the transformer.

4.2 Molecular simulation of transformers for nanomaterials

With the continuous development of nanotechnology, researchers found that adding nano-particles to the traditional mineral insulating oil can form a stable sol system, which cannot only improve the dielectric strength of the insulating oil, but also improve the heat dissipation of the insulating oil. In 1995, nano-particles were added to transformer oil for the first time to form a solid-liquid two-phase nanofluid, which named nano-modified insulating oil. Nano-modified insulating oil has obvious advantages in terms of electrical voltage, ageing condition, and moisture resistance than ordinary transformer oil, which has broad research prospects.

With the development of computer science, molecular dynamics simulation gradually began to apply nano-modified transformers, which cannot only make nano-modified insulating oil, but also make nano-modified transformer insulating paper. The viscosity of nano-modified insulating oil from the microscopic point of view was studied through molecular dynamics simulation in [24], firstly, it determined the appropriate transformer oil composition ratio, then the nano-modified insulating oil model was constructed by using the molecular simulation software amorphous modelling tool, secondly, the root mean square displacement was calculated by molecular dynamics simulation to calculate the diffusion coefficient, and then the viscosity was obtained according to the Einstein's formula. Finally, the influence of temperature on the

viscosity of nano-modified insulating oil was quantitatively described from molecular level, and the viscosity of nano-modified transformer oil was simulated under different working conditions.

In order to improve the thermal stability of transformer insulating paper, nano- Al_2O_3 was used to modify the insulating paper in [25], the effects of nano- Al_2O_3 on the thermal stability of insulating paper were studied by molecular simulation and experimental methods: the modification mechanism of nano- Al_2O_3 on cellulose paper was analysed, the variation of microcosmic parameters of the modified cellulose was studied by using molecular dynamics simulation, at the same time, macroscopic thermal ageing tests on modified and unmodified insulating paper were carried out. The simulation and experimental results show that thermal stability of insulating paper cellulose modified by nano- Al_2O_3 has a better thermal stability. The simulation results provide theoretical support for the research on the properties of nano-modified insulating paper.

Molecular simulation can be used quickly to modify the microstructure of the material or add nano-particles according to the project needs. The comparative analysis of the insulation properties before and after modification can greatly reduce the cycle and cost of material development. The material preparation process can be incorporated into the molecular simulation to better guide the engineering research and development of new insulation materials.

5 Conclusion

The development of molecular simulation provides innovative ideas for researchers. The complementing research method of molecular simulation and experiment, which can provide certain reference for solving many problems existing in the field of oil-paper insulation system of transformers. Especially in the application in plant insulating oil and nano-modified insulating oil, we can modify the microstructure of the material or add nanoparticles according to the actual needs, and compare the insulation performance before and after the modification, it can shorten the development cycle of new materials, reduce development costs, and better ensure the optimisation and reliability of new insulation properties. This approach is bound to have expansive research prospects.

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