

Biodegradation performance of environmentally-friendly insulating oil

Jun Yang¹, Yan He², Shengwei Cai², Cheng Chen², Gang Wen^{3,5}, Feipeng Wang³, Fan Fan³, Chunxiang Wan³, Liya Wu³ and Ruitong Liu⁴

¹ State Grid Corporation of China, Beijing 100031, China;

² China Electric Power Research Institute, Wuhan 430074, China;

³ Chongqing University, Chongqing 400044, China;

⁴ State Grid Liaoning Electric Power Research Institute, Shenyang 110006, China.

⁵ wengang@cqu.edu.cn

Abstract. In this paper, biodegradation performance of rapeseed insulating oil (RDB) and FR3 insulating oil (FR3) was studied by means of ready biodegradation method which was performed with Organization for Economic Co-operation and Development (OECD) 301B. For comparison, the biodegradation behaviour of 25# mineral insulating oil was also characterized with the same method. The testing results shown that the biodegradation degree of rapeseed insulating oil, FR3 insulating oil and 25# mineral insulating oil was 95.8%, 98.9% and 38.4% respectively. Following the "new chemical risk assessment guidelines" (HJ/T 154 - 2004), which illustrates the methods used to identify and assess the process safety hazards inherent. The guidelines can draw that the two vegetable insulating oils, i.e. rapeseed insulating oil and FR3 insulating oil are easily biodegradable. Therefore, the both can be classified as environmentally-friendly insulating oil. As expected, 25# mineral insulating oil is hardly biodegradable. The main reason is that 25# mineral insulating oil consists of isoalkanes, cyclanes and a few arenes, which has few unsaturated bonds. Biodegradation of rapeseed insulating oil and FR3 insulating oil also remain some difference. Biodegradation mechanism of vegetable insulating oil was revealed from the perspective of hydrolysis kinetics.

1. Introduction

Transformers, circuit breakers, current and voltage transformers in electric power delivery systems are usually filled with insulating oil, which is the key to guarantee electrical insulation and heat dissipation [1-3]. Due to the excellent insulation performance, good coolant, low wastage and price, mineral-based transformer oils have been widely applied in power transmission. Lots of transformers are located in populated areas, shopping centres, and near waterways. This brings the result that the leakage of transformer oil may cause considerable environmental disaster [4-6]. In 2009, a big exploding underwater resulted from a short circuit in the hydroelectric power station, Sayano-Shushenskaya Russia has caused more than 100 tons mineral insulating oil leaking into the Yenisey basin [7].

This accident as well other similar cases have promoted global governments and researchers focusing on the development of environmentally-friendly insulating oils, e.g. several vegetable insulating oils. These oils are expected as biodegradable and they are usually obtained from natural products such as rapeseeds, peanuts, soybeans, etc. After treatments like alkaline refinement, vacuum



distillation, and bleaching [8-10], the vegetable oils can be prepared with sufficient electrical properties that meet the requirements from electrical power industry [11-12].

To evaluate the biodegradation property of vegetable insulating oils, the Ready Biodegradability Tests (RBTs) are the useful methods for evaluating environmental performance of insulating oil within a specific time-span [13]. Based on different principles, there are six RBTs (301A-F) methods in the OECD guidelines. Due to the fact that nearly all insulating oils are poorly water-soluble, this work takes the method of OECD 301B for evaluation because it is one of the easiest way and is feasible for testing insulating oils that are nonvolatile and easy to be absorbed [13]. The biodegradation process of vegetable insulating oil was analysed from the perspective of hydrolysis kinetics.

2. Materials and methods

2.1. Test substance

The FR3 insulating oil (Cargill, USA), rapeseed insulating oil (by the authors) and 25# mineral insulating oil (Karamay, China) were used as received. The FR3 oil is prepared from soybean (acknowledged by the manufacture). The rapeseed insulating oil is prepared by the authors' group from raw rapeseed oil via three refinement procedures: alkaline refinement, vacuum distillation, and bleaching [9].

2.2. Biological medium and inoculums

The CO₂ evolution test (i.e. 301B) is one of the six Ready Biodegradation Tests (RBTs) proposed by OECD based on the removal of compounds measured as the production of the catabolic end-product carbon dioxide. The ready biodegradation was determined based on the reduction in CO₂ evolution in a biological medium within 28 days. The composition and mass concentration of the biological medium used in this work is carbon-free and the details are listed in Table 1. Biological medium was prepared on the basis of literature [14]. Besides, inoculums were collected from the primary sedimentation tank in a wastewater treatment plants in Chongqing city. In order to guarantee the concentration of bacteria in the inoculum, the inoculum was preconditioned using the following steps: (1) Remove rough particles and surface supernatants; (2) Wash the inoculum by the biodegradation medium and repeat several times; (3) Aerate the inoculum for 5-7 days at 22°C in darkness. After preconditioned, the inoculum was examined by the plate count agar method, and the bacteria number density was limited between 4×10^7 and 8.5×10^7 CFU/ml.

