

## Article

# Biomass-Derived Ester-Rich Insulating Fluids from Soybean and Canola Oils: Route-Specific Synthesis and Preliminary Performance Screening

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## Abstract

The valorization of vegetable-oil biomass into bio-based functional fluids offers a sustainable route for replacing petroleum-derived insulating liquids in power equipment. In this study, soybean and canola oils were used as renewable lipid feedstocks and converted into biomass-derived ester fluids through acid-catalyzed transesterification with methanol, ethanol, 1-propanol, and 1-butanol. The obtained ester-rich products were subjected to a combined physicochemical, dielectric, and thermal screening workflow, including kinematic viscosity at 40 °C ( $\nu_{40}$ ), acid value, breakdown voltage (BDV), differential scanning calorimetry (DSC; 2–8 °C min<sup>−1</sup> under N<sub>2</sub>), and oxygen bomb calorimetry. Transesterification effectively upgraded the vegetable oils into low-viscosity ester-rich product fluids for most alcohol routes, with soybean methyl ester (SME) reaching  $4.41 \pm 0.02$  mm<sup>2</sup> s<sup>−1</sup> and selected canola-derived esters showing viscosities of 5.81–6.81 mm<sup>2</sup> s<sup>−1</sup>. However, the functional performance of the biomass-derived fluids was strongly governed by the alcohol route. SME exhibited the most favorable balance between dielectric and physicochemical properties, delivering the highest BDV of  $64.90 \pm 9.74$  kV, exceeding the IEC 60156 threshold of 30 kV, while maintaining a low acid value of  $0.0103 \pm 0.0006$  mg KOH g<sup>−1</sup>. In contrast, propyl- and butyl-derived esters showed substantially lower BDV values of  $\leq 14.98$  kV, whereas ethanol-derived products retained near-neat-oil viscosities and were unsuitable for BDV testing under the applied conditions. Although propyl- and butyl-derived ester-rich products reduced kinematic viscosity, their markedly lower BDV values were likely associated with route-dependent product heterogeneity, lower alcohol–oil miscibility, possible residual polar impurities, and moisture sensitivity; therefore, they were regarded as non-optimized screening outcomes rather than IEC-compliant transformer-fluid candidates. DSC analysis provided comparative thermal-response descriptors under nitrogen, with methylation producing more coherent endothermic features. The combustion heats of the ester-rich products were concentrated at approximately 39–41 MJ kg<sup>−1</sup>, lower than that of the mineral-oil reference in this dataset, suggesting combustion heat was used only as a preliminary energy-density descriptor and was not interpreted as direct evidence of improved fire safety. From an engineering-safety perspective, the lower combustion heat of the bio-esters may reduce the potential fire-

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load contribution during fault-related fire scenarios, although full fire-safety qualification requires additional flash-point, fire-point, and aging evaluations. Overall, this work demonstrates that alcohol route selection is a critical factor in converting vegetable oil biomass into high-value bio-based insulating fluids. Among the tested formulations, soybean methyl ester is the most promising baseline candidate for further development as a biodegradable, sustainable transformer fluid.

**Keywords:** vegetable-oil biomass; biomass-derived ester fluid; soybean methyl ester; transesterification; bio-based insulating liquid; breakdown voltage; transformer fluid; sustainable functional fluid

## 1. Introduction

- Soybean and canola oils were valorized into biomass-derived ester-rich products insulating fluids.
- Alcohol-route transesterification strongly governed viscosity, dielectric strength, and thermal behavior.
- Soybean methyl ester showed the best balance of low viscosity and high breakdown voltage.
- Propyl and butyl ester routes reduced viscosity but compromised dielectric reliability.
- Vegetable-oil biomass can serve as a renewable platform for sustainable transformer fluids.

Transformers are critical assets in modern power systems, enabling voltage regulation, reliable distribution, and continuous grid operation. The insulating liquid in transformers serves multiple indispensable roles, including electrical insulation, heat dissipation, arc suppression, and gas absorption, all of which directly influence the stability and safety of power delivery. Any disruption caused by transformer failure can lead to significant economic losses and even catastrophic safety incidents. Among these factors, the reliability and durability of the insulating fluid are central to ensuring the long-term functionality of transformers. When the dielectric strength of insulating fluids falls below the IEC 60156 standard threshold of 30 kV, the risk of breakdown increases significantly, leading to higher maintenance costs and unexpected outages [1].

Conventional mineral oils, derived from petroleum fractions such as alkanes, naphthenes, and aromatics, remain the dominant insulating fluids because of their low kinematic viscosity and well-established performance [2]. Nevertheless, mineral oils are non-biodegradable, flammable, and prone to generating toxic volatile compounds at high temperatures or during faults, raising safety and environmental concerns [3–5]. Furthermore, moisture accelerates transformer aging and shortens insulation life, ultimately compromising grid reliability. These challenges underscore the urgency of developing sustainable, safer, and more resilient alternatives [2–5].

Vegetable oil-derived natural esters have attracted attention as sustainable alternatives to mineral oils. Compared with petroleum-based counterparts, natural esters have higher flash and fire points (nearly twice those of mineral oils), superior water solubility, and dielectric constants that promote a more uniform electric field distribution [4,5]. They are also compatible with cellulose insulation, which extends the thermal aging life of transformer paper by absorbing moisture and lowering hot-spot temperatures [6–8]. Their use extends beyond traditional power systems to offshore wind energy, underwater operations, and environmentally sensitive areas, such as carbon-neutral smart cities [7,8].

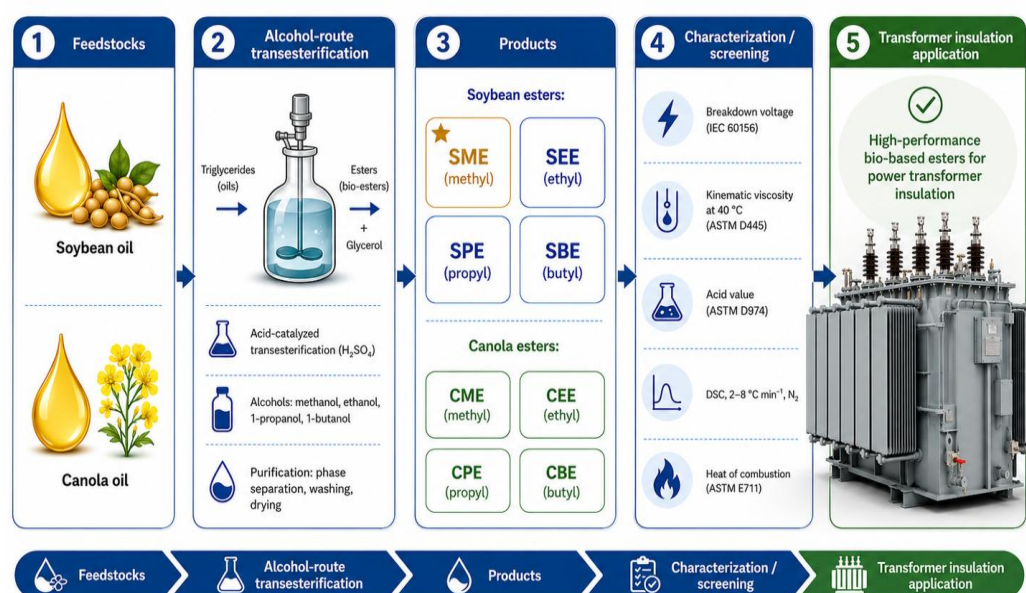
Despite these advantages, vegetable esters face practical limitations. Their higher kinematic viscosity impedes convective cooling, leading to localized hot spots, and their low pour-point temperatures hinder operation in cold climates [9–11]. Moreover, their high content of unsaturated fatty acids results in poor oxidative stability, making them susceptible to degradation and acid formation during service. These drawbacks limit their widespread industrial deployment, underscoring the need for chemical modification strategies to tailor their physicochemical and dielectric properties [4,5,12].

Alcohol-based transesterification has emerged as a promising approach to enhancing the insulating properties of vegetable oils. By converting triglycerides into short-chain fatty acid esters, this process dramatically reduces kinematic viscosity, lowers acid value, and improves flow properties. Importantly, the choice of alcohol dictates the outcome: a. Methanol often yields high dielectric strength and stable kinematic viscosity. b. Under the present acid-catalyzed conditions, ethanol-derived products may be limited by alcohol–oil phase behavior, water sensitivity, and incomplete conversion, whereas propanol and butanol can reduce kinematic viscosity but may compromise dielectric reliability if residual polar species or heterogeneous products remain. c. Propanol and butanol reduce kinematic viscosity but may compromise breakdown voltage [13–15].

In the context of transformer fluids, calorimetric characterization offers a quantitative approach. This study links the esterification route to key performance indicators, including dielectric strength, kinematic viscosity, and oxidative stability. Previous studies have shown that the practical development of vegetable oil-based insulating fluids depends on achieving a suitable balance among electrical robustness, flow behavior, and service stability, while also addressing broader environmental and sustainability considerations [16–18]. Accordingly, this study provides a direct, systematic comparison of soybean and canola oils transesterified with methanol, ethanol, 1-propanol, and 1-butanol under standardized laboratory conditions. The resulting fluids were evaluated for thermal behavior by differential scanning calorimetry (DSC), combustion energy by oxygen bomb calorimetry, physicochemical properties, including acid value and kinematic viscosity at 40 °C ( $\nu_{40}$ ), and dielectric performance by IEC 60156 breakdown-voltage testing.

