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Influence of Molecule Structure on Lightning Impulse Breakdown of Ester Liquids

Huaqiang Li [1,*], Linfeng Xia [1], Shengwei Cai [2], Zhiqiang Huang [3], Jiaqi Li [4] and Lisheng Zhong [1,*]

[1] State Key Laboratory of Electrical Insulation and Power Equipment, Xi'an Jiaotong University, Xi'an 710049, China; xialinfeng@ha.sgcc.com.cn
[2] State Key Laboratory of Power Grid Environmental Protection, China Electric Power Research Institute Wuhan Branch, Wuhan 430074, China; caishengwei@epri.sgcc.com.cn
[3] Transformer Division CHINT Electric Co., Ltd., Shanghai 201614, China; hzhiq@chint.com
[4] Department of Smart Grid Information Engineering, School of Electrical Engineering, Hefei University of Technology, Hefei 230009, China; 2019212235@hfut.edu.cn
* Correspondence: lhqxjtu@mail.xjtu.edu.cn (L.H.); lszhong@mail.xjtu.edu.cn (Z.L.)

Abstract: Ester liquids are environmentally friendly insulating oils, and they can be used as an alternative to mineral oil in transformers, even though in most countries spills of ester oils must be treated like spills of mineral oil. Furthermore, the breakdown characteristics of ester liquids are worse than those of mineral oils in heterogeneous electric fields. In this paper, we present a comprehensive experimental research on both positive and negative lightning impulse breakdown properties in point-plane geometries with gaps varying from 1 mm to 50 mm. The breakdown voltages and streamer velocities of five kinds of ester liquids, including natural ester, synthetic ester, and three kinds of single component esters have been measured. The results show that the double bonds have no effect on the breakdown voltage of ester liquids. The average streamer velocities of mono-esters are faster than that of other esters under positive polarity, and the breakdown voltages of all esters are close.

Keywords: streamer; breakdown; ester liquids; natural ester; lightning impulse

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Citation: Li, H.; Xia, L.; Cai, S.; Huang, Z.; Li, J.; Zhong, L. Influence of Molecule Structure on Lightning Impulse Breakdown of Ester Liquids. *Energies* **2021**, *14*, 1061. https://doi.org/10.3390/en14041061

Academic Editor: Huseyin Hiziroglu

Received: 26 January 2021
Accepted: 3 February 2021
Published: 18 February 2021

1. Introduction

Ester liquids, such as natural ester, synthetic ester, and mono-ester, are environmentally friendly insulating oils. In recent years, many traditional mineral oil transformers have been retrofilled by natural or synthetic ester, which can prolong the life of insulating paper in transformers. However, the utilization of nature or synthetic ester will also lead to problems, such as higher temperature rise, insulation dielectric loss, lower insulation resistance of transformers, and so on [1]. In addition, the electrostatic charging tendency of natural ester insulating oil is also higher than that of mineral insulating oil [2]. Additionally, in most countries, local regulations require that spills of ester oils must be treated like spills of mineral oil.

Furthermore, in heterogeneous electric fields, the breakdown characteristics of ester liquids are not as good as mineral oils. In addition, the lightning impulse breakdown voltage of ester liquids with different molecular structures has been rarely studied. Therefore, it is necessary to carry out the fundamental research on esters liquids breakdown properties under point-plane gaps.

Studies on the breakdown and pre-breakdown phenomena of liquids have been conducted since 1950 s [3]. Like in gases, the different stages establishing the breakdown of liquids is generally called "streamers" also [4], but physical mechanisms of streamers involved in liquids certainly widely differ from in gases. The identification and modeling of physical mechanisms in liquids are less advanced compared to gases as well. The development of streamers in liquid can be divided into two stages: initiation (also called ignition and inception) and propagation. According to the different streamer velocity and shape, Streamers in liquids can be classified in first, second, third, and fourth modes depending on their velocity under positive voltage, and in primary and secondary modes under negative voltage for same reasons [5,6], as shown in Table 1.

Table 1. Streamer development modes of liquids.

Polarity	Modes	Streamer Velocities
Positive	1st	About 100 m/s
	2nd	1–5 km/s
	3rd	10–30 km/s
	4th	>100 km/s
Negative	primary	About 1 km/s
	secondary	>5 km/s

Studies on the breakdown characteristics of ester liquids began in the 2000 s [7,8]. Since the traditional transformer mineral oil has accumulated abundant research data, the studies of ester liquids usually take mineral oil as a sample at the same time for data calibration.

At present, there are many studies on natural and synthetic esters [7–25]. Under uniform or quasi-uniform electric fields the breakdown voltages of natural esters are close to that of mineral oils [8]. However, it is quite different under heterogeneous fields, such as when point-plane and point-sphere electrodes are applicated. Under the nonuniform field, with positive lightning voltage, at 5–25 mm electrode gaps, the breakdown voltages of natural and synthetic esters are close to those of mineral oils [9–11]; at 50–150 mm gaps, the breakdown voltages of natural and synthetic esters are lower than that of mineral oils [10]. However, in [12] it was shown that, at 50 mm gaps, with positive lightning voltage, the breakdown voltages of natural are close to that of mineral oils. With negative lightning voltage, at 5–150 mm gaps, the breakdown voltages of natural and synthetic esters are close to that of mineral oils [10]. In addition, the long pulse or switching wave breakdown voltage of natural ester and synthetic ester is also inferior to that of mineral oil in large gap heterogeneous field [7,9,12,13], but at 2–50 mm gaps, the initiation voltages of natural and synthetic esters are close to that of mineral oils [14–16].

Mono-ester is also called low-viscosity natural ester or synthetic ester, and it was called mono-ester in this paper according to IEC 62770. Under the non-uniform field, with positive lightning voltage, at 25 mm electrode gaps, the breakdown voltages of mono-ester are slightly lower than that of natural ester, and the streamer velocity of mono-ester are higher than that of natural ester; with negative lightning voltage, the breakdown voltages and streamer velocity of mono-ester are close to those of natural ester [9–11,18]. At 30 mm gaps, the streamer velocities of mono-ester are higher than that of mineral oil [17]. With negative lightning voltage, at 100 mm electrode gaps, the breakdown voltages and streamer velocity of mono-ester are close to those of natural ester [12].

In order to enhance the breakdown voltage of ester liquids, a large number of nano-additives have been studied [26], including Fe_3O_4 [27–30], TiO_2 [31–34], SO_2 [34–37], h-BN [38], BN [39], and Al_2O_3 [40,41]. These nano-additives improve the breakdown voltage of insulating oil, however, agglomeration, dispersion techniques, long-term stability, mass production, and cost are still a challenging.

As a whole, for the breakdown of liquids, at least four mechanisms can be identified: (1) bubble, (2) microexplosive, (3) ionization, and (4) electrothermal. From the experimental, the liquid phase transition, ionization, electrode size, liquid volume, static pressure, liquid molecular structure and so on have a significant influence on the experimental results, so scholars cannot obtain unified experimental data, and the previous research objects were mixtures of esters, which never included single component esters. Therefore, in this paper, single-component esters and commercial ester liquids are listed as the research object to study the effect of molecular structure on the breakdown of ester liquids.