Table 1. Composition and mass concentration of the biological medium.

| Composition | Concentration ρ (g/l) |
|---|----------------------------|
| KH ₂ PO ₄ | 8.5 |
| K ₂ HPO ₄ | 2.338 |
| Na ₂ HPO ₄ • 2H ₂ O | 1.064 |
| NH ₄ Cl | 5.0 |
| MgSO ₄ • 7H ₂ O | 22.5 |
| CaCl ₂ • 2H ₂ O | 2.15 |
| H ₃ BO ₃ | 1.43 |
| FeSO ₄ • 7H ₂ O | 1.897 |
| ZnSO ₄ • H ₂ O | 1.97 |
| CuSO ₄ • 5H ₂ O | 1.21 |
| (NH ₄) ₆ Mo ₇ O ₂₄ • 4H ₂ O | 2.498 |

2.3. Experimental setup

The experiment setup is illustrated in Figure 1[15], which contains the following four parts. In gas washing device (2-5), KOH and Ba(OH)₂ solution is adopted to remove CO₂ intake and to test the

absorption respectively. In device (6), biodegradation reaction is carried out. In CO₂ absorption device (7), Ba(OH)₂ solution is used to absorb CO₂ that produced during degradation process. Titration device (8) is used to measure the CO₂ production.

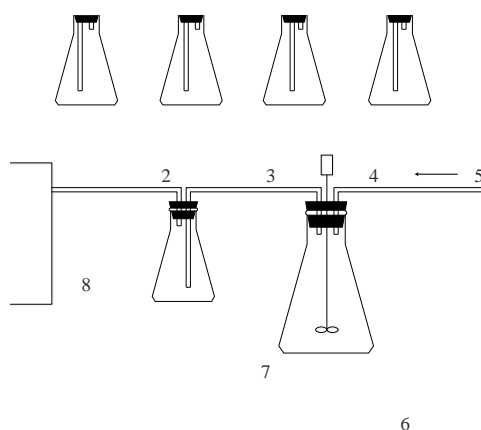


Figure 1. Sketch for the biodegradation test.

The biodegradation test is structured by several experimental and control groups. The experimental group has six biodegradation reaction samples, i.e. two 25# mineral insulating oil samples (adding inoculum with 25# mineral insulating), two FR3 insulating oil samples (adding inoculum with FR3 insulating oil) and two rapeseed insulating oil samples (adding inoculum with rapeseed insulating oil). For comparison, control group contains a blank reaction bottle in which only inoculum was added. Appropriate amount of inoculum and biological medium was mixed with volume of 200ml and was added into a 301B bottle. The reaction temperature was controlled at 28°C, and the stirring rate was 200 r/min. A 0.0125 mol/L Ba(OH)₂ solution with volume of 100 mL was packed in an absorption bottle which was used to absorb the CO₂ evolved. A 0.05 mol/L HCl solution was titrated into the absorption bottle by using phenolphthalein as indicator. CO₂ evolution was menstruated by titrating the volume of HCl solution. The equation (1) is used to calculate the CO₂ produced during biodegradation (mg).

$$m_1 = \frac{(0.0125 \times 100 \times 2 - 0.05 \times V) \times 44}{2} = 1.1 \times (50 - V) \quad (1)$$

Where m_1 is CO₂ produced during biodegradation (mg), V is the HCl titration volume (mL).

3. Results and discussion

3.1. Test cycle

Following the OECD 301B guidelines, every cycle of the insulating oil biodegradation was determined as 28 d and the amount of the produced CO₂ was checked once per 2 days during the first 10 days followed by once per 6 days during the rest 18 days. The equation (1) is used to calculate the CO₂ produced during biodegradation (mg). Two parallel samples for each oil were placed to taking the average value. The amount of produced CO₂ of insulating oil during biodegradation is summarized in Table 2.