The practical significance of this work lies in identifying natural ester formulations that can simultaneously meet key performance requirements for transformer liquids, including adequate dielectric strength, low kinematic viscosity, low acidity, and acceptable thermal behavior. Moreover, bio-based insulating fluids have attracted increasing attention for their biodegradability, environmental compatibility, and relevance to sustainable resource utilization and circular economy strategies [19–21]. By integrating dielectric, physicochemical, and calorimetric analyses, this study establishes structure–property relationships to screen bio-based insulating fluids and identifies soybean methyl ester as a particularly promising formulation for further development of natural ester transformer liquids.

The overall experimental design is summarized in Figure 1. Soybean and canola oils were selected as renewable vegetable-oil biomass feedstocks and converted into alkyl ester fluids through acid-catalyzed transesterification using methanol, ethanol, 1-propanol, and 1-butanol. The resulting ester-rich products were then subjected to an integrated screening protocol, including acid value, kinematic viscosity at 40 °C ( $\nu_{40}$ ), IEC 60156 breakdown voltage, DSC thermal analysis, and oxygen bomb calorimetry. This workflow was designed to link alcohol-route-dependent conversion behavior with application-oriented performance criteria for sustainable transformer insulating fluids.



**Figure 1.** Schematic workflow for the route-specific synthesis of ester-rich products from soybean and canola oil biomass and the preliminary screening of their physicochemical, dielectric, and thermal properties as potential insulating fluid candidates.

## 2. Materials and Methods

### 2.1. Sample Sources

Four types of dielectric fluid samples were used in this study: a commercial Shell dielectric fluid (purchased from Hemou Industrial Co., Taichung, Taiwan), a transformer dielectric fluid (Formosa Plastics Corp., Yunlin County, Taiwan), refined soybean salad oil (Taiwan Sugar Corp., Tainan, Taiwan), and refined canola oil (Delicious One Day Co., Taoyuan, Taiwan). All oils were obtained from commercial sources to ensure consistent quality and reproducible results. Before experimental use, the oils were stored in sealed containers under controlled laboratory conditions (25 °C, low humidity) to minimize moisture uptake and oxidative degradation.

### 2.2. Acid-Catalyzed Transesterification and Product Preparation

Transesterification of refined soybean or canola oils was performed using sulfuric acid–alcohol systems under controlled thermal and mixing conditions. Methanol, ethanol, 1-propanol, and 1-butanol ( $\geq 99.5\%$ , anhydrous grade) served as both reactants and solvents. Methanol was purchased from Merck (Taipei, Taiwan); ethanol from Chan Mao Trading Co., Ltd. (Taichung, Taiwan); 1-propanol from Echo Chemical Co., Ltd. (Taipei, Taiwan); and 1-butanol from Union Chemical Works Ltd. (Hsinchu, Taiwan). Sulfuric acid (95–98%, analytical grade) served as the homogeneous catalyst. To minimize water-induced catalyst deactivation and side reactions, all alcohols were pre-dried over activated 3 Å molecular sieves for at least 24 h before use and were verified to contain less than 0.10 wt% water by Karl Fischer titration. All glassware was oven-dried at 105 °C for at least 2 h and cooled in a desiccator immediately before use.

For each alcohol system, the oil-to-alcohol molar ratio, sulfuric acid loading, reaction temperature, and reaction time were selected based on intrinsic differences among the alcohols, including polarity, boiling point, miscibility with triglyceride-rich oils, steric effects, and expected acid-catalyzed transesterification reactivity. Methanol generally provides better miscibility and faster transesterification than longer-chain alcohols. In con-

trast, ethanol, 1-propanol, and 1-butanol require more severe or prolonged conditions because of their lower polarity, poorer miscibility with the oil phase, and greater steric hindrance. Accordingly, the reaction conditions were adjusted as follows: methanol, oil-to-alcohol molar ratio of 1:6 with 1 wt%  $\text{H}_2\text{SO}_4$ ; ethanol, 1:12 with 1.5 wt%  $\text{H}_2\text{SO}_4$ ; 1-propanol, 1:9 with 3 wt%  $\text{H}_2\text{SO}_4$ ; and 1-butanol, 1:9 with 5 wt%  $\text{H}_2\text{SO}_4$ . These conditions were not intended to impose identical reaction severity across all alcohol systems, but rather to obtain isolable ester-rich products from each alcohol under practical laboratory conditions. Therefore, the potential influence of these synthesis conditions on the final physicochemical and dielectric properties was taken into account when interpreting the results.

The temperature–time schedules were selected based on each alcohol's boiling point, the need to maintain sufficient alcohol–oil contact, and preliminary laboratory trials confirming stable mixing, manageable evaporation, and visually acceptable phase behavior. The methanol system was operated near reflux because of methanol's low boiling point and relatively high transesterification efficiency. For ethanol and 1-propanol, the selected temperatures were below or near their boiling ranges to minimize excessive alcohol loss while maintaining adequate reaction rates over an extended reaction period. For 1-butanol, higher temperature and longer reaction time were required due to its lower polarity, reduced miscibility with the oil phase, and slower reaction kinetics. The optimized temperature–time schedules were therefore set as follows: 70 °C for 4 h for methanol; 70 °C for 24 h for ethanol; 77 °C for 24 h for 1-propanol; and 110 °C for 48 h for 1-butanol.

Transesterification was performed in a dry three-neck round-bottom flask with a working volume of 250–500 mL, equipped with a reflux condenser, thermometer or thermocouple, and mechanical or magnetic stirring. The reaction mixture was heated in a thermostatically controlled bath and stirred at 400–600 rpm. After completion of the reaction, the mixture was cooled to approximately 40 °C under continuous stirring and then transferred to a separatory funnel. The mixture was allowed to stand for 24 h to promote phase separation. The alcohol- and catalyst-containing phase was removed, and the ester-rich phase was collected for purification. The crude ester-rich products were washed repeatedly with small portions of deionized water preheated to approximately 70 °C (about 10 mL per wash) until the wash water reached neutral pH. Warm water was used to reduce the viscosity of the ester-rich phase, enhance the removal of residual sulfuric acid, alcohol, glycerol, and other polar by-products, and facilitate cleaner phase separation. This step was particularly important for the higher-viscosity 1-propyl and 1-butyl ester systems. The use of 70 °C water was limited to the purification step and was not applied as an additional reaction treatment. The washed ester-rich product was then concentrated by rotary evaporation under reduced pressure to remove residual alcohol and volatile impurities. The product was dried at 70 °C for 1 h to remove residual moisture introduced during washing. Finally, the purified ester-rich product samples were stored over 1 wt% activated 3 Å molecular sieves prior to thermal, physicochemical, and dielectric characterization.

### 2.3. Acid Value (ASTM D974)—Consolidated Procedure

The acid value of the esterified and reference oils was determined by color-indicator titration with a standardized alcoholic potassium hydroxide (KOH) solution. In this study, standardized alcoholic KOH refers to an approximately 0.01 N KOH solution prepared in ethanol or isopropanol, protected from atmospheric  $\text{CO}_2$ , and standardized against a primary standard, such as potassium hydrogen phthalate, before use to determine its exact normality. The measured normality and correction factor were recorded and used to calculate the acid value [22–24].

A neutral solvent composed of ethanol and diethyl ether at a 1:1 volume ratio was used to ensure complete dissolution of the oil- and ester-rich product samples and to pro-

vide a clear phenolphthalein endpoint. Although ASTM D974 commonly uses an alcoholic titration medium, the ethanol/diethyl ether mixture was adopted as a practical solvent system because esterified oils and reference vegetable oils were more miscible in this mixed solvent than in ethanol alone. The solvent mixture was pre-neutralized with KOH to a faint, persistent pink color in the presence of phenolphthalein indicator. If necessary, a trace amount of acid was added to return the solvent to a colorless state before sample titration. Phenolphthalein solution (1% w v<sup>-1</sup> in ethanol) was used as the indicator.

For each analysis, approximately 10.0 g of the oil sample was weighed on an analytical balance to the nearest 0.1 mg. The sample was dissolved in the pre-neutralized ethanol/diethyl ether solvent and titrated with the standardized alcoholic KOH solution to a faint pink endpoint that persisted for at least 30 s. Titrations were performed in 50–100 mL stoppered Erlenmeyer flasks using a class-A burette or an autotitrator. Deionized water was used only for rinsing when necessary. For samples with very low or very high acidity, the sample mass was adjusted to keep titrant consumption within 0.2–10.0 mL [23–25].

#### 2.4. Breakdown Voltage (BDV) Testing

The dielectric breakdown strength of the esterified oil samples was measured using a portable automatic oil ester-rich products (BA75, BAUR GmbH, Sulz, Austria) rated at 75 kV. The procedure followed the manufacturer's standard method for insulating liquids. Freshly prepared dielectric fluids, free of visible water contamination or particulates, were used for each test. However, visual inspection alone cannot confirm transformer-grade dryness or the absence of trace polar impurities. In the present study, the final water content of each purified ester-rich product was not quantified by Karl Fischer titration immediately before BDV testing. Therefore, the BDV results should be interpreted as preliminary screening data rather than full transformer-fluid qualification results. Before measurement, the clean, dry test vessel was rinsed with a small portion of the same sample, then filled with 100 mL of the test liquid. The filled vessel was allowed to stand for at least 30 min to allow entrained air bubbles to escape before testing. Electrodes were inspected, cleaned with lint-free wipes (using a mild solvent if necessary), and spaced at  $2.5 \pm 0.05$  mm, as verified with a calibrated gauge. The electrodes were fully immersed and in stable contact with the sample. The instrument was programmed to apply a linearly increasing voltage from 0 kV at a rate of 2–3 kV s<sup>-1</sup> until electrical breakdown occurred. Breakdown voltage values were automatically recorded by the device. If any external flashover or abnormal discharge trace was visually detected, that trial was discarded and repeated after re-equilibration of the sample. Six independent breakdown measurements were performed for each oil sample under identical test conditions. The dielectric strength of each specimen was expressed as the mean  $\pm$  standard deviation of the six recorded breakdown voltages [1].

