A Study on the Law of Gas Production by Pyrolysis of Mixed Insulating Oil under Simulated Overheating Condition

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Abstract. To analyze the law of decomposition and gas production of mixed insulating oil under the action of heat energy, this research conducted the decomposition test of mineral insulating oil, vegetable insulating oil and mixed insulating oil at different hot-spot temperatures through the thermal fault simulation test, compared and analyzed the gas production characteristics and differences of the three insulating oils under the action of heat energy, and analyzed the pyrolysis gas production mechanism of vegetable insulating oil. According to the test results, it can be found that under the condition of no insulating paper and metal catalyst, the characteristic gases produced by the three oils under the action of heat energy are the same, mainly H₂, CH₄, C₂H₄, C₂H₆, CO, CO₂. When the temperature is higher than 700°C, a small amount of C₂H₂ will be produced; when the temperature is low overheated, the pyrolysis characteristic gases of mineral insulating oil are mainly H₂ and CH₄, while the characteristic gases of vegetable insulating oil and mixed insulating oil are H₂ and C₂H₆; when heated, vegetable insulating oil is more easily to produce H₂ than mineral insulating oil; under the same conditions, the CO and CO₂ produced in the vegetable insulating oil are much more than that of the mineral insulating oil, dozens of times more at high temperature; the mixed oil presents similar characteristics to the vegetable insulating oil, which is consistent with the relatively large proportion of vegetable oil in the mixed oil.

Keywords: Mixed insulation oil; Simulation; Overheat; Pyrolysis gas production; Law.

1. Introduction
In electrical equipment, insulating oil mainly plays the role of insulation, heat dissipation and protection. Based on different chemical compositions, common insulating oils are mainly mineral insulating oil, vegetable insulating oil and mixed insulating oil[1]. The mineral insulating oil has a low viscosity and sound cooling performance, but its flash point is as low as about 150°C (closed type). In case of a serious overheating or discharge failure inside the electrical equipment, there will probably be a fire or explosion accident. As a result, in special areas such as mines, residential areas, high-rise buildings, military facilities, etc., electrical equipment using mineral insulating oil has potential fire safety hazards[2-3].

Plant insulating oil mainly comes from soybean, rapeseed, peanut, camellia seed, palm coconut, etc., and its main component is natural ester[4]. The vegetable insulating oil has a biodegradation rate of reaching 97%, and the flash point is>300°C. The electrical equipment has strong overload capacity, so as to effectively improve the fire resistance of electrical equipment. However, because of the high freezing point (about -20°C), high viscosity and poor oxidation resistance of vegetable insulating oil, its application is under great limitation[5-7]. As environmental protection performance requirement of electrical equipment is increasing as the development of society, vegetable insulating oils have shown
obvious advantages, and the corresponding research work has also been intensified. At present, there are more than 1 million vegetable insulating oil transformers in operation throughout the world [8-10].

In winter, in cold areas with low temperatures, the minimum starting temperature of electrical equipment will be lower than the freezing point temperature of vegetable insulating oil, so vegetable insulating oil cannot be used as an insulating medium [11]. In order to make full use of the performance characteristics of mineral insulating oil, such as low freezing point, strong oxidation resistance, good biodegradability of vegetable insulating oil, high flash point, strong overload capacity, the author of this article prepared a low freezing point hybrid insulating oil with mineral insulating oil and natural ester vegetable insulating oil. The mass mixing ratio of vegetable insulating oil and mineral insulating oil is 7:3, and the freezing point of the mixed oil is -41.0°C.

To analyze the law of decomposition and gas production of mixed insulating oil under the action of thermal energy, so as to provide a basis for the diagnosis and analysis of thermal faults in electrical equipment, through the thermal failure simulation test, and without the action of other materials and electric field, the paper carried out respectively the decomposition and gas production tests of mineral insulating oil, vegetable insulating oil and mixed insulating oil at different hot spot temperatures.

2. Test Part

2.1. Test Instrument and Material

Test materials: new mineral oil (hydrogenated), new vegetable insulating oil (rapeseed-based) and new mixed oil (70% vegetable oil + 30% mineral oil).

Test instrument: gas-chromatograph GC1430 (Japan Shimadzu Company), muffle furnace (Hebi Wanbang Instrument Co., Ltd.), peristaltic pump (Dalian Siqi Science & Technology Co., Ltd.), and electromagnetic stirrer (Shanghai).