Figure 2 shows the CO₂ production during the three oils' biodegradation process. During the first 2 days, CO₂ production of rapeseed insulating oil and FR3 insulating oil reached maximum values which are 0.3715 mg, and 0.385mg respectively. This is because biological medium provides sufficient nutrients, and bacteria growth is very well (log phase) within this period. As time goes by, the biological medium is gradually consumed and bacteria growth is gradual transition from log phase to stationary phase. As expected, the CO₂ production decreases to 0.301mg and 0.319mg respectively from the second day to the sixth day. The test substance is greatly consumed and bacteria growth

begins to death phase after 6 days of biodegradation test. On the seventh and eighth days, the CO₂ production shows a dramatic decline. Ultimately, the CO₂ production reduced gradually to 0.

Table 2. The amount of produced CO₂ of insulating oil during biodegradation (mg).

| Time / d | FR3 insulating oil | | rapeseed insulating oil | | 25#mineral insulating oil | |
|----------|--------------------|--------|-------------------------|--------|---------------------------|--------|
| | (1) | (2) | (1) | (2) | (1) | (2) |
| 2 | 0.384 | 0.386 | 0.375 | 0.368 | 0.082 | 0.085 |
| 4 | 0.351 | 0.355 | 0.341 | 0.346 | 0.13 | 0.126 |
| 6 | 0.32 | 0.318 | 0.301 | 0.3 | 0.094 | 0.088 |
| 8 | 0.11 | 0.125 | 0.11 | 0.103 | 0.076 | 0.069 |
| 10 | 0.065 | 0.073 | 0.063 | 0.061 | 0.038 | 0.036 |
| 16 | 0.0011 | 0.0012 | 0.0013 | 0.0012 | 0.0013 | 0.0011 |
| 22 | 0.001 | 0.0012 | 0.001 | 0.0012 | 0.0011 | 0.0014 |
| 28 | 0.001 | 0.0011 | 0.0012 | 0.0011 | 0.001 | 0.0011 |

On the other hand, the CO₂ production of 25# mineral insulating oil is only 0.0835 mg within the first two days of biodegradation process. The CO₂ production of 25# mineral insulating oil reaches a maximum value which is 0.128 mg from third day to fourth day. Bacteria growth is in its stationary phase and the number of bacterial reaches a peak. In addition, biological medium provides sufficient nutrients. Afterwards, CO₂ production of 25# mineral insulating oil reduces gradually to 0 in the end.

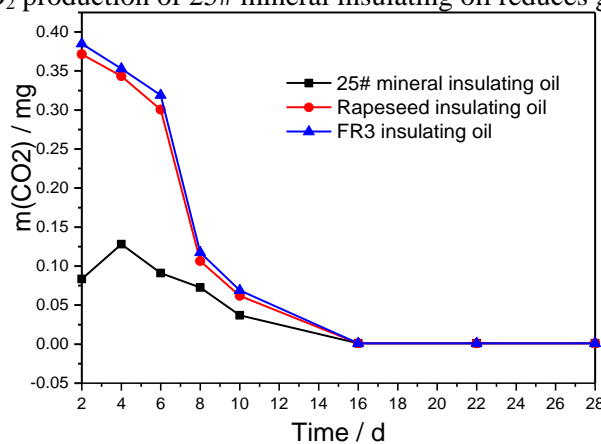


Figure 2. The CO₂ production during the three oils' biodegradation process.

Following the OECD 301B guidelines, the biodegradation degree of insulating oil can be calculated by equation 2. In addition, m_1 is the CO₂ production which has been obtained from equation 1.

$$D = \frac{m_1}{ThCO_2 \times m_2} \quad (2)$$

where D is biodegradation degree of insulating oil (%); m_2 is the amount of test substance (mg); ThCO₂ is the theoretical CO₂ evolution (mg/mg).

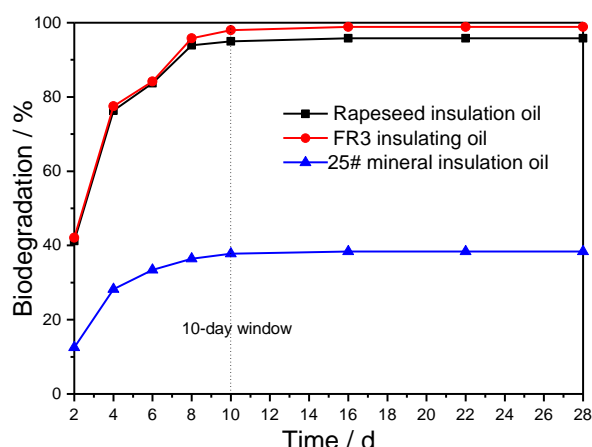


Figure 3. Biodegradation degree of the three oils' biodegradation process.