2. Materials and Methods

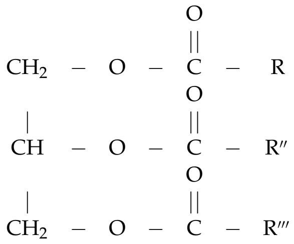
2.1. Investigated Liquid Dielectrics

Five types of ester liquids and one traditional naphthenic based mineral oil were investigated in this work: Synthetic ester Midel 7131, which is a mixture of pentaerythritol esters and is made by M&I Materials Ltd., Manchester, United Kingdom; rapeseed-based natural ester, which is a mixture of triglyceride esters and is made by Guangdong Zhuoyuan New Material Technology Co., Ltd., Zhongshan, China; glycerin trioleate, ethyl oleate, and ethyl linoleate, which are made by Shanghai Gaoming Chemical Co., Ltd., Shanghai, China; and Mineral KI25X, which is made by the PetroChina lubricant company, Karamay, China. Their molecular structures are shown in Equations (1)–(5), where the R, R′, R″, and R″′ stands for multiple hydrocarbon chains. Midel 7131® is a synthetic ester conforming to IEC 61099, and it has four ester groups indicated by '–COOR' at the end of a cross structure, and the four 5–10 length hydrocarbon chains could be either the same or different. Natural ester is refined from vegetable oil, which mainly originated from soya bean, rapeseed, and sunflower. Its main ingredient is triglycerides, which are fatty molecules formed by glycerol, three saturated and unsaturated fatty long-chain fatty acids conforming to IEC 62770. The fat has up to 22 carbon-length chains containing 1–3 double bonds, as shown in Equation (1). Glycerin trioleate is a special kind of triglyceride, and its molecule formed by glycerol and three oleic acid (which has 18 carbon-length chains containing one double bond), as shown in Equation (2). Ethyl oleate and ethyl linoleate are mono-esters-type conforming to IEC 62770, and both have 18 carbon length chains, whereas ethyl oleate contains one double bond, and ethyl linoleate contains two double bonds, as shown in Equations (4) and (5). All ester liquids are more polar than traditional mineral oil with the hydrocarbon-based molecular structure. For ester liquids, the relative permittivity is, therefore, higher, and the volume resistivity is lower than that of mineral oil. The differences in molecular structures of the above esters are shown in Table 2.

Table 2. The difference of ester molecular structure.

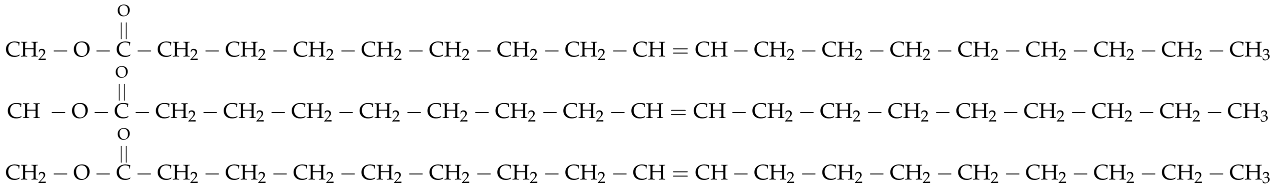
Properties	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate
Main components	Pentaerythritol esters mixture	Triglycerides mixture	Glycerin trioleate	Ethyl oleate	Ethyl linoleate
Carbon length of fatty acids	5–10	16–22	18	18	18
Double bonds in molecule	0	0–9	3	1	2
Ester bonds in molecule	4	3	3	1	1

A highly refined naphthenic based mineral oil KI25X was tested during all the experiments, as the benchmark for cross-comparison between esters and mineral oil.



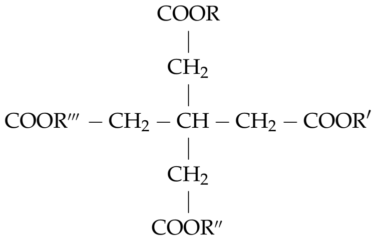
$$\begin{array}{ccccccc} & & & & \mathrm{O} & & \\ & & & & \| & & \\ \mathrm{CH_2} & - & \mathrm{O} & - & \mathrm{C} & - & \mathrm{R} \\ & & & & \mathrm{O} & & \\ | & & & & \| & & \\ \mathrm{CH} & - & \mathrm{O} & - & \mathrm{C} & - & \mathrm{R''} \\ & & & & \mathrm{O} & & \\ | & & & & \| & & \\ \mathrm{CH_2} & - & \mathrm{O} & - & \mathrm{C} & - & \mathrm{R'''} \end{array} \quad (1)$$

Triglyceride ester



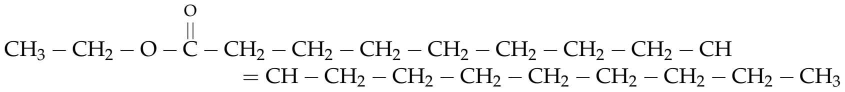
$$\begin{array}{l} \mathrm{CH_2-O-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3} \\ \mathrm{CH\ -O-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3} \\ \mathrm{CH_2-O-\overset{\overset{\large O}{\|}}{C}-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH=CH-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_2-CH_3} \end{array} \quad (2)$$

Glycerin trioleate



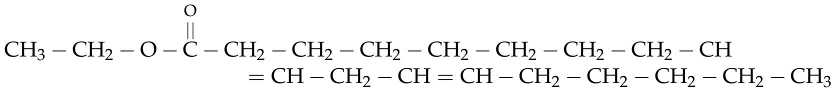
$$\begin{array}{c} COOR \\ | \\ CH_2 \\ | \\ COOR''' - CH_2 - CH - CH_2 - COOR' \\ | \\ CH_2 \\ | \\ COOR'' \end{array} \tag{3}$$

Pentaerythritol ester



$$\begin{array}{l} CH_3 - CH_2 - O - \overset{\overset{O}{\|}}{C} - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH \\ \qquad\qquad\qquad\qquad = CH - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \end{array} \tag{4}$$

Ethyl oleate



$$\begin{array}{l} CH_3 - CH_2 - O - \overset{\overset{O}{\|}}{C} - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH_2 - CH \\ \qquad\qquad\qquad\qquad = CH - CH_2 - CH = CH - CH_2 - CH_2 - CH_2 - CH_2 - CH_3 \end{array} \tag{5}$$

Ethyl linoleate

The basic properties of the investigated liquids are given in Table 3. For comparison, the properties of silicone oil are also listed.

Table 3. Basic properties of the investigated liquids and silicone oil.

Properties	Unit	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate	Mineral Oil	Silicone Oil
Density (20 °C)	kg/m^3	0.97	0.92	0.92	0.87	0.88	0.88	0.96
Viscosity (0 °C)	mm^2/s	240	234	236	22.1	21.9	38	93
Viscosity (40 °C)		28	36	37	6.3	6.3	8.1	39
Viscosity (100 °C)		5.0	7.9	8.0	2.2	2.1	2.6	15
Heat capacity (20 °C)	kJ/kg·K	1.88	1.85	1.85	1.95	1.95	1.86	1.51
Thermal conductivity (20 °C)	W/m·K	0.144	0.177	0.177	0.132	0.132	0.126	0.157
water content	ppm	20	15	15	12	12	5	8
tan δ (90 °C)		0.03	0.02	0.04	0.04	0.04	0.001	0.001
relative permittivity		3.2	3.2	3.2	2.95	2.95	2.2	2.5

Mineral oil, synthetic ester, and natural ester were from the insulating oil manufacturers, and glycerin trioleate, ethyl laurate, ethyl oleate, and ethyl linoleate came from a same chemical manufacturer. Although the impulse lightning breakdown voltages of insulating liquids are normally not sensitive to water or particle contamination, we still filtered and dehydrated these liquids to ensure the consistency of the experimental conditions.