2.2. Test Method

2.2.1. Establishment of the thermal failure simulation test equipment

As shown in Figure 1, the test equipment is composed of a peristaltic pump, a muffle furnace, a syringe, a three-way valve, oil pipelines and a sample bottle. Except that the inlet and outlet pipes of the peristaltic pump and the inlet pipe of the syringe are hoses, all other pipes are stainless steel pipes. The peristaltic pump provides power for the flowing of the oil sample, and the muffle furnace provides a high-temperature environment to heat the stainless steel tube inserted therein and the oil sample flowing in the tube. The heating time of the muffle furnace to the oil flow can be regulated by adjusting the oil flow rate and the length of the stainless steel pipe section inserted into the muffle furnace. Through this, it can ensure that after the oil sample flows through the muffle furnace, its temperature is consistent with the furnace temperature. By using the sealing property of the syringe and the piston action of the core, the oil sample and the gas generated flowing out of the muffle furnace are collected. The length of the stainless steel tube drawn from the muffle furnace is about 100 cm, which ensures that the oil sample can have enough cooling time after flowing out of the muffle furnace. When flowing into the syringe, its temperature is close to the ambient temperature of the test chamber.

2.2.2. Preparation of the mixed insulation oil

Weigh 3 pieces of mineral insulating oil and 7 pieces of rapeseed-based vegetable insulating oil, put them in a clean glass beaker, stir for 30 minutes on an electromagnetic stirrer, get sonicated in an ultrasonic cleaner for 30 minutes, and then keep it static for 24h.

2.2.3. Treatment of the insulation oil for test

Take enough mineral insulating oil, vegetable insulating oil, and mixed insulating oil respectively with 1000mL glass grinding mouth bottles, heat and degas in a vacuum drying oven for 3h (133Pa, 85°C), cool to room temperature, cover the grinding plug and set aside for future application. After treatment, the gas content in the oil is lower than 1.0% (V/V). Measure untreated mineral insulating oil,
vegetable insulating oil and mixed insulating oil. The air content in the oil should be 6.6% ~ 7.1% (V/V).

![Figure 1. Thermal failure simulation test equipment.](image)

2.2.4. Test of characteristic gas production law under the condition of overheated insulation oil

Lubricate a 500ml syringe with treated oil sample to maintain good lubrication and sealing performance of the syringe core, take 200ml of sample oil with the syringe according to the operation steps in GB/T 7252-2001 Guidelines for the Analysis and Judgment of Dissolved Gases in Transformer Oil, connect with the “2” outlet of the three-way valve through a hose, and then add 350 ml sample oil into the sample bottle.

Adjust the length of the heating pipe section inserted into the muffle furnace, and set the three-way valve at the “1-3” communicated position, set the temperature of the muffle furnace according to the specific requirement, start the peristaltic pump after the temperature in the furnace stabilizes to the set value, and set the oil flow rate through the speed of the peristaltic pump. The insulating oil in the sample bottle flows into the muffle furnace through the peristaltic pump, flows out after it is heated to the same temperature as the muffle furnace and then enters the waste liquid bottle. After the oil volume in the waste liquid bottle is greater than 30 mL, place the three-way valve at the “1-2” communicated position, the sample oil flows into the syringe and time with a stopwatch, place the three-way valve at the “1-3” communicated position at 15 minutes, and then the experiment is finished.

Take out the syringe and seal the syringe outlet with a rubber cap, place it in the lab for 12h, mix evenly the oil in the syringe with the original 200ml oil, prepare the sample oil for test.

Re-set the temperature of the muffle furnace, and carry out the test under 200°C, 300°C, 400°C, 500°C, 550°C, 600°C, 650°C, 700°C, 750°C; change the oil sample; carry out the test of mineral insulating oil, vegetable insulating oil, and mixed insulating oil respectively.

See Table 1 for the set values of temperature, oil flow rate and heating pipe length for pyrolysis test.