Figure 3 shows the biodegradation degrees of the three oils' biodegradation process. During the first two days, biodegradation degrees of the rapeseed insulating oil, the FR3 insulating oil and the 25# mineral insulating oil are 41.2%, 42.1% and 12.5% respectively. According to the criterion of the positive result in OECD 301B test, a compound fulfilled the 10-day window and with a biodegradation degree value of 60% or more was classified as "readily and rapidly" biodegradable compound. The biodegradation degree of rapeseed insulating oil, FR3 insulating oil is more than 60% which is classified as rapid biodegradation in a 10-day window within 28 days [14]. However, the biodegradation degree of 25# mineral insulating oil is only 37.8% in this period. Ultimately, biodegradation degree of rapeseed insulating oil and FR3 insulating oil tends to 100%.

It can be seen from Figure 4 that the biodegradation degree of rapeseed insulating oil, FR3 insulating oil is more than 25# mineral insulating oil within 28 days' degradation process. Biodegradation degree of rapeseed insulating oil, FR3 insulating oil and 25# mineral insulating oil is 95.8%, 98.9% and 38.4% respectively. In "new chemical risk assessment guidelines" (HJ/T 154 - 2004), it can be seen that the two vegetable insulating oils, i.e. rapeseed insulating oil and FR3 insulating oil can easily be biodegraded. However, their biodegradation degrees are different. In the following, the difference of biodegradation degree between FR3 insulating oil and rapeseed insulating oil will be explained.

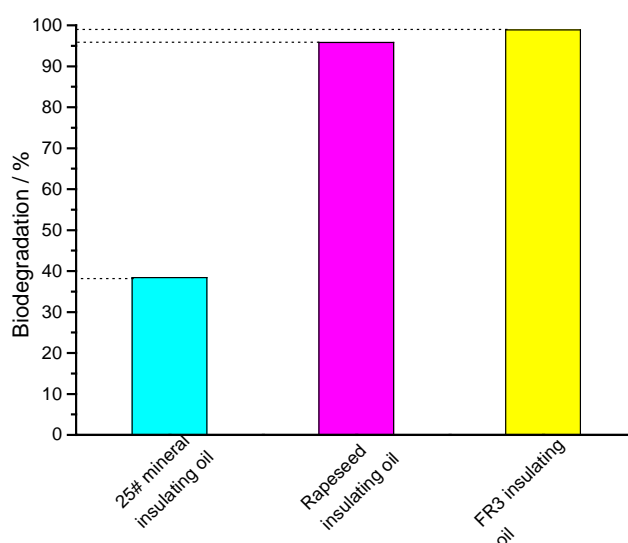


Figure 4. Biodegradation degree of the three oils' in 28d degradation process.

3.2 The mechanism of insulating oil biodegradation

The biodegradation process of insulating oil includes three phases: the hydrolysis of ester, the oxidation of long chain hydrocarbon, the oxidation and ring-opening of aromatic hydrocarbon [13]. The three phases are closely related to the activation energy of test substance. The experimental results show that biodegradation degree of 25# mineral insulating oil is less than rapeseed insulating oil and FR3 insulating oil, which is mainly because 25# insulating oil consists of isoalkane, cyclanes and a few arenes. Besides, it contains a few unsaturated bond. Therefore, the hydrolysis reaction of 25# mineral insulating oil is very difficult. However, rapeseed insulating oil and FR3 insulating oil mainly consist of triglyceride, which can be hydrolysed in alkaline, acidic and even neutral conditions. The activation energy of hydrolysis and the hydrolysis rate that meet the Arrhenius's law can be written in the following form [16].

$$K = A \cdot \exp\left(-\frac{E_a}{RT}\right) \quad (3)$$

Where k is the rate constant; T is the absolute temperature (in kelvins); A is the pre-exponential factor, a constant for each chemical reaction; E_a is the activation energy for the reaction (kJ mol⁻¹); R is the universal gas constant (kJ mol⁻¹ K⁻¹). During the biodegradation process, the variable of A, R and T remain unchanged. Therefore, the activation energy is inversely proportional to the hydrolysis rate of test substance, and it can be reflected by iodine value. Hydrolysis rate is positively correlated with iodine value [17]. Obviously, hydrolysis rate is positively correlated with iodine value. The iodine value of rapeseed insulating oil is 120 (lg/100g), and the iodine value of FR3 insulating oil is 130 (lg/100g). Hence, the hydrolysis rate of FR3 insulating oil is greater than the rapeseed insulating oil. Therefore, the biodegradation degree of FR3 insulating oil is more than rapeseed insulating oil.