2.2. Experimental Method

Figure 1 schematically shows the test cell and point-plane electrode systems. A cubic test cell (made of transparent Perspex with volume of 3 L) was used to hold the liquid samples and point-plane electrodes. Needle electrodes made of lanthanum tungsten alloy containing 1.5% lanthanum oxide was used, and the tip radius of curvature for the needle electrodes was guaranteed to be in the range of (50 ± 5) µm after using a microscope. The plane electrode is made of brass with a diameter of 80 mm and edge radius of 10 mm.

A Marx generator provided positive and negative standard lightning impulse voltage (1.2/50 µs). The waveforms of breakdown voltage and flashover voltage were recorded by a potential divider and an oscilloscope. The breakdown time can be observed from the voltage waveform of the oscilloscope, as shown in Figure 2. During breakdown tests, a current limit resistor (5 kΩ) was added in the circuit to limit the breakdown current, and further protect the liquid sample and point electrode.

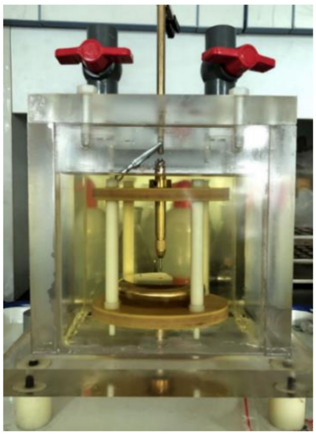


Figure 1. Test cell and point-plane electrode.

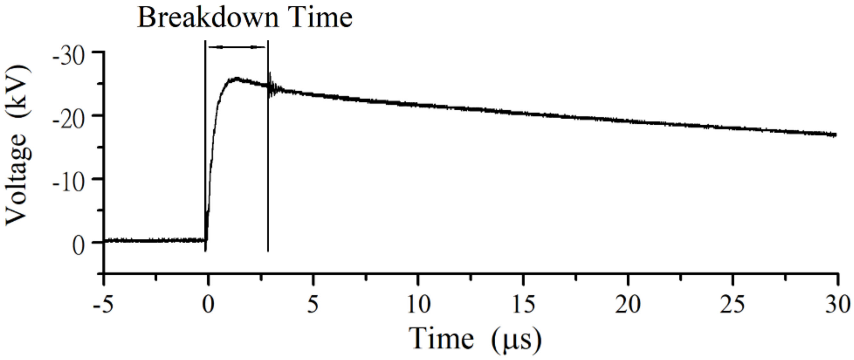


Figure 2. Impulse voltage waveform during breakdown.

The gaps were arranged with 1 mm, 5 mm, 15 mm, 25 mm, and 50 mm. For each gap, 20 times of lighting impulse breakdown were carried out. According to our previous exploratory trials, it was acceptable to replace the liquid sample and point needle electrode after 20 tests. The change of needle electrode before and after the test is shown in Figure 3. All the experiments were carried out at room temperature and ambient pressure.

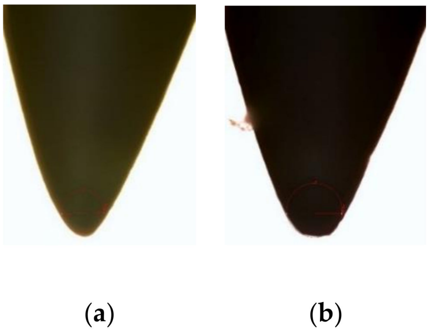

(**a**) (**b**)

Figure 3. lanthanum tungsten needle electrodes before and after 20 tests: (**a**) before tests; (**b**) after tests.

In this paper, there was a concern with respect to the positive and negative impulse lightning breakdown voltage and streamer propagation velocity. The experimental data were processed by Weibull distribution.

Breakdown voltage was measured by using step up rising voltage procedure. The initial voltage was set at the expected breakdown voltage of about 50–80%. Voltage level increased step-by-step (one shot per step) with the increment of about 2.5 kV or 5 kV depending on the gap distance or expected breakdown voltage. Twenty breakdowns per sample were carried out before changing the electrode and liquid sample. At least a

2 min break was given between breakdowns to make the discharge by-products and gas bubbles diffuse.

Two-parameter Weibull distribution is used to describe the breakdown results of the insulating oils. The distribution function is expressed as:

$$F(x) = 1 - \mathrm{e}^{-(\frac{x}{\alpha})\beta} \tag{6}$$

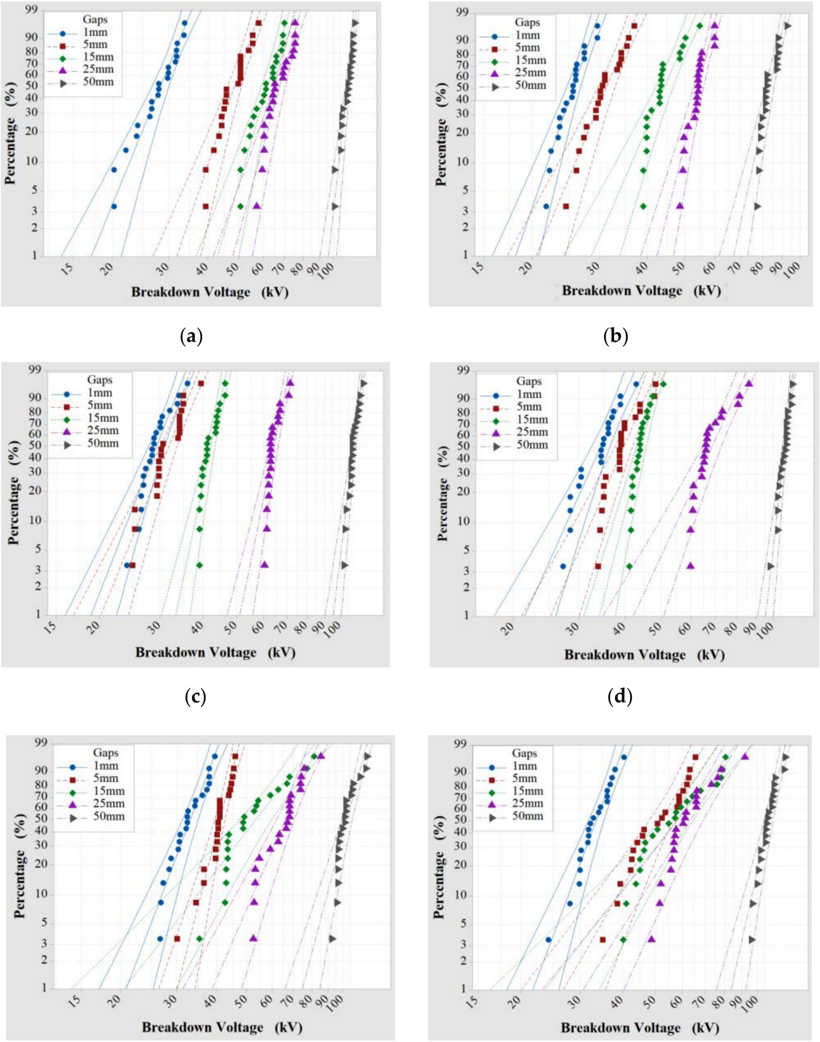
where α is the scale parameter; β is the shape parameter; x is a variable; and F is the failure probability.