### Table 1. Pyrolysis test condition of the insulation oil.

| NO. | Test temperature(°C) | Oil flow rate(mL/min) | Oil flow rate(cm/min) | Length of heating pipe section(cm) |
|-----|----------------------|-----------------------|-----------------------|-----------------------------------|
| 1   | 200                  | 1.67                  | 23.6                  | 21.0                              |
| 2   | 300                  | 1.67                  | 23.6                  | 21.0                              |
| 3   | 400                  | 0.85                  | 12.0                  | 11.0                              |
| 4   | 500                  | 0.85                  | 12.0                  | 11.0                              |
| 5   | 600                  | 0.37                  | 5.22                  | 5.0                               |
| 6   | 700                  | 0.37                  | 5.22                  | 5.0                               |
| 7   | 800                  | 0.37                  | 5.22                  | 5.0                               |
According to the requirements of GBT 7252-2001 *Guidelines for the Analysis and Judgment of Dissolved Gas in Transformer Oil*, take the test sample oil to determine the content of the dissolved gas in it, and then analyze the law of the characteristic decomposition gas of insulating oil in the case of local high temperature and overheating.

### 3. Test Result and Analysis

#### 3.1. Results of Insulation Oil Pyrolysis Test

When the temperature is lower than 550°C, the insulating oil flowing from the muffle furnace into the syringe contains no bubbles. When the temperature is at 600°C, air bubbles begin to emerge out of the insulating oil entering the syringe. A higher temperature generates more bubbles. After the bubbles burst, light white gas will be released. From 400°C, the color of the insulating oil entering the syringe gradually darkens and presents a dark brown color at 750°C, indicating that the insulating oil has been severely deteriorated. As to the oil-immersed high-voltage electrical equipment, the thermal faults are usually classified into low-temperature thermal faults (<300°C), medium-temperature thermal faults (300°C to 700°C) and high-temperature thermal faults (>700°C) based on the hot spot temperature. Because of the heat energy, the hydrocarbon and aliphatic groups in the insulating oil will pyrolyze and produce gas. Gas production is slow at low temperatures, and most of the gas produced is dissolved in oil. Gas production is violent at high temperature, and part of the gas is dissolved in the oil, and the other part of the gas escapes from the oil in the form of bubbles.

The test results show that, under the action of thermal stress, the breaking of the chemical bonds of the insulating oil will produce gases, such as H$_2$, CH$_4$, C$_2$H$_4$, C$_2$H$_6$, C$_2$H$_2$, CO and CO$_2$. The data in Table 2 to Table 4 are the test results of the content of characteristic gas components generated by the pyrolysis of insulating oil and dissolved in the oil. This data does not include the content of gas components in the gas phase.

**Table 2. Results of pyrolysis gas production test of mineral insulating oil.**

| Gas component content (μL/L) | Pyrolysis temperature (°C) |
|-----------------------------|---------------------------|
|                             | 200 | 300 | 400 | 500 | 550 | 600 | 650 | 700 | 750 |
| H$_2$                       | 18  | 61  | 93  | 376 | 510 | 751 | 2375| 6825| 9496|
| CH$_4$                      | 15  | 32  | 916 | 4857| 7357| 11151| 47650| 168675| 176666|
| C$_2$H$_4$                  | 0   | 1.5 | 124 | 2350| 4715| 10785| 98735| 637650| 1302975|
| C$_2$H$_6$                  | 0.2 | 0.8 | 596 | 4465| 6572| 13608| 60953| 360750| 392590|
| C$_2$H$_2$                  | 0   | 0   | 0   | 0   | 0   | 325 | 475 |
| CO                          | 23  | 89  | 1442| 3022| 3157| 3578 | 4635 | 6096 | 8475 |
| CO$_2$                      | 392 | 451 | 2514| 3955| 6025| 9908 | 11820| 13184| 18873|

**Table 3. Results of the pyrolysis gas production test of rapeseed-based vegetable insulating oil.**

| Gas component content (μL/L) | Pyrolysis temperature (°C) |
|-----------------------------|---------------------------|
|                             | 200 | 300 | 400 | 450 | 500 | 550 | 600 | 650 | 700 | 750 |
| H$_2$                       | 145 | 355 | 557 | 774 | 1204| 1797| 6507| 8789| 12641| 28759|
| CH$_4$                      | 4.3 | 121 | 418 | 731 | 2070| 2851| 14511| 55539| 126112| 213050|
| C$_2$H$_4$                  | 1.9 | 13.8| 313 | 815 | 3848| 4984| 132695| 441507| 830280| 2158762|
| C$_2$H$_6$                  | 7.4 | 3924| 11397| 14068| 18965| 24710| 126486| 289663| 383350| 934563|
| C$_2$H$_2$                  | 0   | 0   | 0   | 0   | 0   | 0   | 556 | 785 |
| CO                          | 64  | 913 | 2505| 5524| 13000| 20064| 73378| 175678| 259930| 418756|
| CO$_2$                      | 825 | 1977| 5507| 6350| 16340| 41617| 425686| 557821| 832934| 1268560|
3.2. Analysis of Gas Production Rules