#### 2.5. Kinematic Viscosity at 40 °C ( $v_{40}$ ) (ASTM D445)—Consolidated Procedure

The kinematic viscosity of the raw vegetable oils and acid-catalyzed esterified products was determined at 40 °C in accordance with ASTM D445 [26]. All measurements were performed using calibrated Cannon–Fenske glass capillary viscometers with traceable certification. The viscometers used, and their respective calibration constants (C), were as follows: U289 (C = 0.008456 mm<sup>2</sup> s<sup>-2</sup>), U452 (C = 0.007629 mm<sup>2</sup> s<sup>-2</sup>), and U540 (C = 0.008106 mm<sup>2</sup> s<sup>-2</sup>).

Samples were introduced into the viscometer tubes after gentle homogenization to ensure representative composition and avoid air entrapment. All glassware was rinsed with volatile, water-free solvents (hexane and isopropanol) and dried prior to use. Analyses were conducted in a constant-temperature water bath maintained at  $40.00 \pm 0.05$  °C,

monitored using a Class A thermometer or a calibrated temperature probe. Efflux time was recorded with a stopwatch of 0.01 s resolution or an automated viscometer timer [26].

For each measurement, the sample flow time was recorded in triplicate, and the kinematic viscosity was calculated as

$$\nu = C \times t \quad (1)$$

where  $\nu$  is the kinematic viscosity ( $\text{mm}^2 \text{s}^{-1}$ ) and  $t$  is the measured flow time (s). The average of three consecutive readings, with a relative deviation of  $\pm 0.2\%$ , was reported. Before measurement, any sample containing visible particulates was filtered through a dry, inert membrane, and samples were tightly capped to minimize moisture absorption and solvent loss [25].

## 2.6. Oxygen Bomb Calorimetry—Heat of Combustion

Heat of combustion was measured with an oxygen bomb calorimeter (Parr Instrument Co. IL, USA) in accordance with ASTM E711 [26]. The calorimeter was first calibrated with certified benzoic acid standards to determine the system energy equivalent ( $W$ ,  $\text{J } ^\circ\text{C}^{-1}$ ). For each test,  $1.000 \pm 0.005$  g of well-mixed sample was weighed into a clean crucible, and a 10 cm iron ignition wire was mounted across the bomb electrodes, contacting the sample but not the crucible. The sealed bomb was flushed and then charged to 25 atm of  $\text{O}_2$ . It was placed in a bucket containing 2.0 L of deionized water and equilibrated until the baseline drift stabilized.

Ignition was initiated electrically, and temperature was continuously recorded from the pre-ignition baseline through the post-peak period. The corrected temperature rise was calculated using ASTM E711 drift corrections (pre- and post-ignition) [26]. After cooling, the bomb was vented, and the residual wire length was measured to determine the wire correction. The bomb and crucible were thoroughly rinsed, and all washings were combined to a final volume of 100 mL. The solution was then titrated with standardized sodium carbonate, using methyl orange to quantify the acid produced (mainly  $\text{HNO}_3$ ) [21].

The heat of combustion for each run was calculated as [26]

$$T_c = T_f - T_i \quad (2)$$

$$H_c = \frac{T_c \times W - e_1 - e_2 - e_3}{M} \quad (3)$$

$$H_g = 4.184T_c \quad (4)$$

where  $T_i$  is the initial temperature at ignition,  $T_f$  is the final temperature after complete combustion, and  $T_c$  is the net temperature rise.  $W$  ( $\text{cal } ^\circ\text{C}^{-1}$ ) is the calorimeter energy equivalent, determined by standardization with benzoic acid and representing the heat required to raise the system temperature by  $1^\circ\text{C}$ .  $e_1$  (cal) is the ignition-wire heat correction;  $e_2$  (cal) is the correction for heat released by oxidation of residual nitrogen in the bomb (nitric acid formation);  $e_3$  (cal) is the correction for heat released by oxidation of sulfur species in the oil (sulfuric acid formation).  $M$  (g) is the test-oil mass.  $H_g$  ( $\text{J g}^{-1}$ ) denotes the heat of combustion, expressed in calories per gram; conversion to SI units in  $\text{J g}^{-1}$  (divide by 4.184), and then to  $\text{MJ kg}^{-1}$ . All measurements were performed in triplicate ( $n = 3$ ) and are presented as the mean  $\pm$  SD. Runs were repeated if incomplete combustion, leakage, or atypical drift was observed; daily checks included verification that benzoic acid remained within established control limits. All operations were conducted in a fume hood behind the calorimeter shield, in accordance with manufacturer and institutional safety procedures.

### 2.7. Differential Scanning Calorimetry Analysis

Differential scanning calorimetry (DSC) was performed using a TA Instruments Q20 DSC system (TA Instruments, DE, USA) to obtain comparative thermal-response descriptors of the reference oils, neat vegetable oils, and route-derived ester-rich products. Approximately 1.1–1.5 mg of each sample was hermetically sealed in aluminum pans. A nitrogen purge of 50 mL min<sup>-1</sup> was maintained throughout the analysis. Heating scans were conducted from 30 °C to 500 °C at heating rates of 2, 4, 6, and 8 °C min<sup>-1</sup>.

Because the DSC measurements were conducted under nitrogen, the observed thermal events were interpreted primarily as volatilization-related transitions, phase/structural transitions, and thermal decomposition under inert conditions, rather than as direct evidence of oxidative stability. Onset temperature, peak temperature, and enthalpy were extracted from the thermograms for comparative screening. Although the heating-rate program was consistent with the general framework of ASTM E698, activation energy and full kinetic parameters were not calculated in this study; therefore, the DSC results were not interpreted as a complete ASTM E698 kinetic analysis [27–29].

### 2.8. Statistical Analysis

All quantitative data are presented as the mean ± standard deviation (SD). Break-down voltage (BDV) was measured with six replicate determinations for each sample tested, whereas kinematic viscosity, acid value, and heat of combustion were measured in triplicate. Because this study was designed as a preliminary screening investigation and no statistical grouping letters or *p*-values are reported in the tables, the statistical analysis was limited to descriptive statistics. No inferential comparisons, including ANOVA (Version 9.4, SAS Institute Inc., Cary, NC, USA), Duncan's multiple range test, data transformation, or nonparametric post hoc testing, were applied in the revised manuscript. This simplified presentation is intended to avoid unsupported statistical interpretation and to maintain consistency between the Section 2 and the reported tabulated results [28,29].

## 3. Results and Discussion

### 3.1. Physicochemical Quality: Acid Value and Kinematic Viscosity at 40 °C

Acid-catalyzed alcohol transesterification markedly altered the physicochemical profiles of both soybean- and canola-based fluids by converting triglycerides into lower-molecular-weight fatty acid alkyl esters. As summarized in Table 1, neat soybean and canola oils exhibited high kinematic viscosities at 40 °C ( $32.78 \pm 0.87$  and  $35.09 \pm 1.35$  mm<sup>2</sup> s<sup>-1</sup>, respectively), consistent with their triglyceride-dominant structures. After transesterification, kinematic viscosity was substantially reduced across most alcohol routes, reaching  $4.41 \pm 0.02$  mm<sup>2</sup> s<sup>-1</sup> for soybean methyl ester (SME) and 5.81–6.81 mm<sup>2</sup> s<sup>-1</sup> for the principal canola-derived ester-rich products (Table 1).

1. Acid values remained low across the esterified products, indicating limited hydrolysis during reaction and effective purification. For soybean-derived fluids, acid value decreased from  $0.0174 \pm 0.0008$  mg KOH g<sup>-1</sup> in the neat oil to  $0.0103 \pm 0.0006$  mg KOH g<sup>-1</sup> for SME, while canola butyl ester (CBE) reached an especially low value of  $0.0015 \pm 0.0008$  mg KOH g<sup>-1</sup> (Table 1). Although canola methyl ester (CME) showed a higher acid value than the other canola-derived ester-rich products, it remained lower than that of the neat canola oil. This result suggests that methyl transesterification reduced the feedstock's initial acidity, but that CME may have retained more residual acidic species or hydrolysis-derived free fatty acids than CEE, CPE, and CBE after purification. Because methyl esterification was carried out under a shorter reaction time and lower catalyst loading than the longer-chain alcohol systems, small differences in residual catalyst removal, ester-rich products hydrolysis, or free fatty acid partitioning

during washing may have contributed to the relatively higher acid value of CME. Nevertheless, the measured acid value of CME remained within the low-acidity range considered acceptable for preliminary screening.