The scale parameter α is the breakdown field strength of insulating oil, when the failure probability is 63.2%. The dispersion of breakdown data can be expressed by shape parameter β. The larger the shape parameter beta is, the smaller the dispersion of breakdown data is. All probability distribution figures in this paper are 95% confidence intervals.

3. Results

3.1. Positive Impulse Lightning Breakdown Voltage

The 95% confidence interval Weibull failure probability distributions of positive lightning breakdown voltages for insulating liquids are shown in Figure 4.



(**a**) (**b**)

(**c**) (**d**)

(**e**) (**f**)

Figure 4. Weibull failure probability distribution of positive breakdown voltages of insulating liquid samples: (**a**) Mineral oil; (**b**) Synthetic ester; (**c**) Natural ester; (**d**) Glycerin trioleate; (**e**) Ethyl oleate; (**f**) Ethyl linoleate.

The 50% positive breakdown voltage, V_{pb}, was calculated, and the results are shown in Table 4.

Table 4. The 50% positive breakdown voltages of insulating liquids (kV).

Electrode gaps/mm	Mineral Oil	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate
1	28.3	25.6	29.3	34.3	33.2	33.5
5	48.6	31.2	31.8	39.6	41.1	51.9
15	61.7	44.2	42.1	44.2	53.3	57.8
25	67.6	54.4	64.2	68.3	66.0	63.3
50	110.7	83.3	109.3	107.5	103.2	107.8

For the convenience of visual observation, the 50% positive breakdown voltages of insulating liquids are drawn as Figure 5.

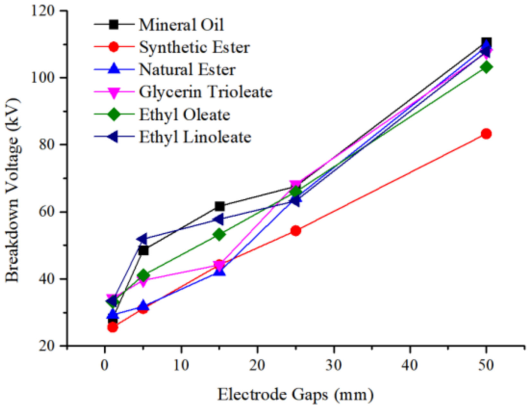


Figure 5. The 50% positive breakdown voltages of insulating liquids.

It can be seen from Figure 5, as a whole, the positive lightning breakdown voltage of the synthetic ester is lower than others. Additionally, at 1–15 mm gaps, although there are great differences in V_{pb}, there are no obvious rules; at 25 mm and 50 mm gaps, the V_{pb} of mineral oil is slightly higher than that of ester liquids, and the V_{pb} of all ester liquids are close to each other, except for synthetic ester. It should be noted that in our previous studies, the V_{pb} of mineral oil is 1.28 times that of natural ester, contrasting to 1.01 times that in this paper. The difference is that the container and grounding electrode used in this paper are smaller than previous studies (80 mm vs. 120 mm, 3 L vs. 25 L). The results of previous studies are also shown in Figure 6.

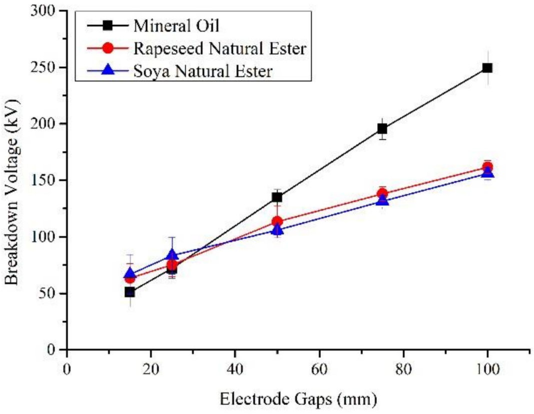


Figure 6. The average positive breakdown voltages of insulating liquids.

Average streamer propagation velocity (v_a) is calculated by the ratio of gap distance d to breakdown time T_b. Table 5 presents the results of average streamer propagation velocity under positive polarity.

Table 5. Positive average streamer velocities of insulating liquids (km·s^{-1}).

Electrode Gaps/mm	Mineral Oil	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate
1	0.56	0.44	0.33	0.47	0.65	0.57
5	1.63	1.07	1.12	1.13	1.54	1.98
15	1.98	1.52	1.46	1.43	2.08	2.05
25	2.06	1.78	1.60	1.60/14.04	2.09	2.06
50	2.29	2.56	1.75	2.23/15.19	2.23	2.25

It can be seen from Table 5, at 1–15 mm gaps, the streamer velocities of mineral oil and mono-esters are faster than other esters, the same as Devins [42]. At 25 mm gaps, streamer velocities of mineral oil and mono-esters are still faster than others, except for glycerin trioleate. At 50 mm gaps, streamer velocities of mineral oil, mono-esters, and synthetic ester are similar, and streamers of natural ester are slower than mineral oil, mono-esters, and synthetic ester. Moreover, at 25 mm and 50 mm gaps, glycerin trioleate has two different streamer velocities, with the slower one is similar with other esters and the faster one is faster than any other insulating liquids. This means that there are two modes (2nd and 3rd) of streamer under this condition. However, there are no significant differences between the breakdown voltage of glycerin trioleate and other insulating liquids at 25 mm and 50 mm gaps.

3.2. Negative Impulse Lightning Breakdown Voltage

The 95% confidence interval Weibull failure probability distribution of the negative lightning breakdown voltages (V_{nb}) for insulating liquids is shown in Figure 7.

The 50% negative breakdown voltages, V_{nb}, were calculated, and the results are shown in Table 6.

Table 6. The 50% negative breakdown voltages of insulating liquids (kV).

Electrode gaps/mm	Mineral Oil	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate
1	29.8	25.9	25.8	25.8	27.9	27.9
5	61.7	37.0	41.1	42.1	38.3	38.6
15	113.2	63.2	69.6	69.2	63.4	62.0
25	149.6	88.9	96.7	95.7	87.0	91.2
50	257.2	149.6	166.0	166.3	170.7	167.7