3.2.1. Hydrocarbons and hydrogen

The test results show that when low temperature overheating occurs, the pyrolysis characteristic gases of mineral insulating oil are mainly H₂ and CH₄, while the characteristic gases of vegetable insulating oil and mixed insulating oil are H₂ and C₂H₆. When the medium-to-high temperature overheating occurs, the content of dissolved gas in the oil is very high, indicating that the pyrolysis gas production is very large. When the temperature reaches 700°C, C₂H₂ is produced in the three oils, showing obvious high-energy failure characteristics.

| Gas component | Pyrolysis temperature (°C) |
|---------------|----------------------------|
|               | 200 300 400 450 500 550 600 650 700 750 |
| H₂            | 270 351 606 769 1049 3833 5936 6205 6572 11760 |
| CH₄           | 9.9 211 262 439 653 5329 18760 38640 68160 198000 |
| C₂H₆          | 25 27 247 625 1349 5256 56784 152040 469320 1035360 |
| C₂H₄          | 62 4011 6264 7368 9167 16418 64540 144600 301080 457200 |
| C₂H₂          | 0 0 0 0 0 0 0 0 279 444 |
| CO            | 195 1062 2821 5735 6543 20196 69860 73920 88195 94600 |
| CO₂           | 1836 2187 7389 9158 13612 42075 175140 365505 379930 382840 |

When heated, the vegetable insulating oil is more likely to produce H₂ than mineral insulating oil. When the temperature is lower than 500°C, the H₂ content produced by vegetable insulating oil and mixed insulating oil is 4 to 7 times that of mineral insulating oil. When the temperature is higher than 500°C, the H₂ content produced by the vegetable insulating oil and the mixed insulating oil is 2 to 3 times the H₂ content produced by the mineral insulating oil. The relative content of H₂ in the characteristic gas decreases with the increase of the hot spot temperature. This is because the rate of pyrolysis of H₂ is lower than that of other hydrocarbon characteristic gases.

In order to facilitate the analysis, the relative contents of CH₄, C₂H₄, and C₂H₆ are used to find the distribution law of the contents of the three gases when the temperature is overheated, as shown in Table 5.

| Type of insulating oil | Gas relative content(%) | Pyrolysis temperature (°C) |
|------------------------|-------------------------|----------------------------|
|                        | 400 500 550 600 650 700 750 |
| Mineral oil            | CH₄ 56.0 41.6 39.5 31.4 23.0 14.4 13.9 |
|                        | C₂H₄ 7.6 20.1 25.3 30.3 47.6 54.6 55.3 |
|                        | C₂H₆ 36.4 38.3 35.2 38.3 29.4 31.0 30.8 |
| vegetable oil          | CH₄ 3.4 8.3 8.8 5.3 7.1 9.4 6.4 |
|                        | C₂H₄ 2.6 15.5 15.3 48.5 56.1 62.0 65.3 |
|                        | C₂H₆ 94.0 76.2 75.9 46.2 36.8 28.6 28.3 |
| Mixed oil              | CH₄ 3.9 5.8 19.7 13.4 11.5 8.2 11.7 |
|                        | C₂H₄ 3.6 12.1 19.5 40.5 45.3 56.0 61.2 |
|                        | C₂H₆ 92.5 82.1 60.8 46.1 43.2 35.8 27.1 |

Based on the data in Table 5, for mineral insulating oil, the relative content of CH₄ decreases sharply with the increase of hot spot temperature; the opposite is true for C₂H₄; while C₂H₆ is relatively stable. When the hot spot temperature reaches 650°C, the C₂H₄ content approaches 50%. For vegetable insulating oil, the relative content of C₂H₆ decreases rapidly with the increase of hot spot temperature; the opposite is true for C₂H₄; CH₄ is relatively stable. When the hot spot temperature reaches 600°C, the content of C₂H₄ approaches 50%. At about 50°C lower than mineral oil, namely the temperature is 50°C lower than that of the mineral oil, the production of C₂H₄ from the pyrolysis of vegetable
insulating oil is greatly increased. The mixed oil shows characteristics rather similar to those of vegetable insulating oil, which is in line with the relatively large proportion of vegetable oil in the mixed oil.