4. Conclusions

In this paper, biodegradation performance of the rapeseed insulating oil, FR3 insulating oil and 25# insulating oil was studied by means of rapid biodegradation method, which was performed following OECD 301B. The results indicate that 25# mineral insulating oil is hardly biodegradable. The main reason is that 25# mineral insulating oil consists of isoalkanes, cyclanes, arenes, which have a few unsaturated bonds. The biodegradation degree of FR3 insulating oil is higher than rapeseed insulating oil because FR3 insulating oil can more easily hydrolyze. Test results show that the biodegradation degrees of 25# mineral insulating oil, FR3 insulating oil and rapeseed insulating oil are 38.4%, 98.9% and 95.8% respectively. "New chemical risk assessment guidelines" (HJ/T 154 - 2004) indicates that the chemical substances of rapeseed insulating oil and FR3 insulating oil can be more easily biodegraded, thus rapeseed insulating oil and FR3 insulating oil are classified as environmentally-friendly insulating oils.

Acknowledgment

The authors gratefully acknowledge the financial support from the national grid technology project (GY71-15-043).

References

- [1] Mukaiyama Y, Nonaka F, Takagi I, et al. 1991 Development of a perfluorocarbon liquid immersed prototype large power transformer with compressed SF₆ gas insulation *IEEE Transactions on Power Delivery* **6**(3) 1108-1116
- [2] Stebbins R D, Myers D S, Shkolnik A B 2003 Furanic compounds in dielectric liquid samples: review and update of diagnostic interpretation and estimation of insulation ageing *International Conference on Properties and Applications of Dielectric Materials*, 2003 IEEE 921-926
- [3] Wang X, Wang Z D. 2012 Study of dielectric behavior of ester transformer liquids under ac voltage *IEEE Transactions on Dielectrics & Electrical Insulation* **19**(6) 1916-1925
- [4] Rouse T O 1998 Mineral insulating oil in transformers *IEEE Electrical Insulation Magazine*

14(3) 6-16

- [5] Lukić J, Orlović A, Spiteller M, et al. 2006 Re-refining of waste mineral insulating oil by extraction with N -methyl-2-pyrrolidone *Separation & Purification Technology* **51(2)** 150-156
- [6] Hoai P M, Ngoc N T, Minh N H, et al. 2010 Recent levels of organochlorine pesticides and polychlorinated biphenyls in sediments of the sewer system in Hanoi Vietnam *Environmental Pollution* **158(3)** 913-920
- [7] Seleznev V S, Liseikin A V, Bryksin A A, et al. 2014 What caused the accident at the Sayano-Shushenskaya hydroelectric power plant (SSHPP): A seismologist's point of view *Seismological Research Letters* **85(4)** 817-824
- [8] Sun D, Yang F, Liu Z, et al. 2010 Preparation of insulating oil from vegetable oil and its electrical characteristics *China Oils & Fats* **35** 11
- [9] Suleiman A A, Muhamad N A, Bashir N, et al. 2017 Moisture effect on conductivity of kraft paper immersed in power transformer vegetable-based insulation oils. *Iet Generation Transmission & Distribution* **11(9)** 2269-2274
- [10] Elkin I, Hildgen P 2013 Selective Synthesis of Glyceryl Tris[9,10-(threo)-dihydroxyoctadecanoate] *Journal of the American Oil Chemists Society* **90(10)** 1465-1474
- [11] T.V. Oommen 2002 Vegetable oils for liquid-filled transformers *IEEE Electrical Insulation Magazine* **18(1)** 6-11
- [12] Mansour D E A, Ammar A M 2017 Performance evaluation of environmentally friendly insulating oil under accelerated aging tests *Power Systems Conference. IEEE 2017 MEPCON* 927-931
- [13] Elzbieta Beran 2008 Experience with evaluating biodegradability of lubricating base oils *Tribology International* **41(12)** 1212-1218
- [14] He M, Mei C F, Sun G P, et al. 2016 The Effects of Molecular Properties on Ready Biodegradation of Aromatic Compounds in the OECD 301B CO2 Evolution Test *Archives of Environmental Contamination & Toxicology* **71(1)** 1-13
- [15] Wang K, Fang J H, Chen B S, et al. 2004 Fast Method For The Evaluation of Biodegradability of Lubricating Oils *Acta Petrolei Sinica* **20(6)** 74-78
- [16] Choi S H, Kim K S, Huh C S 2015 Dissolved Gas Analysis of Environment-Friendly Vegetable Insulating Oils **28(4)** 238-243
- [17] Hui Sun, Xiuyang Lu, Liang Chen 2007 Comparison of hydrolysis kinetics of different vegetable oils in near-critical water *Journal of Chemical Industry and Engineering (China)* **58(4)** 925-929