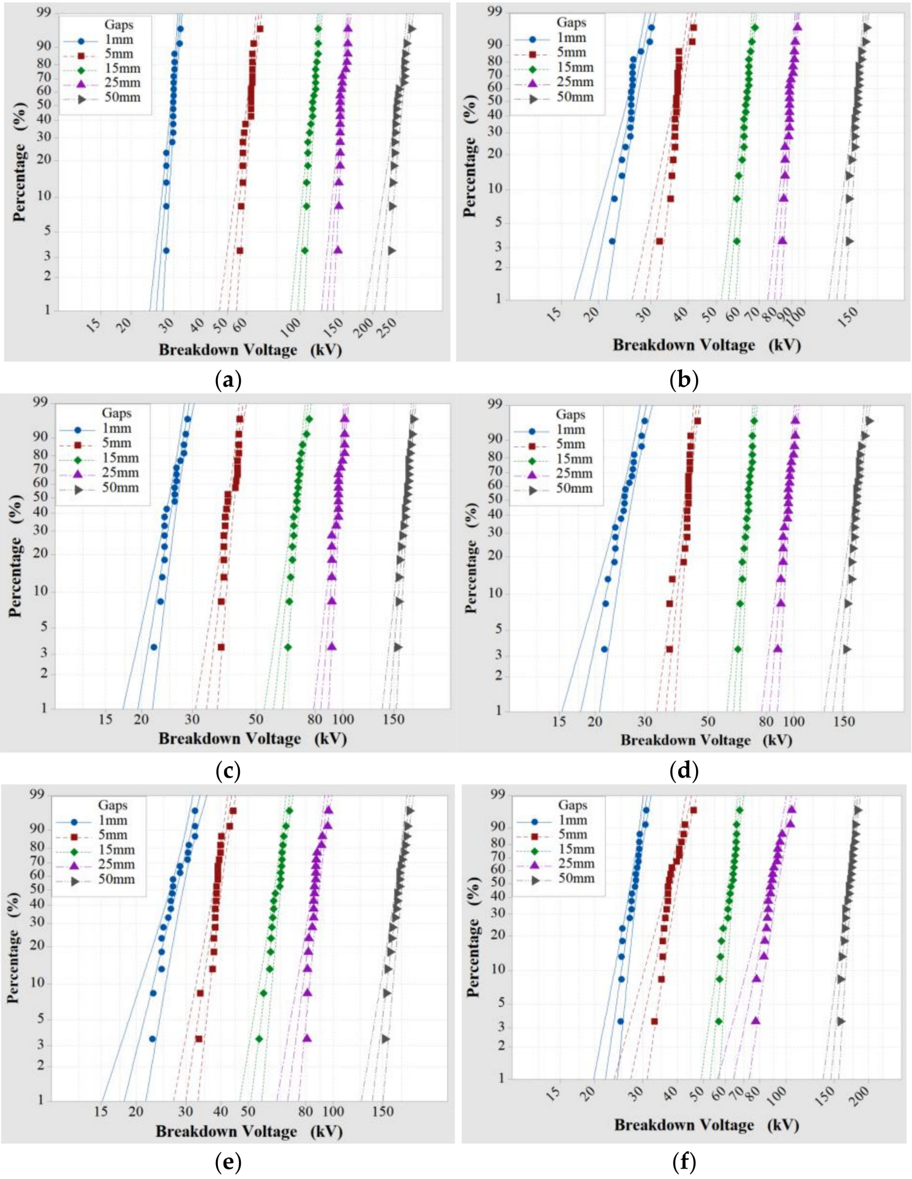
For the convenience of visual observation, the 50% negative breakdown voltages of insulating liquids are drawn as shown in Figure 8.

It can be seen from Table 6 that the negative breakdown voltages of mineral oil are always higher than those of ester liquids, and the differences increase with the extension of gaps distance. As the results of positive breakdown voltage show, the negative breakdown voltage of synthetic ester is still slightly lower than other insulating liquids, consistent in [11]. In addition, the negative breakdown voltages of other esters are quite close.

Table 7 presents the results of the average streamer propagation velocities of insulating liquids under negative polarity.

Table 7. Negative streamer average velocities of insulating liquids (km·s^{-1}).

Electrode gaps/mm	Mineral Oil	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate
1	0.14	0.35	0.36	0.47	0.42	0.45
5	0.44	0.66	0.84	0.87	0.92	1.01
15	0.94	0.69	1.04	0.98	0.95	1.05
25	0.98	0.71	1.10	1.10	0.97	1.10
50	1.17	0.87	1.12/3.85	1.21/5.36	1.19	1.17



(**a**) (**b**) (**c**) (**d**) (**e**) (**f**)

Figure 7. Weibull failure probability distribution of negative breakdown voltages of insulating liquid samples: (**a**) Mineral oil; (**b**) Synthetic ester; (**c**) Natural ester; (**d**) Glycerin trioleate; (**e**) Ethyl oleate; (**f**) Ethyl linoleate.

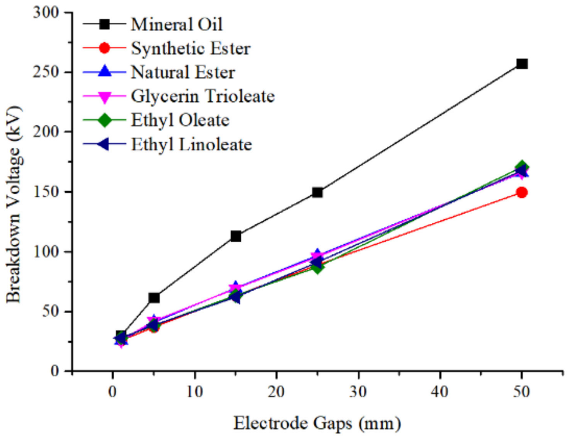


Figure 8. The 50% negative breakdown voltages of insulating liquids.

It can be seen from Table 7 that the streamer velocity at negative polarity is less than that of positive polarity. The streamer velocities of synthetic ester are lower than those of other insulating oils, including other ester liquids, same as [11]. At 1–5 mm gaps, the streamer velocities of mineral oil are less than those of ester liquids. At 15–25 mm gaps, the streamer velocities of mineral oil are similar with other ester liquids except synthetic ester. At a 50 mm gap, the streamer velocities of mineral oil are similar with mono-esters. Additionally, at a 50 mm gap, natural ester and glycerin trioleate have two different streamer velocities, with the slower one is similar with other esters and the faster one is faster than any other insulating liquids. This means that there are two modes (primary and secondary) of streamer under this condition. However, there are no significant differences between the breakdown voltages of natural ester and glycerin trioleate and other insulating liquids at 50 mm gaps.

3.3. Data Dispersion

In order to more clearly show the deviation of the breakdown voltage experiment of insulating liquid, the modified relative standard deviation (*RSD*) was used to describe the data dispersion, and the relative standard deviation (*RSD*) of 50% breakdown voltage is defined as follows:

$$RSD = \frac{S}{50\%V_b} \times 100\% = \frac{\sqrt{\frac{\sum_{i=1}^{n}(x_i - 50\%V_b)^2}{n-1}}}{50\%V_b} \times 100\% \tag{7}$$

where S is the standard deviation; $50\%V_b$ is the 50% breakdown voltage; n is the number of breakdown tests.

The relative standard deviations of positive and negative breakdown voltages are shown in Tables 8 and 9, respectively.

Table 8. The *RSD* of 50% positive breakdown voltages.

Electrode Gaps/mm	Mineral Oil	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate
1	14.9%	8.6%	10.3%	12.3%	12.5%	11.7%
5	11.1%	9.5%	12.0%	10.7%	9.6%	18.4%
15	10.4%	10.8%	5.8%	5.5%	23.4%	23.0%
25	9.1%	9.6%	4.8%	10.9%	13.7%	16.6%
50	4.4%	9.1%	3.4%	3.4%	7.2%	6.2%

Table 9. The *RSD* of 50% negative breakdown voltages.