3.2.2. CO and CO2

As the temperature increases, the content of CO and CO2 in insulating oil also increases. The content of CO and CO2 produced by pyrolysis in vegetable insulating oil and mixed insulating oil is higher than the corresponding gas content in mineral insulating oil. The analysis of the test data is shown in Table 6.

| Parameters                  | Pyrolysis temperature (℃) |
|-----------------------------|----------------------------|
|                             | 200 | 300 | 400 | 500 | 550 | 600 | 650 | 700 | 750 |
| Ratio of vegetable oil to mineral oil CO | 2.8 | 10.3 | 1.7 | 4.1 | 6.4 | 20.5 | 37.9 | 42.6 | 49.4 |
| Ratio of mixed oil to      | 8.5 | 11.9 | 1.9 | 2.2 | 6.4 | 19.5 | 15.9 | 14.5 | 11.2 |
| mineral oil CO2             | 2.1 | 2.2 | 2.2 | 4.1 | 6.9 | 42.9 | 47.2 | 63.2 | 67.2 |
| Ratio of mixed oil to      | 4.7 | 4.8 | 2.9 | 3.4 | 6.9 | 17.7 | 30.9 | 28.8 | 20.3 |
| mineral oil CO2/CO          | 17.0 | 5.1 | 5.7 | 1.3 | 1.9 | 2.8 | 2.6 | 2.1 | 2.2 |
| vegetable oil CO2/CO        | 12.9 | 2.1 | 2.2 | 1.3 | 2.1 | 5.8 | 3.2 | 3.2 | 3.0 |
| mixed oil CO2/CO            | 9.4 | 2.1 | 2.6 | 2.1 | 2.1 | 2.5 | 4.9 | 4.3 | 4.0 |

According to Table 6, it can be found that the content of CO and CO2 generated in vegetable insulating oil is much higher than the content of the corresponding gases in mineral insulating oil under the same conditions, and even dozens of times higher at high temperatures. The characteristics of mixed insulating oil are similar to those of vegetable insulating oil. When the temperature is lower than 600°C, the ratio of CO2 and CO content in the three insulating oils shows no obvious regularity. At high temperatures, the CO2/CO ratio of mineral insulating oil is about 2.2, the CO2/CO ratio of vegetable insulating oil is about 3.2, and the CO2/CO ratio of mixed insulating oil is about 4.5.

3.2.3. Three-ratio method

The three-ratio method refers to selecting three pairs of faulty gases from the characteristic gas components of insulating oil to calculate their content ratios, and then express them with different codes according to the ratio range, so as to diagnose the nature of the fault with the corresponding relationship between the coding rule and the fault type. According to GB/T 7252-2001 Guidelines for the Analysis and Judgment of Dissolved Gases in Transformer Oil, this paper will adopt the ratios of C2H2/C2H4, CH4/H2, C2H4/C2H6 of the five gases H2, CH4, C2H4, C2H6, and C2H2. The data analysis results are shown in Table 7 and Table 8.

For mineral insulating oil, when the temperature is 200°C and 300°C, the ratio of C2H4/C2H6 is meaningless because of the low content of C2H2 and C2H6, so it is not calculated. The data in Table 8 shows that for mineral insulating oil, when the temperature is 400°C, 500°C, 550°C, and 600°C, the code of the three ratios is 020. According to GB/T 7252-2001 Guidelines for Analysis and Judgment of Dissolved Gases in Transformer Oil, the fault type is low temperature overheating (150~300°C), which do not match. When the temperature is 650°C and 700°C, the three-ratio code is 021; when the temperature is 750°C, the three-ratio code is 022. This is consistent with GB/T 7252-2001 Guidelines for Analysis and Judgment of Dissolved Gases in Transformer Oil. The three-ratio code for the most temperature points of vegetable insulating oils and mixed insulating oils does not conform to the judgment result of GB/T 7252-2001. Therefore, it is not possible to directly diagnose the overheating fault of vegetable insulating oil and mixed insulating oil according to GB/T 7252-2001. The three-ratio range and coding rules should be adjusted accordingly through a large number of simulation tests.
and the accumulation of electrical equipment operating data and fault diagnosis experience.