In contrast, ethanol-derived products (SEE and CEE) retained viscosities comparable to those of the parent oils, strongly suggesting incomplete conversion or persistent multiphase structures under the applied conditions (Table 1). The ethyl ester samples were retained in Table 1 as transparent evidence of an unsuccessful conversion route, but they were classified as conversion-limited outliers and excluded from application-oriented dielectric interpretation. Therefore, the unusually high kinematic viscosities of the ethanol-derived products should not be interpreted as a normal alcohol-chain-length trend. Both SEE and CEE retained kinematic viscosities close to those of the parent soybean and canola oils, indicating incomplete transesterification or the persistence of triglyceride-rich/multiphase structures under the present ethanol reaction conditions. In contrast, the methyl, propyl, and butyl ester routes produced substantially lower viscosities, consistent with more effective conversion of triglycerides into lower-molecular-weight alkyl esters. Thus, the ethyl ester samples were treated as conversion-limited outliers rather than as evidence of a monotonic relationship between alcohol chain length and kinematic viscosity. Because direct compositional characterization was not performed for all route-derived products in the present study, the sample names should be regarded as operational labels for the ester-rich phases obtained from each alcohol route rather than as confirmation of chemically pure alkyl esters. In particular, the ethanol-derived products retained kinematic viscosities close to those of the parent soybean and canola oils, indicating incomplete conversion or the persistence of triglyceride-rich and/or multiphase structures under the applied conditions. Therefore, SEE and CEE should be interpreted as conversion-limited products rather than well-defined ethyl ester fluids. Overall, methyl esterification proved the most robust route, simultaneously achieving low viscosity and low acidity across both feedstocks (Table 1).

**Table 1.** Acid value and kinematic viscosity at 40 °C of reference insulating oils, neat vegetable oils, and acid-catalyzed transesterified products (mean  $\pm$  SD).

| Fluid                      | Acid Value<br>(mg KOH g <sup>-1</sup> ) | KV<br>40 °C (mm <sup>2</sup> s <sup>-1</sup> ) |
|----------------------------|-----------------------------------------|------------------------------------------------|
| Shell transformer fluid    | 0.0142 $\pm$ 0.0005                     | 8.73 $\pm$ 0.04                                |
| Dielectric fluid           | 0.0176 $\pm$ 0.0002                     | 10.15 $\pm$ 0.02                               |
| Soybean oil                | 0.0174 $\pm$ 0.0008                     | 32.78 $\pm$ 0.87                               |
| Soybean methyl ester (SME) | 0.0103 $\pm$ 0.0006                     | 4.41 $\pm$ 0.02                                |
| Soybean ethyl ester (SEE)  | 0.0127 $\pm$ 0.0011                     | 32.77 $\pm$ 0.09                               |
| Soybean propyl ester (SPE) | 0.0066 $\pm$ 0.0008                     | 8.42 $\pm$ 0.06                                |
| Soybean butyl ester (SBE)  | 0.0096 $\pm$ 0.0005                     | 4.98 $\pm$ 0.02                                |
| Canola oil                 | 0.0539 $\pm$ 0.0014                     | 35.09 $\pm$ 1.35                               |
| Canola methyl ester (CME)  | 0.0228 $\pm$ 0.0008                     | 6.81 $\pm$ 0.02                                |
| Canola ethyl ester (CEE)   | 0.0022 $\pm$ 0.0010                     | 31.86 $\pm$ 0.21                               |
| Canola propyl ester (CPE)  | 0.0063 $\pm$ 0.0007                     | 5.81 $\pm$ 0.01                                |
| Canola butyl ester (CBE)   | 0.0015 $\pm$ 0.0008                     | 6.06 $\pm$ 0.06                                |

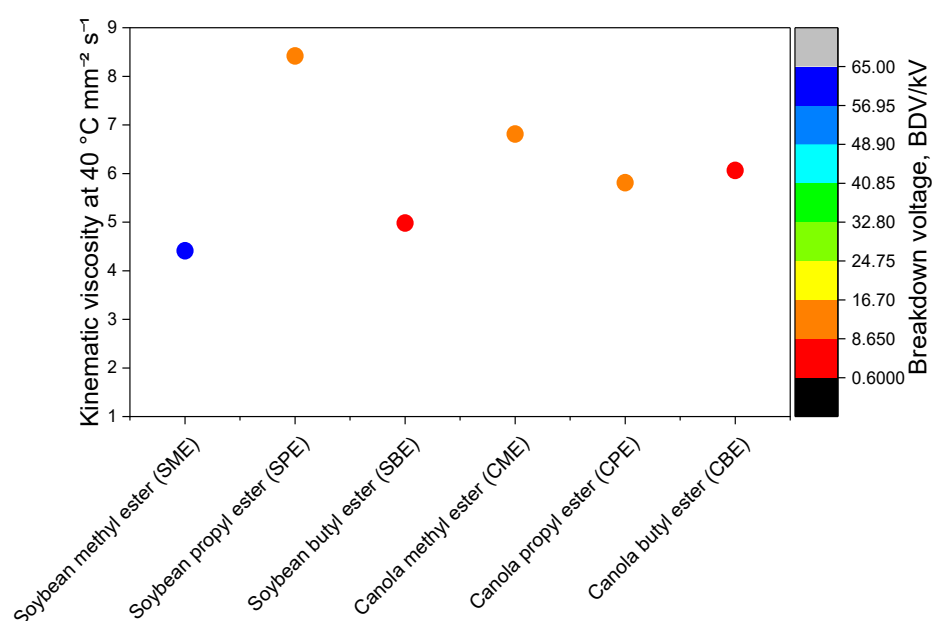
Remarks: Transformer dielectric fluid (provided by Formosa Plastics Corporation, Yunlin County, Taiwan).

### 3.2. Dielectric Strength: Breakdown Voltage and Formulation Dependence

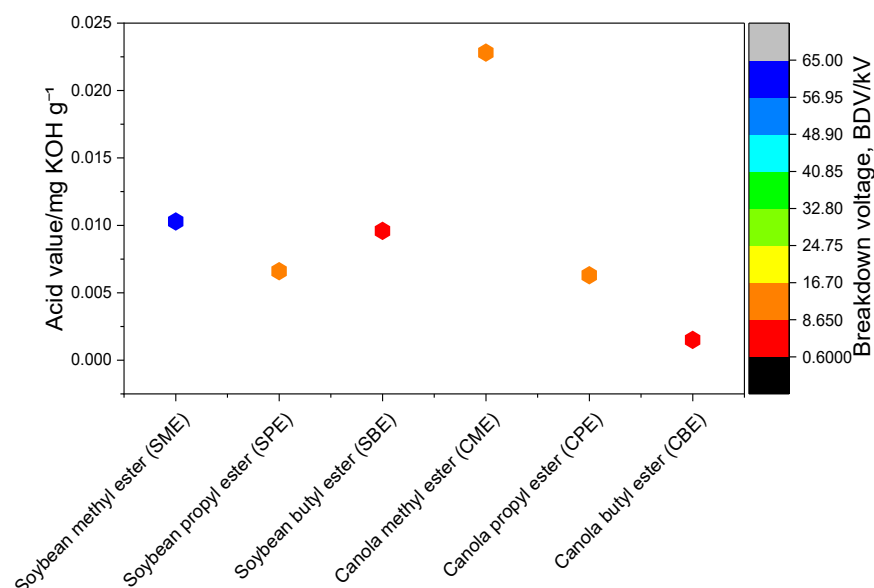
Despite broadly similar reductions in kinematic viscosity, breakdown voltage was highly sensitive to alcohol type and feedstock (Table 2). Soybean methyl ester exhibited the highest dielectric strength, with a breakdown voltage of 64.90  $\pm$  9.74 kV, exceeding the

IEC 60156 minimum requirement of 30 kV by more than a factor of two (Table 2). In contrast, propyl- and butyl-derived ester-rich products exhibited markedly lower breakdown voltages, and the soybean and canola butyl esters approached non-insulating behavior under the present test conditions (Table 2). The very low BDV values of SBE and CBE indicate that these samples approached non-insulating behavior. This behavior may be associated with residual moisture, residual acid or catalyst, residual alcohol or glycerol, sulfur-containing species, incomplete purification, and product heterogeneity, as well as route-specific compositional effects. Because final Karl Fischer water content and residual polar-impurity analyses were not performed for each purified product, these factors are discussed as plausible explanations rather than confirmed mechanisms. Although several esterified products exhibited reduced kinematic viscosity, most breakdown voltage values in Table 2 did not meet the IEC 60156 minimum requirement for insulating liquids. Therefore, these formulations should not be considered acceptable transformer-fluid candidates under the present preparation conditions. Rather, they represent unsuccessful or non-optimized esterification routes within the scope of this screening study. Only soybean methyl ester satisfied the IEC 60156 criterion, indicating that it was the only formulation in this dataset that combined sufficiently low kinematic viscosity with acceptable dielectric strength.

The correlation plots further indicate that low kinematic viscosity alone is insufficient to ensure high dielectric strength. Although breakdown voltage generally decreased with increasing kinematic viscosity, soybean methyl ester was a clear positive outlier, achieving both low kinematic viscosity and high breakdown voltage (Figure 2). Similarly, breakdown voltage showed only a weak association with acid value, suggesting that acid value alone is not a reliable predictor of dielectric breakdown in these ester-rich product systems (Figure 3). Collectively, these results highlight that dielectric reliability is governed not only by bulk rheological properties but also by chemistry-specific and microstructural factors, including the esterification route, moisture control, removal of residual polar impurities, and product homogeneity.



**Figure 2.** Relationship between breakdown voltage (BDV) and kinematic viscosity at 40 °C ( $v_{40}$ ) for transesterified soybean/canola ester-rich products and reference fluids.