Electrode Gaps/mm	Mineral Oil	Synthetic Ester	Natural Ester	Glycerin Trioleate	Ethyl Oleate	Ethyl Linoleate
1	3.9%	7.5%	7.6%	9.7%	11.2%	6.7%
5	5.2%	5.5%	5.6%	5.6%	6.4%	8.2%
15	4.2%	3.7%	4.4%	3.6%	6.1%	5.5%
25	3.2%	3.2%	3.8%	4.2%	5.1%	8.2%
50	5.5%	3.9%	3.8%	4.3%	5.8%	4.4%

It can be seen from Tables 8 and 9, at 1–25 mm gaps, the relative standard deviations of positive breakdown voltages are much larger than that of negative breakdown voltages, and this means that the stability of the positive experimental results is worse than those of the negative. At 50 mm gap, the relative standard deviation of positive breakdown decreases and is close to that of negative breakdown voltage.

4. Discussion

For the positive breakdown, the dispersion of positive breakdown voltages in 1–15 mm gaps is large, and there are no obvious rules between ester liquids and mineral oil. This implies that the space charge may be involved in the breakdown process. Similar to the polarity effect in gas, there are positive ions that accumulate near the positive needle tip and, thus, space charges are formed. Due to the influence of impurities in engineering insulating liquids, the dispersion of liquid in small areas are not uniform, and so the space charge is unstable. Consequently, the positive breakdown voltages are irregular. As the gaps and voltages in the gaps increase, the space charge tends to be saturated, and its influence on electric field distribution is reduced. Thus, at 25–50 mm gaps, the experimental results are stable gradual with the increase of gap and the breakdown voltages are close to the intrinsic breakdown voltages of insulating liquids. According to the report from Lesaint [43], the inception mechanism of positive and negative polarity streamers may be the same. Thus, if the space charges affect the breakdown voltages, this means that the inception voltages of positive streamer should be a little higher than that of negative streamer at smaller electrode gaps. According to the data in [15], at 15 mm gaps, for both ester liquids and mineral oil, our hypothesis is true. Namely, at 20 mm gaps, with the decrease influence of space charge, the inception voltages of positive streamer are similar to negative streamers.

For the negative breakdown, the negative breakdown voltages of mineral oil are always higher than those of ester liquids, and these of ester liquids are similar to each other. Under the same experimental conditions, the differences of breakdown voltages between ester liquids and mineral oil undoubtedly resulted from the difference of their molecular structures. The largest difference between ester liquids and mineral oil are the ester bonds. That means the ester bond plays a decisive role in the lower negative breakdown voltage of ester liquids. The synthetic ester has the most ester bonds in the same volume, so its breakdown voltages are the lowest, same as [17].

Li calculated the ionization potential of ester molecules [44]. The molecules ionization potentials range of ester insulating oil are 7.94 to 6.77 eV, and the largest contribution is double bond. The molecule with more double bond has lower ionization potential. In this paper, the double bond has little effect on the negative breakdown voltage of ester insulating oil. Cornering the differences in ethyl oleate and ethyl linoleate, their molecular structures are almost identical, except the double bonds of ethyl oleate is almost half of ethyl linoleate. In addition, natural ester and glycerin trioleate also have different double bonds. But their breakdown voltage is basically the same. That means the molecular ionization has little effect on the breakdown mechanism of ester insulating oil.

According to the discussion above, molecular ionization is unlikely to be the main mechanism of the breakdown of ester liquids. In addition, among liquid breakdown mechanisms [45], the ionic dissociation mechanism has the strongest correlation with ester bond.

The ester liquids are polar medium. Thus, a small part of them is separate into ions. The ion concentration n_0 is shown in Equation (8):

$$n_0 = \sqrt{\frac{N_0 v_0}{\xi}} \mathrm{e}^{-u_0/2\mathrm{k}T} \tag{8}$$

where n_0 is the ion concentration; v_0 is the relative thermal vibrational frequency between atomic clusters; ξ is the composite coefficient of ions; u_0 is the activation energy of ion pair dissociation; k is the Boltzmann constant; T is the absolute temperature.

Mineral oil is a non-polar medium, making it difficult to separate into ions. Therefore, ester liquids contain more ion pairs than mineral oil. During the process of breakdown, these ions are less stable than molecules, and easier to release electrons, consequently strengthening the process of collision ionization, and reducing breakdown voltage. Therefore, the negative impulse breakdown voltages of ester liquids are lower than those of mineral oil.

Under the action of external electric field, the activation energy of ion pair dissociation decreases with the increase of field strength, as described by the Poole–Frenkel effect. The effect is shown in Equations (9) and (10):

$$n_0 = \sqrt{\frac{N_0 v_0}{\xi}} \mathrm{e}^{-(u_0 - \Delta u_0)/2\mathrm{k}T} \tag{9}$$

$$\Delta n_0 = \sqrt{\frac{q^3 E}{\pi \varepsilon_0 \varepsilon_\mathrm{r}}} \tag{10}$$

where q is the charge of ions; E is the electric field strength; ε_0 is the permittivity of vacuum; ε_r is the relative dielectric constant.

It can be seen from Equations (9) and (10), with the increase of electric field, the potential energy of ion dissociation will decrease, and more ions will be found in ester oil. Thus, the difference among the breakdown voltages between ester liquids and mineral oil increases.

5. Conclusions

Breakdown properties, including breakdown voltage and streamer velocities of natural ester, synthetic ester, and three kinds of single component esters under positive and negative lightning impulse in heterogeneous electric fields, were studied in this paper. The conclusions are as follows:

1. The positive lightning breakdown voltage of the synthetic ester is lower than others. At 1–15 mm gaps, there are no obvious rules; at 25 mm and 50 mm gaps, the V_pb of mineral oil is slightly higher than that of ester liquids, and the V_pb of all ester liquids are close to each other except for synthetic ester. At 1–15 mm gaps, the streamer velocities of mineral oil and mono-esters are faster than other esters. At 25 mm and 50 mm gaps, glycerin trioleate have two different streamer velocities, but there are no significant influences on the breakdown voltage.
2. The negative breakdown voltages of mineral oil are always higher than those of ester liquids, and the differences increase with the extension of gaps distance. The V_nb of synthetic ester is still slightly lower than other insulating liquids. The V_nb of other esters are very close. The streamer velocity of negative polarity is less than that of positive polarity. The streamer velocities of synthetic ester are lower than those of other insulating oils. At 1–5 mm gaps, the streamer velocities of mineral oil are less than those of ester liquids. At 15–25 mm gaps, the streamer velocities of mineral oil are similar with other ester liquids except synthetic ester. At a 50 mm gap, the streamer velocities of mineral oil are similar with mono-esters. At a 50 mm gap, natural ester and glycerin trioleate have two different streamer velocities, but there are no significant influences on the breakdown voltage.
3. The space charge may be involved in the positive breakdown process. Thus, the positive breakdown voltages are irregular. As the gaps increase, the influence of space charge on electric field distribution reduces. At 1–25 mm gaps, the relative standard deviations of positive breakdown voltages are much larger than those of negative breakdown voltages. At a 50 mm gap, the relative standard deviation of positive breakdown decreases.
4. The ionic dissociation may contribute to the breakdown mechanism of ester liquids. Ester liquids can separate into ions. However, mineral oil is hard to separate. The ions strengthen the process of collision ionization, and reduce the breakdown voltage. Therefore, the negative impulse breakdown voltages of ester liquids are lower than those of mineral oil. With the increase of the electric field, the potential energy of ion dissociation will decrease, and more ions will be found in the ester oil. Thus, the difference of the breakdown voltages between ester liquids and mineral oil increases.