Table 7. Calculation results of the three ratios of characteristic gas components.

| Type of insulating oil | Ratio | Pyrolysis temperature (°C) |
|------------------------|-------|---------------------------|
|                        |       | 200 | 300 | 400 | 500 | 550 | 600 | 650 | 700 | 750 |
| C₂H₂/C₂H₄               |       |     |     |     |     |     |     |     |     |     |
| Mineral oil             |       |     |     |     |     |     |     |     |     |     |
| CH₄/H₂                  | 0.81  | 0.51 | 9.80 | 12.91 | 14.42 | 14.81 | 20.12 | 24.73 | 18.62 |     |
| C₂H₂/C₂H₆               |       |     |     |     |     |     |     |     |     |     |
| Vegetable oil           |       |     |     |     |     |     |     |     |     |     |
| C₂H₂/C₂H₄               | 0     | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0.0007 |
| CH₄/H₂                  | 0.34  | 0.75 | 1.72 | 1.59 | 2.23 | 6.32 | 9.98 |     |     |     |
| C₂H₂/C₂H₆               |       |     |     |     |     |     |     |     |     |     |
| Mixed oil               |       |     |     |     |     |     |     |     |     |     |
| C₂H₂/C₂H₄               | 0.037 | 0.60 | 0.43 | 0.62 | 1.39 | 3.48 | 6.23 | 10.37 | 16.84 |     |
| CH₄/H₂                  | 0.007 | 0.039 | 0.15 | 0.32 | 0.88 | 1.05 | 1.56 |     |     |     |

Table 8. Coding combination of the three ratios of characteristic gas components.

| Type of insulating oil | Coding combination | Pyrolysis temperature (°C) |
|------------------------|--------------------|---------------------------|
|                        |                    | 200 | 300 | 400 | 500 | 550 | 600 | 650 | 700 | 750 |
| C₂H₂/C₂H₄               |                    |     |     |     |     |     |     |     |     |     |
| Mineral oil             |                    |     |     |     |     |     |     |     |     |     |
| CH₄/H₂                  | 0                  | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    |
| C₂H₂/C₂H₆               |                    |     |     |     |     |     |     |     |     |     |
| Vegetable oil           |                    |     |     |     |     |     |     |     |     |     |
| C₂H₂/C₂H₄               | 0                  | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    | 0    |
| CH₄/H₂                  | 0.34               | 0.75 | 1.72 | 1.59 | 2.23 | 6.32 | 9.98 |     |     |     |
| C₂H₂/C₂H₆               |                    |     |     |     |     |     |     |     |     |     |
| Mixed oil               |                    |     |     |     |     |     |     |     |     |     |
| C₂H₂/C₂H₄               | 0.037              | 0.60 | 0.43 | 0.62 | 1.39 | 3.48 | 6.23 | 10.37 | 16.84 |     |
| CH₄/H₂                  | 0.007              | 0.039 | 0.15 | 0.32 | 0.88 | 1.05 | 1.56 |     |     |     |

3.3. Analysis of Pyrolysis Gas Production Mechanism

Because the mass fraction of vegetable insulating oil in the mixed insulating oil is relatively large, the pyrolysis gas production characteristics are more similar to those of vegetable insulating oil, and there is no “unique” gas production law. Therefore, the pyrolysis mechanism analysis suggests that the mineral insulating oil and vegetable insulating oil that make up the mixed insulating oil decompose and produce gas respectively under the action of heat energy, and there is no interaction that affects the gas production. The gas production mechanism of mineral insulating oil under the action of thermal energy is the chain scission and dehydrogenation reaction of hydrocarbons [12,13]. This has been well known by professionals. Therefore, this paper analyzes the pyrolysis gas production mechanism of vegetable insulating oil.