**Figure 3.** Relationship between breakdown voltage (BDV) and acid value for transesterified soybean/canola ester-rich products and reference fluids.

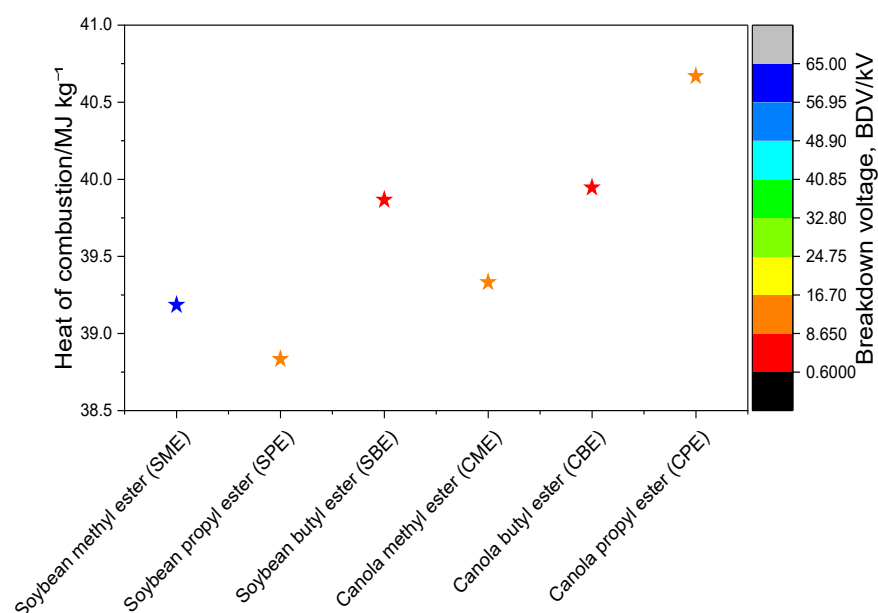
**Table 2.** Breakdown voltage (IEC 60156) and heat of combustion (ASTM E711) for transesterified ester-rich products and reference fluids (mean  $\pm$  SD where applicable).

| Fluid                      | BDV (kV)         | Heat of Combustion (MJ kg <sup>-1</sup> ) |
|----------------------------|------------------|-------------------------------------------|
| Shell transformer fluid    | N/A              | 44.93 $\pm$ 0.12                          |
| Dielectric fluid           | N/A              | 43.73 $\pm$ 0.80                          |
| Soybean oil                | N/A              | 39.06 $\pm$ 0.03                          |
| Soybean methyl ester (SME) | 64.90 $\pm$ 9.74 | 39.18 $\pm$ 0.13                          |
| Soybean ethyl ester (SEE)  | N/A              | 38.86 $\pm$ 0.33                          |
| Soybean propyl ester (SPE) | 10.73 $\pm$ 0.22 | 38.83 $\pm$ 0.09                          |
| Soybean butyl ester (SBE)  | 0.80 $\pm$ 0.00  | 39.86 $\pm$ 0.15                          |
| Canola oil                 | N/A              | 39.52 $\pm$ 0.23                          |
| Canola methyl ester (CME)  | 12.90 $\pm$ 2.14 | 39.33 $\pm$ 0.04                          |
| Canola ethyl ester (CEE)   | N/A              | 39.20 $\pm$ 0.41                          |
| Canola propyl ester (CPE)  | 14.98 $\pm$ 0.50 | 40.66 $\pm$ 0.23                          |
| Canola butyl ester (CBE)   | 1.10 $\pm$ 0.00  | 39.94 $\pm$ 0.23                          |

Remarks: Dielectric fluid (provided by Formosa Plastics Corporation, Yunlin County, Taiwan).

### 3.3. Heat of Combustion and Implications for Fire Load

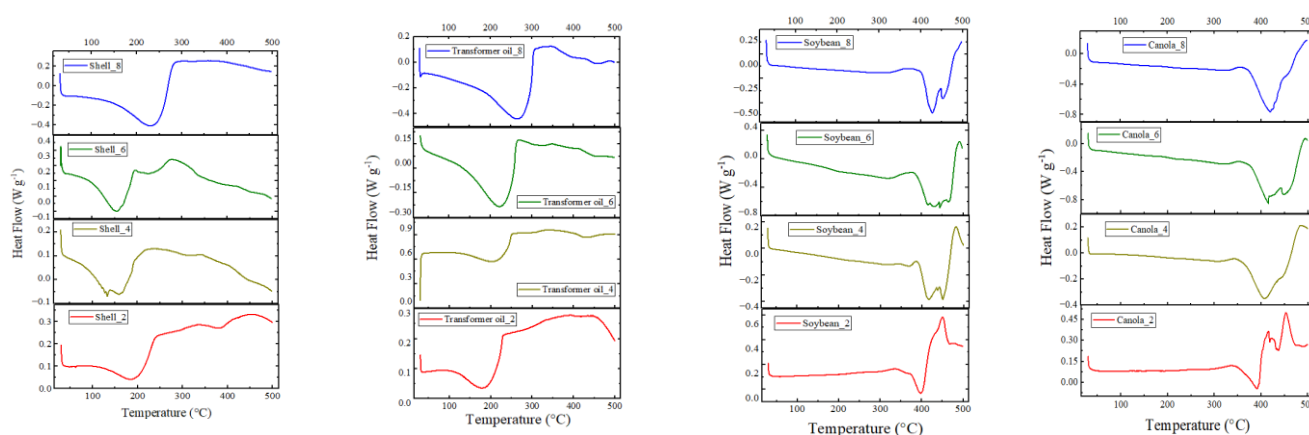
Bomb calorimetry showed that the ester-rich products clustered around 39–41 MJ kg<sup>-1</sup>, whereas the mineral-oil reference exhibited a higher heat of combustion in this dataset (Table 2). These results provide useful preliminary information on stored chemical energy per unit mass. However, the heat of combustion alone is insufficient to assess the fire safety of transformer fluids. Fire behavior also depends on flash point, fire point, ignition temperature, vapor pressure, heat-release rate, combustion dynamics, and fault-condition behavior. Therefore, the lower heat of combustion observed for the ester-rich products should be interpreted only as a complementary energy-density descriptor, not as direct evidence of improved fire safety. No meaningful correlation was observed between BDV and heat of combustion, indicating that combustion energetics were not predictive of dielectric performance within this screening dataset (Figure 4).



**Figure 4.** Relationship between breakdown voltage (BDV) and heat of combustion for transesterified soybean/canola ester-rich products and reference fluids.

### 3.4. DSC Analyses of Reference Transformer Oils and Neat Vegetable Oils (Benchmark Behavior)

DSC thermal analyses of the reference transformer oils and neat vegetable oils show distinct endothermic features across heating rates of 2–8 °C min<sup>−1</sup> (Figure 5). Under an inert nitrogen purge, these endothermic events primarily reflect volatilization-related transitions and thermally induced decomposition rather than oxidative reactions. Shifts in onset and peak temperatures with heating rate are consistent with kinetic and transport limitations typical of complex hydrocarbon and triglyceride mixtures. The corresponding endothermic descriptors ( $T_o$ ,  $T_p$ , and  $\Delta H$ ) for the reference transformer oils are summarized in Table 3, providing a benchmark for interpreting how transesterification alters thermal-response signatures.



**Figure 5.** DSC thermograms of reference transformer oils and neat vegetable oils measured at heating rates of 2–8 °C min<sup>−1</sup> under N<sub>2</sub> (comparative overlays).

**Table 3.** DSC endothermic descriptors (1Endo/2Endo onset temperature  $T_o$ , peak temperature  $T_p$ , and enthalpy  $\Delta H$ ) of reference transformer oils measured at heating rates of 2–8 °C min<sup>−1</sup> under N<sub>2</sub>.

| Fluid                    | Heating Rate (°C min <sup>−1</sup> ) | Sample Mass (mg) | 1Endo $T_o$ (°C) | 1Endo $T_p$ (°C) | 1Endo $\Delta H$ (J g <sup>−1</sup> ) | 2Endo $T_o$ (°C) | 2Endo $T_p$ (°C) | 2Endo $\Delta H$ (J g <sup>−1</sup> ) |
|--------------------------|--------------------------------------|------------------|------------------|------------------|---------------------------------------|------------------|------------------|---------------------------------------|
| Shell trans-former fluid | 2                                    | 1.49             | 95.77            | 201.36           | 266.50                                | N/A              | N/A              | N/A                                   |
|                          | 4                                    | 1.52             | 54.55            | 160.16           | 213.20                                | N/A              | N/A              | N/A                                   |
|                          | 6                                    | 1.51             | 49.81            | 155.07           | 164.70                                | N/A              | N/A              | N/A                                   |
|                          | 8                                    | 1.48             | 63.08            | 242.34           | 338.00                                | N/A              | N/A              | N/A                                   |
| Dielectric fluid         | 2                                    | 1.52             | 97.19            | 195.82           | 241.30                                | N/A              | N/A              | N/A                                   |
|                          | 4                                    | 1.52             | 112.83           | 218.97           | 243.50                                | N/A              | N/A              | N/A                                   |
|                          | 6                                    | 1.45             | 38.91            | 223.37           | 404.70                                | N/A              | N/A              | N/A                                   |
|                          | 8                                    | 1.51             | 41.28            | 270.75           | 395.80                                | N/A              | N/A              | N/A                                   |

### 3.5. DSC Signatures of Soybean-Derived Ester-Rich Products: Effect of Alcohol Selection

Soybean-derived alkyl esters exhibited route-dependent DSC responses across 2–8 °C min<sup>−1</sup> (Figure 6), with quantitative endothermic descriptors summarized in Table 4. Neat soybean oil displayed high-temperature endothermic transitions consistent with the broad decomposition behavior of unsaturated triglyceride mixtures (Table 4; Figure 5). After methylation, SME showed a well-defined first endothermic event at lower onset and peak temperatures with moderate enthalpy values across heating rates, consistent with reduced molecular weight and a narrower compositional distribution following transesterification (Table 4; Figure 6).