In future research, we will carry out further work to improve the breakdown voltage of ester liquids, such as adding additives or modify their molecules, and so on.

Author Contributions: Conceptualization, L.H., C.S. and H.Z.; investigation, L.H. and X.L.; resources, H.Z.; data curation, X.L. and J.L.; writing, L.H.; supervision, Z.L.; funding acquisition, C.S. All authors have read and agreed to the published version of the manuscript.

Funding: This research was funded by [Open Fund of State Key Laboratory of Power Grid Environmental Protection, State Key Laboratory of Power Grid Environmental Protection, China Electric Power Research Institute Wuhan Branch, Wuhan 430074, China], grant number [GYW51201801177]. This research was funded by [China Postdoctoral Science Foundation], grand number [2019M653630].

Institutional Review Board Statement: Not applicable.

Informed Consent Statement: Not applicable.

Data Availability Statement: The data presented in this study are available on request from the corresponding author. The data are not publicly available due to fund requirements.

Acknowledgments: The fund supports from Open Fund of State Key Laboratory of Power Grid Environmental Protection (no. GYW51201801177), State Key Laboratory of Power Grid Environmental Protection, China Electric Power Research Institute Wuhan Branch, Wuhan 430074, China. This research was partly supported by the China Postdoctoral Science Foundation, no. 2019M653630. All support is gratefully acknowledged.

Conflicts of Interest: The authors declare no conflict of interest.

References

1. Garcia, B.; Ortiz, A.; Renedo, C.; Burgos, J.C.; Gomez, D.G.; Rosa, D.P. Application of biodegradable fluids as liquid insulation for distribution and power transformers. In Proceedings of the 2020 IEEE International Conference on Environment and Electrical Engineering and 2020 IEEE Industrial and Commercial Power Systems Europe (EEEIC/I&CPS Europe), Madrid, Spain, 9–12 June 2020; pp. 1–6.
2. Zdanowski, M. Electrostatic Charging Tendency Analysis Concerning Retrofilling Power Transformers with Envirotemp FR3 Natural Ester. *Energies* **2020**, *13*, 4420. [CrossRef]
3. Sharbaugh, A.H.; Devins, J.C.; Rzad, S.J. Progress in the Field of Electric Breakdown in Dielectric Liquids. *IEEE Trans. Electr. Insul.* **1978**, 249–276. [CrossRef]
4. Beroual, A.; Zahn, M.; Badent, A.; Kist, K.; Schwabe, A.J.; Yamashita, H.; Yamazawa, K.; Danikas, M.; Chadband, W.D.; Torshin, Y. Propagation and structure of streamers in liquid dielectrics. *IEEE Electr. Insul. Mag.* **1998**, *14*, 6–17. [CrossRef]
5. Hebner, R.E. Measurement of Electrical Breakdown in Liquids. In *The Liquid State and its Electrical Properties*; Springer: Boston, MA, USA, 1988; pp. 519–537.
6. Lesaint, O.; Massala, G. Positive streamer propagation in large oil gaps: Experimental characterization of propagation modes. *IEEE Trans. Dielectr. Electr. Insul.* **1998**, *5*, 360–370. [CrossRef]
7. Duy, C.T.; Lesaint, O.; Denat, A.; Bonifaci, N. Streamer propagation and breakdown in natural ester at high voltage. *IEEE Trans. Dielectr. Electr. Insul.* **2009**, *16*, 1582–1594. [CrossRef]
8. Rapp, K.; Corkran, J.; McShane, C.P.; Prevost, T.A. Lightning Impulse Testing of Natural Ester Fluid Gaps and Insulation Interfaces. *IEEE Trans. Dielectr. Electr. Insul.* **2009**, *16*, 1595–1603. [CrossRef]
9. Peppas, G.D.; Charalampakos, V.P.; Gonos, I.F.; Pyrgioti, E.C.; Pyrgioti, E. Electrical and optical measurements investigation of the pre-breakdown processes in natural ester oil under different impulse voltage waveforms. *IET Sci. Meas. Technol.* **2016**, *10*, 545–551. [CrossRef]
10. Huang, Z.; Chen, X.; Li, J.; Wang, F.; Zhang, R.; Mehmood, M.A.; Liang, S.; Jiang, T. Streamer characteristics of dielectric natural ester-based liquids under long gap distances. *AIP Adv.* **2018**, *8*, 105129. [CrossRef]
11. Liu, Q.; Wang, Z.D. Streamer characteristic and breakdown in synthetic and natural ester transformer liquids under standard lightning impulse voltage. *IEEE Trans. Dielect. Electr. Insul.* **2011**, *18*, 285–294. [CrossRef]
12. Ngoc, M.N.; Lesaint, O.; Bonifaci, N.; Denat, A.; Hassanzadeh, M. A comparison of breakdown properties of natural and synthetic esters at high voltage. In Proceedings of the 2010 Annual Report Conference on Electrical Insulation and Dielectic Phenomena, West Lafayette, IN, USA, 17–20 October 2010; pp. 1–4.
13. Dang, V.-H.; Beroual, A.; Perrier, C. Investigations on streamers phenomena in mineral, synthetic and natural ester oils under lightning impulse voltage. *IEEE Trans. Dielectr. Electr. Insul.* **2012**, *19*, 1521–1527. [CrossRef]
14. Rozga, P. Streamer propagation in small gaps of synthetic ester and mineral oil under lightning impulse. *IEEE Trans. Dielectr. Electr. Insul.* **2015**, *22*, 2754–2762. [CrossRef]
15. Rozga, P.; Stanek, M. Characteristics of streamers developing at inception voltage in small gaps of natural ester, synthetic ester and mineral oil under lightning impulse. *IET Sci. Meas. Technol.* **2016**, *10*, 50–57. [CrossRef]