The pyrolysis and gas production behavior of insulating materials are determined by their chemical composition and molecular structure [14-16]. The main component of the rapeseed-based insulating oil used in this test is triglyceride. Triglyceride is obtained by esterification of three fatty acid molecules and one glycerol molecule [17], and its molecular structure is shown in Figure 2. Where R stands for hydrocarbon chain, and the R on the three ester groups can be the same, but generally different. For vegetable insulating oil, the higher the degree of fatty acid molecule saturation, the more stable the chemical properties of the corresponding oil, but the worse its low-temperature fluidity [18]. Table 9 lists the types and contents of fatty acids contained in the vegetable insulating oil used in the test. The content of monounsaturated fatty acids is 55.9%, which is relatively high.
Figure 2. Triglyceride molecular formula of vegetable insulating oil.

Table 9. Fatty acid contents of vegetable oil.

| Type of fatty acids | Saturated fatty acid | Monounsaturated fatty acid | Bisunsaturated fatty acids | Triunsaturated fatty acids |
|---------------------|----------------------|--------------------------|--------------------------|--------------------------|
| Content of fatty acids | 7.9 | 55.9 | 22.1 | 11.1 |

There are single bonds (C-C, C-H, O-H, H-H, C-O) and C=O double bonds in the molecular structure of vegetable insulating oil, but there are very few C=C and triple bonds (C≡C). The bond energies of various bonds are listed in Table 10 [19]. The bond energy determines the stability of the chemical bond. The greater the energy of the bonds, the more stable the bond, and it is not easy to be destroyed.

Table 10. Bond energies of different chemical bonds.

| Chemical bonds | H - H | C - H | C - C | C = C | C≡C | C - O | C = O | H - O |
|----------------|-------|-------|-------|-------|-----|-------|-------|-------|
| Bond energy (kcal/mol) | 104.2 | 94 - 103 | 70 - 100 | 147 | 194 | 84 | 174 | 110.6 |

Generally, the thermal decomposition of insulating oil mainly depends on the amount of energy it receives. The thermal cracking reaction is a strongly endothermic reaction. At low temperatures, the thermal energy of the insulating oil is not enough to damage these bonds. Therefore, the normal deterioration of the insulating oil results in the formation of a very small amount of H₂, CH₄, C₂H₆, etc. However, when the temperature rises, thermal energy will break many carbon-oxygen bonds and hydrocarbon-bonds, and produce a large amount of low-molecular hydrocarbon gases, H₂, CO and CO₂.

Under the action of thermal energy, triglyceride decomposes and produces free radical groups CH₃(CH₂)ₙ COO• and CH₃(CH₂)ₙ CO•. The group CH₃(CH₂)ₙ COO• produces n-alkanes and isoolefin by decarboxylation, disproportionation and deethylation, and the group CH₃(CH₂)ₙ CO• produces alkanes and olefins by deethone, disproportionation and deethylation, as shown in equations 1 ~ 6.

\[
\text{CH}_3(\text{CH}_2)_n\text{COO}^- \rightarrow \text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2\text{CH}_2^- + \text{CO}_2 \quad (1)
\]

\[
\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2\text{CH}_2^- \rightarrow \text{CH}_3(\text{CH}_2)_{n-4}\text{CH}_2\text{CH}_2^- + \text{CH}_2 = \text{CH}_2 \quad (2)
\]

\[
2\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2\text{CH}_2^- \rightarrow \text{CH}_3(\text{CH}_2)_{n-2}\text{CH}=\text{CH}_2 + \text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2\text{CH}_3 \quad (3)
\]

\[
\text{CH}_3(\text{CH}_2)_n\text{CO}^- \rightarrow \text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2^- + \text{CH}_2 = \text{CO} \quad (4)
\]

\[
\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2^- \rightarrow \text{CH}_3(\text{CH}_2)_{n-4}\text{CH}_2^- + \text{CH}_2 = \text{CH}_2 \quad (5)
\]

\[
2\text{CH}_3(\text{CH}_2)_{n-2}\text{CH}_2^- \rightarrow \text{CH}_3(\text{CH}_2)_{n-3}\text{CH}=\text{CH}_2 + \text{CH}_3(\text{CH}_2)_{n-3}\text{CH}_2\text{CH}_3 \quad (6)
\]

As CO₂ gas is produced during decomposition, vegetable insulating oil produces more CO₂ gas than mineral insulating oil. During the thermal decomposition process of hydrocarbon chain of vegetable insulating oil, the following reaction occurs:

\[
\text{RH} + \text{e} \rightarrow \text{R}^- + \text{H}^- \quad (7)
\]