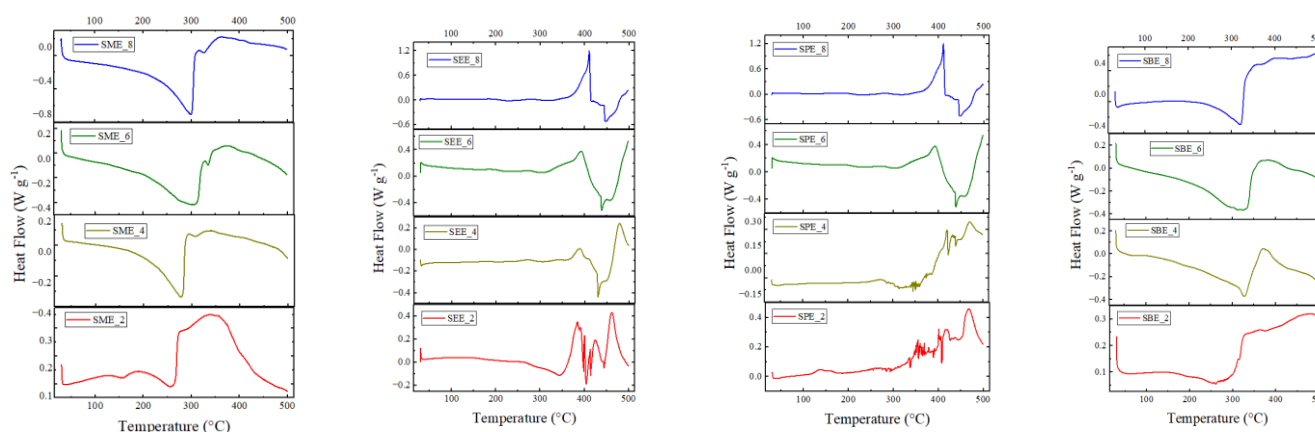
In contrast, ethanol- and propyl-derived soybean ester-rich products showed broader, higher-temperature endothermic features, suggesting greater heterogeneity and multiple thermal pathways (Table 4; Figure 6). The ethanol-derived product also retained near-neat-oil kinematic viscosity, supporting the interpretation that incomplete conversion contributed to both rheological and thermal complexity (Tables 1 and 4). Although SBE exhibited a discernible endothermic feature, its dielectric strength was negligible, underscoring that DSC coherence alone does not ensure electrical reliability (Tables 2 and 4; Figure 6).

**Table 4.** DSC endothermic descriptors of soybean oil and soybean-derived alkyl esters (SME, SEE, SPE, SBE) measured at heating rates of 2–8 °C min<sup>−1</sup> under N<sub>2</sub>.

| Fluid                      | Heating Rate (°C min <sup>−1</sup> ) | Sample Mass (mg) | 1Endo $T_o$ (°C) | 1Endo $T_p$ (°C) | 1Endo $\Delta H$ (J g <sup>−1</sup> ) | 2Endo $T_o$ (°C) | 2Endo $T_p$ (°C) | 2Endo $\Delta H$ (J g <sup>−1</sup> ) |
|----------------------------|--------------------------------------|------------------|------------------|------------------|---------------------------------------|------------------|------------------|---------------------------------------|
| Soybean oil                | 2                                    | 1.49             | N/A              | N/A              | N/A                                   | 336.02           | 401.90           | 568.70                                |
|                            | 4                                    | 1.52             | N/A              | N/A              | N/A                                   | 384.35           | 449.34           | 357.00                                |
|                            | 6                                    | 1.51             | N/A              | N/A              | N/A                                   | 377.24           | 465.70           | 486.20                                |
|                            | 8                                    | 1.48             | N/A              | N/A              | N/A                                   | 378.19           | 428.86           | 223.30                                |
| Soybean methyl ester (SME) | 2                                    | 1.52             | 190.07           | 265.21           | 146.6                                 | N/A              | N/A              | N/A                                   |
|                            | 4                                    | 1.52             | 154.06           | 277.76           | 294.2                                 | N/A              | N/A              | N/A                                   |
|                            | 6                                    | 1.45             | 176.80           | 306.32           | 238.4                                 | N/A              | N/A              | N/A                                   |
|                            | 8                                    | 1.51             | 152.63           | 299.87           | 285.3                                 | N/A              | N/A              | N/A                                   |
| Soybean ethyl ester (SEE)  | 2                                    | 1.52             | N/A              | N/A              | N/A                                   | 384.35           | 404.34           | 632.00                                |
|                            | 4                                    | 1.52             | N/A              | N/A              | N/A                                   | 387.67           | 429.64           | 324.10                                |
|                            | 6                                    | 1.45             | N/A              | N/A              | N/A                                   | 392.41           | 438.27           | 550.30                                |
|                            | 8                                    | 1.51             | N/A              | N/A              | N/A                                   | 410.41           | 445.71           | 454.80                                |
|                            | 2                                    | 1.52             | N/A              | N/A              | N/A                                   | 388.61           | 407.85           | 183.10                                |

|                            |   |      |        |        |        |        |        |        |
|----------------------------|---|------|--------|--------|--------|--------|--------|--------|
| Soybean propyl ester (SPE) | 4 | 1.52 | N/A    | N/A    | N/A    | 268.26 | 449.49 | 459.60 |
|                            | 6 | 1.45 | N/A    | N/A    | N/A    | 268.73 | 433.79 | 558.50 |
|                            | 8 | 1.51 | N/A    | N/A    | N/A    | 383.40 | 467.12 | 223.60 |
| Soybean butyl ester (SBE)  | 2 | 1.52 | 144.58 | 299.30 | 311.70 | N/A    | N/A    | N/A    |
|                            | 4 | 1.52 | 213.76 | 329.56 | 331.70 | N/A    | N/A    | N/A    |
|                            | 6 | 1.45 | 173.48 | 330.75 | 337.60 | N/A    | N/A    | N/A    |
|                            | 8 | 1.51 | 188.17 | 322.12 | 224.40 | N/A    | N/A    | N/A    |

Remarks: N/A, The observed differences are not interpreted quantitatively in this work and are therefore omitted from further discussion.



**Figure 6.** DSC thermograms of soybean-derived ester-rich products (SME, SEE, SPE, SBE) measured at heating rates of 2–8 °C min<sup>−1</sup> under N<sub>2</sub> (comparative overlays).

### 3.6. DSC Signatures of Canola-Derived Ester-Rich Products and Feedstock Effects

Canola-derived alkyl esters also exhibited alcohol-dependent DSC thermograms across 2–8 °C min<sup>−1</sup> (Figure 7), with endothermic descriptors summarized in Table 5. Neat canola oil exhibited dominant high-temperature endothermic transitions broadly comparable to those of soybean oil (Table 5; Figure 5). Transesterification altered the profiles, and CME exhibited lower-temperature transitions and reduced enthalpy relative to the neat oil across several heating rates, consistent with molecular simplification (Table 5; Figure 7). However, propyl- and ethyl-derived canola ester-rich products exhibited broader and higher-temperature features at several heating rates (Table 5; Figure 7).

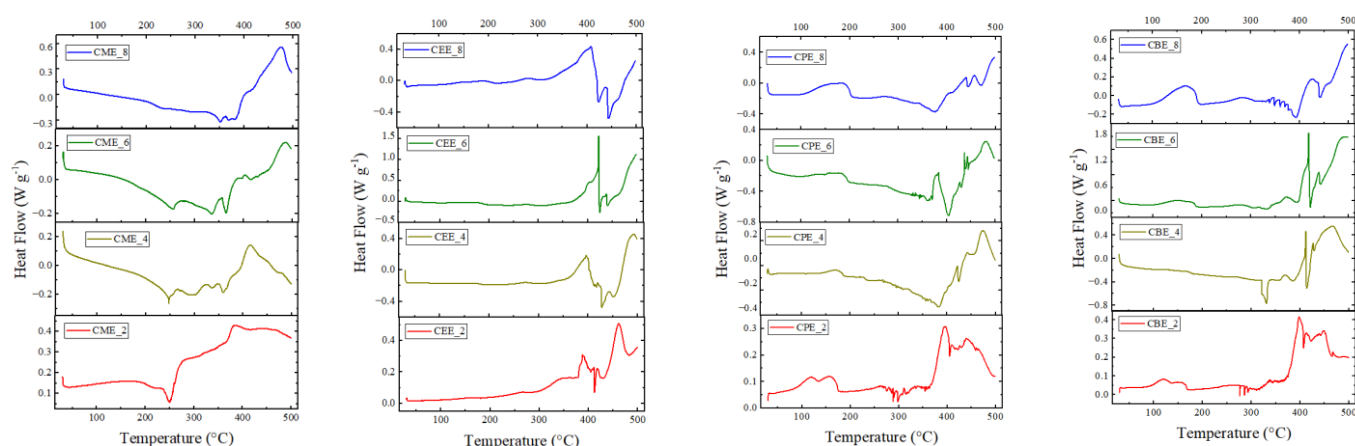
Despite comparable viscosities among CME, CPE, and CBE, their BDV values differed substantially (Tables 1 and 2; Figure 2), indicating that feedstock-specific fatty acid distributions and minor components modulate dielectric behavior even when bulk rheology is similar. These results suggest that optimal alcohol selection may be feedstock-dependent rather than universal.