16. Rozga, P. Streamer propagation and breakdown in a very small point-insulating plate gap in mineral oil and ester liq-uids at positive lightning impulse voltage. *Energies* **2016**, *9*, 467. [CrossRef]
17. Sitorus, H.B.H.; Beroual, A.; Setiabudy, R.; Bismo, S. Pre-breakdown phenomena in new vegetable oil—Based jatropha curcas seeds as substitute of mineral oil in high voltage equipment. *IEEE Trans. Dielectr. Electr. Insul.* **2015**, *22*, 2442–2448. [CrossRef]
18. Rozga, P.; Stanek, M. Comparative analysis of lightning breakdown voltage of natural ester liquids of different viscosities supported by light emission measurement. *IEEE Trans. Dielectr. Electr. Insul.* **2017**, *24*, 991–999. [CrossRef]
19. Unge, M.; Singha, S.; Van Dung, N.; Linhjell, D.; Ingebrigtsen, S.; Lundgaard, L.E. Enhancements in the lightning impulse breakdown characteristics of natural ester dielectric liquids. *Appl. Phys. Lett.* **2013**, *102*, 172905. [CrossRef]
20. Rozga, P.; Tabaka, P. Comparative analysis of breakdown spectra registered using optical spectrometry technique in biodegradable ester liquids and mineral oil. *IET Sci. Meas. Technol.* **2018**, *12*, 684–690. [CrossRef]
21. Haegele, S.; Vahidi, F.; Tenbohlen, S.; Rapp, K.J.; Sbravati, A. Lightning Impulse Withstand of Natural Ester Liquid. *Energies* **2018**, *11*, 1964. [CrossRef]
22. Lu, W.; Liu, Q.; Wang, Z. Mechanisms of streamer leading to breakdown in synthetic ester liquid in uniform field. In Proceedings of the 2017 IEEE 19th International Conference on Dielectric Liquids (ICDL), Manchester, UK, 25–29 June 2017; pp. 1–4.
23. Rozga, P.; Stanek, M.; Rapp, K. Lightning properties of selected insulating synthetic esters and mineral oil in point-to-sphere electrode system. *IEEE Trans. Dielectr. Electr. Insul.* **2018**, *25*, 1699–1705. [CrossRef]
24. Reffas, A.; Moulai, H.; Béroual, A. Comparison of dielectric properties of olive oil, mineral oil, and other natural and synthetic ester liquids under AC and lightning impulse stresses. *IEEE Trans. Dielectr. Electr. Insul.* **2018**, *25*, 1822–1830. [CrossRef]
25. Sitorus, H.B.; Beroual, A.; Setiabudy, R.; Bismo, S. Comparison of streamers characteristics in jatropha curcas methyl ester oil and mineral oil under lightning impulse voltage. In Proceedings of the 2014 IEEE 18th International Conference on Dielectric Liquids (ICDL), Bled, Slovenia, 29 June–3 July 2014; pp. 1–4.
26. Contreras, J.E.; Rodriguez, E.A.; Taha-Tijerina, J. Recent Trends of Nanomaterials for High-Voltage Applications. In *Handbook of Nanomaterials for Industrial Applications*; Elsevier: Amsterdam, The Netherlands, 2018; Volume 39, pp. 724–738. [CrossRef]
27. Segal, V.; Hjortsberg, A.; Rabinovich, A.; Nattrass, D.; Raj, K. AC (60 Hz) and impulse breakdown strength of a colloidal fluid based on transformer oil and magnetite nanoparticles. In Proceedings of the Conference Record of the 1998 IEEE International Symposium on Electrical Insulation (Cat. No.98CH36239), Arlington, VA, USA, 7–10 June 1998; Volume 2, pp. 619–622. [CrossRef]
28. Segal, V.; Rabinovich, A.; Nattrass, D.; Raj, K.; Nunes, A. Experimental study of magnetic colloidal fluids behavior in power transformers. *J. Magn. Magn. Mater.* **2000**, *215*, 513–515. [CrossRef]
29. Nazari, M.; Rasoulifard, M.H.; Hosseini, H. Dielectric breakdown strength of magnetic nanofluid based on insula-tion oil after impulse test. *J. Magn. Magn. Mater.* **2016**, *399*, 1–4. [CrossRef]
30. Li, J.; Liao, R.; Yang, L. Investigation of natural ester based liquid dielectrics and nanofluids. In Proceedings of the 2012 International Conference on High Voltage Engineering and Application, Shanghai, China, 17–20 September 2012; pp. 16–21. [CrossRef]
31. Mansour, D.-E.A.; Atiya, E.G.; Khattab, R.M.; Azmy, A.M. Effect of titania nanoparticles on the dielectric properties of transformer oil-based nanofluids. In Proceedings of the 2012 Annual Report Conference on Electrical Insulation and Dielectric Phenomena, Montreal, QC, Canada, 14–17 October 2012; pp. 295–298. [CrossRef]
32. Pugazhendhi, S. Experimental evaluation on dielectric and thermal characteristics of nano filler added transformer oil. In Proceedings of the 2012 International Conference on High Voltage Engineering and Application, Shanghai, China, 17–20 September 2012; pp. 207–210. [CrossRef]
33. Katiyar, A.; Dhar, P.; Nandi, T.; Maganti, L.S.; Das, S.K. Enhanced breakdown performance of Anatase and Rutile titania based nano-oils. *IEEE Trans. Dielectr. Electr. Insul.* **2016**, *23*, 3494–3503. [CrossRef]
34. Koutras, K.N.; Naxakis, I.A.; Antonelou, A.E.; Charalampakos, V.P.; Pyrgioti, E.C.; Yannopoulos, S.N. Dielectric strength and stability of natural ester oil based TiO_2 nanofluids. *J. Mol. Liq.* **2020**, *316*, 113901. [CrossRef]
35. Jin, H.; Andritsch, T.; Tsekmes, I.A.; Kochetov, R.; Morshuis, P.H.F.; Smit, J.J. Properties of Mineral Oil based Silica Nanofluids. *IEEE Trans. Dielectr. Electr. Insul.* **2014**, *21*, 1100–1108. [CrossRef]
36. Rafiq, M.; Khan, D.; Ali, M. Dielectric properties of transformer oil based silica nanofluids. In Proceedings of the 2015 Power Generation System and Renewable Energy Technologies (PGSRET), Islamabad, Pakistan, 10–11 June 2015; pp. 1–3. [CrossRef]
37. Karthik, R.; Raymon, A. Effect of silicone oxide nano particles on dielectric characteristics of natural ester. In Proceedings of the 2016 IEEE International Conference on High Voltage Engineering and Application (ICHVE), Chengdu, China, 19–22 September 2016; pp. 1–3.
38. Taha, J.; Narayanan, T.N.; Ajayan, P.M.; Contreras, J.E.; Rodriguez, J. Enhanced Dielectric Performance of Nano Boron Nitride Impregnated Cellulosic Insulations. In Proceedings of the ASME 2015 International Mechanical Engineering Congress and Exposition, Houston, TX, USA, 13–19 November 2015; Volume 57533, p. V010T13A031. [CrossRef]
39. Du, B.X.; Li, X.L.; Li, J.; Tao, X.Y. Effects of BN nanoparticles on thermal conductivity and breakdown strength of vegetable oil. In Proceedings of the 2015 IEEE 11th International Conference on the Properties and Applications of Dielectric Materials (ICPADM), Sydney, NSW, Australia, 19–22 July 2015; pp. 476–479.
40. Khaled, U.; Beroual, A. Lightning impulse breakdown voltage of synthetic and natural ester liquids-based Fe_3O_4, Al_2O_3 and SiO_2 nanofluids. *Alex. Eng. J.* **2020**, *59*, 3709–3713. [CrossRef]
41. Beroual, A.; Khaled, U. Statistical Investigation of Lightning Impulse Breakdown Voltage of Natural and Synthetic Ester Oils-Based Fe3O4, Al2O3 and SiO2 Nanofluids. *IEEE Access* **2020**, *8*, 112615–112623. [CrossRef]

42. Devins, J.C.; Rzad, S.J.; Schwabe, R.J. Breakdown and prebreakdown phenomena in liquids. *J. Appl. Phys.* **1981**, *52*, 4531–4545. [CrossRef]
43. Lesaint, O. Prebreakdown phenomena in liquids: Propagation 'modes' and basic physical properties. *J. Phys. D Appl. Phys.* **2016**, *49*, 144001. [CrossRef]
44. Li, J.; Wang, Y.; Wang, F.; Liang, S.; Lin, X.; Chen, X.; Zhou, J. A study on ionization potential and electron trap of vegetable insulating oil related to streamer inception and propagation. *Phys. Lett. A* **2017**, *381*, 3732–3738. [CrossRef]
45. Sun, A.; Huo, C.; Zhuang, J. Formation mechanism of streamer discharges in liquids: A review. *High Volt.* **2016**, *1*, 74–80. [CrossRef]