Where e is the energy acting on RH, and R⁻ and H⁻ are the free radicals of R and H respectively. CH₂=CH₂, the intermediate product of thermal decomposition of vegetable insulation oil, can combine with H₂ to produce C₂H₆. Therefore, vegetable insulation oil will produce more C₂H₆ at medium and low temperatures.
4. Conclusion
In this study, a thermal failure simulation test system was established, and the laws of pyrolysis and gas production of mineral insulating oil, vegetable insulating oil and mixed insulating oil under the condition of oil only were obtained. The characteristic gases produced by the three oils under the action of thermal energy are the same, mainly \( \text{H}_2 \), \( \text{CH}_4 \), \( \text{C}_2\text{H}_4 \), \( \text{C}_2\text{H}_6 \), \( \text{CO} \), and \( \text{CO}_2 \). When the temperature exceeds 700°C, a small amount of \( \text{C}_2\text{H}_2 \) will be produced.

When low-temperature overheating occurs, the pyrolysis characteristic gases of mineral insulating oil are mainly \( \text{H}_2 \) and \( \text{CH}_4 \), while the characteristic gases of vegetable insulating oil and mixed insulating oil are mainly \( \text{H}_2 \) and \( \text{C}_2\text{H}_6 \).

When heated, vegetable insulating oil is more likely to produce \( \text{H}_2 \) than mineral insulating oil. When the temperature is lower than 500°C, the \( \text{H}_2 \) content produced by vegetable insulating oil and mixed insulating oil is 4-7 times that of mineral insulating oil. When the temperature is higher than 500°C, the \( \text{H}_2 \) content of vegetable insulating oil and mixed insulating oil is 2 to 3 times that of mineral insulating oil.

For mineral insulating oil, the relative content of \( \text{CH}_4 \) decreases sharply with the increase of hot spot temperature; the opposite is true for \( \text{C}_2\text{H}_4 \); while \( \text{C}_2\text{H}_6 \) is relatively stable. When the hot spot temperature reaches 650°C, the \( \text{C}_2\text{H}_4 \) content approaches 50%. For vegetable insulating oil, the relative content of \( \text{C}_2\text{H}_6 \) decreases rapidly with the increase of hot spot temperature; the opposite is true for \( \text{C}_2\text{H}_4 \); \( \text{CH}_4 \) is relatively stable. When the hot spot temperature reaches 600°C, the content of \( \text{C}_2\text{H}_4 \) approaches 50%. At about 50°C lower than mineral oil, namely the temperature is 50°C lower than that of the mineral oil, the production of \( \text{C}_2\text{H}_4 \) from the pyrolysis of vegetable insulating oil is greatly increased. The mixed oil shows characteristics rather similar to those of vegetable insulating oil, which is in line with the relatively large proportion of vegetable oil in the mixed oil.

The content of \( \text{CO} \) and \( \text{CO}_2 \) generated in vegetable insulating oil is much higher than the content of the corresponding gases in mineral insulating oil under the same conditions, and even dozens of times higher at high temperatures. The characteristics of mixed insulating oil are similar to those of vegetable insulating oil. When the temperature is lower than 600°C, the ratio of \( \text{CO}_2 \) and \( \text{CO} \) content in the three insulating oils shows no obvious regularity. At high temperatures, the \( \text{CO}_2/\text{CO} \) ratio of mineral insulating oil is about 2.2, the \( \text{CO}_2/\text{CO} \) ratio of vegetable insulating oil is about 3.2, and the \( \text{CO}_2/\text{CO} \) ratio of mixed insulating oil is about 4.5.

The three-ratio code for the most temperature points of vegetable insulating oils and mixed insulating oils does not conform to the judgment result of GB/T 7252-2001. Therefore, it is not possible to directly diagnose the overheating fault of vegetable insulating oil and mixed insulating oil according to GB/T 7252-2001. The three-ratio range and coding rules should be adjusted accordingly through a large number of simulation tests and the accumulation of electrical equipment operating data and fault diagnosis experience.

Acknowledgement
Thanks for the support of the fund project: State Grid Heilongjiang Electric Power Co., Ltd. Key Technology Project (52243718000).

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