**Table 5.** DSC endothermic descriptors of canola oil and canola-derived alkyl esters (CME, CEE, CPE, CBE) measured at heating rates of 2–8 °C min<sup>−1</sup> under N<sub>2</sub>.

| Fluid      | Heating Rate (°C min <sup>−1</sup> ) | Sample Mass (mg) | 1Endo T <sub>o</sub> (°C) | 1Endo T <sub>p</sub> (°C) | 1Endo ΔH (J g <sup>−1</sup> ) | 2Endo T <sub>o</sub> (°C) | 2Endo T <sub>p</sub> (°C) | 2Endo ΔH (J g <sup>−1</sup> ) |
|------------|--------------------------------------|------------------|---------------------------|---------------------------|-------------------------------|---------------------------|---------------------------|-------------------------------|
| Canola oil | 2                                    | 1.49             | N/A                       | N/A                       | N/A                           | 336.96                    | 392.78                    | 401.60                        |
|            | 4                                    | 1.52             | N/A                       | N/A                       | N/A                           | 343.60                    | 412.11                    | 449.00                        |
|            | 6                                    | 1.51             | N/A                       | N/A                       | N/A                           | 349.76                    | 415.32                    | 530.90                        |

|                           |   |      |        |        |        |        |        |        |
|---------------------------|---|------|--------|--------|--------|--------|--------|--------|
|                           | 8 | 1.48 | N/A    | N/A    | N/A    | 353.55 | 420.16 | 340.20 |
| Canola methyl ester (CME) | 2 | 1.52 | 174.91 | 250.82 | 365.50 | N/A    | N/A    | N/A    |
|                           | 4 | 1.52 | 208.55 | 359.40 | 415.80 | N/A    | N/A    | N/A    |
|                           | 6 | 1.45 | 188.65 | 365.03 | 438.10 | N/A    | N/A    | N/A    |
|                           | 8 | 1.51 | 241.72 | 383.16 | 307.90 | N/A    | N/A    | N/A    |
| Canola ethyl ester (CEE)  | 2 | 1.52 | N/A    | N/A    | N/A    | 388.61 | 412.34 | 319.00 |
|                           | 4 | 1.52 | N/A    | N/A    | N/A    | 396.20 | 427.85 | 594.90 |
|                           | 6 | 1.45 | N/A    | N/A    | N/A    | 422.26 | 424.39 | 671.30 |
|                           | 8 | 1.51 | N/A    | N/A    | N/A    | 408.04 | 442.61 | 271.20 |
| Canola propyl ester (CPE) | 2 | 1.52 | N/A    | N/A    | N/A    | 273.94 | 371.79 | 294.00 |
|                           | 4 | 1.52 | N/A    | N/A    | N/A    | 271.10 | 413.78 | 614.40 |
|                           | 6 | 1.45 | N/A    | N/A    | N/A    | 272.52 | 406.01 | 472.40 |
|                           | 8 | 1.51 | N/A    | N/A    | N/A    | 277.73 | 411.81 | 392.60 |
| Canola butyl ester (CBE)  | 2 | 1.52 | N/A    | N/A    | N/A    | 246.46 | 326.68 | 297.50 |
|                           | 4 | 1.52 | N/A    | N/A    | N/A    | 272.52 | 343.00 | 466.40 |
|                           | 6 | 1.45 | N/A    | N/A    | N/A    | 273.94 | 407.14 | 407.50 |
|                           | 8 | 1.51 | N/A    | N/A    | N/A    | 279.15 | 426.24 | 293.50 |

Remarks: N/A, The observed differences are not interpreted quantitatively in this work and are therefore omitted from further discussion.



**Figure 7.** DSC thermograms of canola-derived ester-rich products (CME, CEE, CPE, CBE) measured at heating rates of 2–8 °C min<sup>−1</sup> under N<sub>2</sub> (comparative overlays).

### 3.7. Integrated Endothermic Characteristic at 4 °C min<sup>−1</sup>

At a heating rate of 4 °C min<sup>−1</sup>, the first endothermic event (1Endo) provides a compact descriptor set for cross-comparing thermal response with physicochemical and dielectric metrics (Tables 3–5). SME exhibited a clearly resolved mid-temperature endothermic window, a low acid value, and the highest BDV in the dataset (Tables 1, 2 and 4; Figure 2). While this does not establish causality, the co-occurrence of a coherent 1Endo signature and favorable dielectric behavior supports the use of DSC descriptors as complementary screening indicators when protocols are standardized (Tables 3–5). By contrast, fluids such as SBE and CME exhibited higher onset and/or peak temperatures and/or larger enthalpies without corresponding improvements in BDV, indicating that the association is conditional rather than deterministic (Tables 2, 4 and 5). The coherent SME endothermic window may indicate lower compositional heterogeneity after methyl esterification, but DSC cannot directly predict BDV; dielectric reliability must be interpreted alongside moisture control, residual polar impurities, and product cleanliness.

### 3.8. Structure–Property Relationships and Application-Oriented Performance Window

The effect of alcohol chain length on the desired transformer-fluid properties was not strictly monotonic; however, a clear structure-dependent trend was observed. In principle, increasing the alkyl chain length from methyl to butyl esters may reduce molecular polarity and alter intermolecular packing, thereby improving flow behavior after triglyceride conversion. However, longer-chain alcohols also introduce greater steric hindrance and lower miscibility with the oil phase during transesterification. These factors may reduce conversion efficiency and increase compositional heterogeneity or residual polar impurities, which can adversely affect dielectric reliability even when kinematic viscosity is reduced.

In the present study, methyl esterification provided the most favorable balance, particularly for soybean oil, because soybean methyl ester combined low kinematic viscosity with the highest breakdown voltage. In contrast, the propyl and butyl esters exhibited reduced kinematic viscosity but substantially lower breakdown voltage, indicating that increasing the alkyl chain length did not necessarily improve transformer-fluid performance. Therefore, the alcohol-chain-length effect should be interpreted as a balance among conversion efficiency, viscosity reduction, molecular polarity, and dielectric cleanliness rather than as a simple linear relationship.

Across the dataset, three consistent structure–property trends emerged. First, transesterification effectively reduced kinematic viscosity, but dielectric strength remained highly chemistry-sensitive (Tables 1 and 2; Figures 2 and 3). Second, soybean methyl ester uniquely combined low kinematic viscosity, low acid value, and IEC-compliant breakdown voltage (Tables 1 and 2; Figures 2 and 3). Third, feedstock effects persisted even at similar viscosity levels, indicating that compositional details beyond bulk rheology also modulated dielectric behavior (Tables 1 and 2; Figure 2). From an application perspective, soybean methyl ester was the most direct drop-in candidate among the formulations tested. Based on the present results, a conservative preliminary target range would emphasize a breakdown voltage  $\geq 30$  kV, a kinematic viscosity at 40 °C in the low single-digit  $\text{mm}^2 \text{s}^{-1}$  range, an acid value  $\leq 0.02$  mg KOH  $\text{g}^{-1}$ , stable DSC behavior, and rigorous moisture control (Tables 1–5). Long-term oil–paper aging studies remain essential for service-relevant qualification.

### 3.9. Limitations and Outlook

This limitation should be considered when interpreting the relationship between synthesis route, physicochemical properties, dielectric behavior, and DSC response. Although viscosity, acid value, BDV, and DSC descriptors provide useful preliminary screening information, they cannot fully substitute for direct compositional confirmation. Future work should include GC-FID/GC-MS, HPLC, FTIR, or NMR analysis; ester content determination; mono-, di-, and triglyceride profiling; residual alcohol and free glycerol measurement; residual catalyst/sulfur species analysis; and yield/conversion assessment. These analyses will be necessary to establish more robust structure–property relationships and to support practical qualification of transformer fluids. A further limitation of this study is that the final water content, residual catalyst/sulfur species, residual alcohol, and free glycerol were not quantified for each purified ester-rich product prior to BDV testing. In addition, the commercial reference transformer fluids were not tested for BDV under the same protocol. These missing measurements limit direct dielectric comparison and prevent full transformer-fluid qualification. Future work should include Karl Fischer water-content analysis, residual polar-impurity determination, BDV testing of reference fluids using the same instrument and electrode protocol, dielectric dissipation factor, relative permittivity, volume resistivity, flash/fire point, pour point, oxidative stability, and long-term oil–paper aging evaluation, ignition temperature, vapor pressure, heat-release rate, and realistic fault-condition combustion behavior.

## 4. Conclusions

This study provides a preliminary process–property screening framework for biomass-derived ester-rich insulating-fluid candidates prepared from soybean and canola oils under route-specific acid-catalyzed transesterification conditions. Because methanol, ethanol, 1-propanol, and 1-butanol required different oil/alcohol ratios, catalyst loadings, reaction temperatures, and reaction times, the observed performance differences should be interpreted as outcomes of the combined effects of alcohol identity, reaction severity, conversion efficiency, purification behavior, residual polar species, and product homogeneity, rather than alcohol chain length alone. Among the route-derived products evaluated in this study, soybean methyl ester (SME) showed the most favorable preliminary balance of properties, with an IEC 60156-compliant breakdown voltage (BDV =  $64.90 \pm 9.74$  kV), low kinematic viscosity at 40 °C ( $\nu_{40} = 4.41 \pm 0.02$  mm<sup>2</sup> s<sup>−1</sup>), and low acid value ( $0.0103 \pm 0.0006$  mg KOH g<sup>−1</sup>). In contrast, propyl- and butyl-route products reduced kinematic viscosity but exhibited substantially lower BDV values, while ethanol-derived products retained near-neat-oil viscosities and were therefore regarded as conversion-limited products under the present conditions. The DSC results obtained under nitrogen provided useful comparative thermal-response descriptors, including onset temperature, peak temperature, and enthalpy. Methylation produced more coherent endothermic features than several higher-alcohol routes, which may reflect lower product heterogeneity. However, DSC descriptors should be interpreted only as complementary screening indicators and not as deterministic predictors of dielectric performance or oxidative stability. Similarly, combustion calorimetry showed that the ester-rich products had lower heats of combustion than the mineral-oil reference in this dataset, but this result should be regarded only as preliminary energy-density information and not as sufficient evidence of improved fire safety. Overall, SME is identified as the most promising baseline candidate among the tested route-derived products, but it should not be considered a fully qualified commercial transformer fluid at this stage. Further validation is required, including detailed compositional analysis, determination of ester content, residual alcohol/glycerol and catalyst analysis, final Karl Fischer water content measurement, additional dielectric characterization, flash/fire point testing, pour point evaluation, oxidative stability assessment, cellulose compatibility, and long-term oil–paper aging tests. These future studies are essential to confirm the practical feasibility, service reliability, and engineering applicability of biomass-derived ester-rich insulating fluids.

**Author Contributions:** Conceptualization, C.-P.L.; methodology, T.-W.H.; investigation, T.-W.H.; formal analysis, C.-P.L. and S.-Y.T.; visualization, M.H.; writing—original draft preparation, S.-Y.T.; writing—review and editing, all authors; supervision, C.-P.L. All authors have read and agreed to the published version of the manuscript.

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**Data Availability Statement:** The datasets generated and analyzed during the current study are available from the corresponding author upon reasonable request.

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USA) was used for grammar, spelling, punctuation, and clarity checks. All experimental data, analyses, tables, results, and other figures were generated and prepared by the authors. The authors reviewed all AI-assisted content and take full responsibility for the final manuscript.

**Conflicts of Interest:** The authors declare no conflicts of interest.

## References

1. IEC 60156; Insulating Liquids—Determination of the Breakdown Voltage at Power Frequency—Test Method. International Electrotechnical Commission: Geneva, Switzerland, 2018.
2. Peng, X.; Wang, Q.; Kang, S.; Chen, C.; Li, G.; Wang, K.; Liao, R.; Zhao, X. Research progress in modified mineral oil, natural ester and mixed oil in transformers. *Electr. Mater. Appl.* **2024**, *1*, e12005.
3. Kurzweil, P. Environmental impact and aging properties of natural and synthetic transformer oils under Electrical Stress Conditions. *Adv. Sustain. Syst.* **2021**, *5*, 2100079.
4. Oparanti, S.O.; Rao, U.M.; Fofana, I. Natural esters for green transformers: Challenges and keys for improved serviceability. *Energies* **2023**, *16*, 61.
5. Shen, Z.; Wang, F.; Wang, Z.; Li, J. A critical review of plant-based insulating fluids for transformer: 30-year development. *Renew. Sustain. Energy Rev.* **2021**, *141*, 110783.
6. Karaman, H.S.; Mansour, D.E.A.; Lehtonen, M.; Darwish, M.M.F. Condition assessment of natural ester–mineral oil mixture due to transformer retrofilling via sensing dielectric properties. *Sensors* **2023**, *23*, 6440.
7. Zhang, E.; Zhang, Z.; Wang, F.; Li, J.; Ye, Z.; Li, C. State-of-art review on chemical indicators for monitoring the aging status of oil-immersed transformer paper insulation. *Energies* **2023**, *16*, 1396.
8. Xing, Y.; Hu, Y.; Ma, Y.; Liu, Y.; Dong, M.; Xu, Y. Difference analysis of dissolved gas in natural ester insulating fluids under typical electrical and thermal faults: An experimental study. *High Volt.* **2023**, *8*, 1206–1214.
9. Przybyłek, P. Thermal ageing of dry cellulose paper impregnated with different insulating liquids—Comparative studies of materials properties. *Energies* **2024**, *17*, 784.
10. Das, A. Investigation of electrical breakdown and heat transfer properties of coconut oil-based nanofluids. *Ind. Crops Prod.* **2023**, *197*, 116545.
11. Das, A.K. Analysis of AC breakdown strength of vegetable oils and effect of mineral oil. *Electr. Power Syst. Res.* **2023**, *214*, 108920.
12. Liu, J.; Zhang, H.; Fan, X.; Zhang, Y.; Zhang, C. Aging evaluation for transformer oil-immersed cellulose insulation by using frequency dependent dielectric modulus technique. *Cellulose* **2021**, *28*, 2387–2401.
13. Mustangin, M.; Purwantana, B.; Hidayat, C.; Radi. Development of high free fatty acid crude palm oil as a biodegradable electrical liquid insulator as an alternative to mineral oil-based insulators. *Clean. Eng. Technol.* **2024**, *18*, 100712.
14. Ye, W.; Hao, J.; Zhang, J.; Li, H.; Zhang, J.; Liao, R. Lightning impulse breakdown behavior of natural ester and modified natural ester under long oil gap: An experiment and first-principles simulation analysis. *Ind. Crops Prod.* **2024**, *210*, 118087.
15. Zhang, K.; Huang, Z.; Li, J. Probing the mechanism of antioxidant and oxidative stability properties of gallic acid and its esters in natural esters: Computational investigations and experiments. *Renew. Energy* **2025**, *239*, 122137.
16. Obebe, E.O.; Hadjadj, Y.; Oparanti, S.O.; Fofana, I. Enhancing the performance of natural ester insulating liquids in power transformers: A comprehensive review on antioxidant additives for improved oxidation stability. *Energies* **2025**, *18*, 1690.
17. Oparanti, S.O.; Fofana, I.; Jafari, R.; Zarrougui, R. A state-of-the-art review on green nanofluids for transformer insulation. *J. Mol. Liq.* **2024**, *396*, 124023.
18. Farade, R.A.; Abdul Wahab, N.I.; Mansour, D.E.A. The effect of nano-additives in natural ester dielectric liquids: A comprehensive review on stability and thermal properties. *IEEE Trans. Dielectr. Electr. Insul.* **2023**, *30*, 1478–1497.
19. Li, J.; Zhang, Z.; Zou, P.; Grzybowski, S.; Zahn, M. Preparation of a vegetable oil-based nanofluid and investigation of its breakdown and dielectric properties. *IEEE Electr. Insul. Mag.* **2012**, *28*, 43–50.
20. Beccari, S.; Pipitone, E.; Caltabellotta, S. Analysis of the Combustion Process in a Hydrogen-Fueled CFR Engine. *Energies* **2023**, *16*, 2351.
21. Rao, U.M.; Fofana, I.; Jaya, T.; Rodriguez-Celis, E.M.; Jalbert, J.; Picher, P. Alternative dielectric fluids for transformer insulation system: Progress, challenges, and future prospects. *IEEE Access* **2019**, *7*, 184552–184571.
22. Xue, Y.; Ranjith, P.G.; Chen, Y.; Cai, C.; Gao, F.; Liu, X. Nonlinear mechanical characteristics and damage constitutive model of coal under CO<sub>2</sub> adsorption during geological sequestration. *Fuel* **2023**, *331*, 125690.

23. ASTM D974-22; Standard Test Method for Acid and Base Number by Color-Indicator Titration. ASTM International: West Conshohocken, PA, USA, 2022. <https://doi.org/10.1520/D0974-22>.
24. Uçar, B.; Gholami, Z.; Svobodová, K.; Hradecká, I.; Hönig, V. A comprehensive study for determination of free fatty acids in selected biological materials: A review. *Foods* **2024**, *13*, 1891.
25. ASTM D445-21; Standard Test Method for Kinematic Viscosity of Transparent and Opaque Liquids. ASTM International: West Conshohocken, PA, USA, 2021.
26. Tsai, S.Y.; Su, J.W.; Tong, J.T.; Lin, C.P. Evaluation of suitable mixture proportion compatibility of aviation fuel JET A-1 blended with butanol isomers. *J. Therm. Anal. Calorim.* **2021**, *144*, 403–413.
27. ASTM E698-11; Standard Test Method for Arrhenius Kinetic Constants for Thermally Unstable Materials Using, D.S.C. ASTM International: West Conshohocken, PA, USA, 2020.
28. Tsai, S.Y.; Hsu, Y.C.; Lin, H.Y.; Huang, F.K.; Lin, C.P. Comparison of the effect of *Pleurotus citrinopileatus* extract and vitamin E on the stabilization properties of camellia oil. *J. Therm. Anal. Calorim.* **2017**, *130*, 1281–1292.
29. Lin, C.P.; Liu, Y.H.; Wang, S.X.; Tai, T.C.; Tsai, S.Y. Thermal stability and characteristics of enoki mushroom dietary fiber by autoclaving pretreatment combined with enzymatic hydrolysis. *J. Therm. Anal. Calorim.* **2023**, *148*, 6807–6818.

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