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# Physicochemical, Thermal and Cooling Curve Characterisation of Sulfate Salt–Modified Sesame Oil as a Potential Bio-Based Quenching Medium

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## Abstract

The development of environmentally safe quenching media is critical for sustainable heat treatment operations. Vegetable oils have emerged as promising bio-based alternatives to petroleum-derived quenchants due to their renewability, biodegradability and favourable thermal characteristics; however, their direct industrial application is often limited by inadequate thermal stability and sub-optimal cooling behaviour. In this study, raw sesame oil and sesame oil modified with potassium sulfate ($K_2SO_4$) and sodium sulfate ($Na_2SO_4$) additives were systematically characterised to evaluate their suitability as potential bio-based quenching media. Physicochemical properties, including density, viscosity, acid value and iodine value, were evaluated. Thermal safety characteristics (smoke point, flash point and fire point) were determined using a digital infrared pyrometer, while thermal degradation behaviour was assessed through thermogravimetric and differential thermal analyses (TGA/DTA) to obtain decomposition onset temperatures and maximum mass loss rate temperatures. Cooling behaviour was examined using temperature–time cooling curve analysis. The results show that the incorporation of sulfate salt additives modifies the physicochemical and thermal behaviour of sesame oil, generally leading to improved thermal safety limits and enhanced thermal stability compared with the raw oil. Cooling curves reveal noticeable differences in heat extraction behaviour among the modified oils, indicating that additive concentration improves the cooling characteristics of sesame oil, especially at the vapour blanket stage (0 – 5 sec). The combined findings demonstrate that sulfate salt modification provides an effective route for modifying the properties of sesame oil and establishing its potential as a bio-based quenching medium. The data generated in this study serve as essential baseline information for future application-oriented heat treatment studies.

**Keywords:** Sesame oil, Bio-quenchant, Sulfate salts, Physicochemical properties, Thermal stability, Cooling curve

## 1. Introduction

The continuous drive toward sustainable manufacturing has intensified global efforts to replace petroleum-based industrial fluids with environmentally safe alternatives. In heat treatment operations, quenching media play an important role in determining cooling severity, microstructural transformation and eventually the mechanical performance of metallic components. Conventional quenchants such as water, brine and mineral oils remain widely used; however, each presents inherent drawbacks. Water and brine exhibit excessively high cooling rates that often promote distortion, residual stresses and cracking of steel components, while mineral oils are non-renewable, poorly biodegradable and associated with environmental and health concerns [1–3].

Vegetable oils have emerged as promising bio-based alternatives to mineral oil quenchants owing to their renewability, biodegradability, low volatility and relatively high flash points [4, 5]. Their molecular structure, dominated by triglycerides composed of long-chain fatty acids, provides inherent lubricity and thermal resistance, which are advantageous for quenching applications [6]. Over the past decade, numerous studies have demonstrated the feasibility of vegetable oils such as soybean, palm, sunflower, rapeseed and canola oils as quenching media and metalworking fluids, with cooling performances comparable to or better than conventional mineral oils [7–10].

The utilisation of edible vegetable oils for industrial purposes often raises ethical concerns regarding competition with the food supply. However, industrial deployment does not necessarily rely on food-grade oils. Large volumes of downgraded or non-edible fractions of edible oils are generated annually during processing, storage and frying operations and can be valorised for technical applications [11, 12]. Moreover, the suitability of an oil for quenching is governed primarily by its physicochemical and thermal characteristics such as viscosity, density, acid value, iodine value and thermal stability rather than its nutritional value [13]. Consequently, the industrial adoption of edible oils in non-food sectors has been widely reported without adverse implications for food security [14].

Despite their advantages, raw vegetable oils generally suffer from limitations including insufficient thermal stability, poor oxidation resistance and sub-optimal cooling characteristics for demanding heat treatment processes [15]. These shortcomings restrict their direct application as industrial quenchants. To overcome these challenges, modification of vegetable oils using additives has gained considerable research attention. Additives can tailor viscosity, suppress volatilisation, improve thermal stability and modify heat transfer behaviour during quenching [16, 17].

Among various classes of additives, inorganic salts have shown promise in influencing boiling behaviour and heat extraction mechanisms of quenchants. The presence of dissolved or dispersed ionic species can destabilise vapour blankets, promote early transition to nucleate boiling and enhance convective heat transfer, thereby improving cooling efficiency [18, 19]. Sulfate-based salts such as potassium sulfate ($K_2SO_4$) and sodium sulfate ($Na_2SO_4$) are particularly attractive because of their thermal stability, availability, low cost and reported flame-retardant characteristics [20, 21]. However, systematic studies on their influence when incorporated into vegetable-oil-based quenchants remain scarce.

Sesame oil is a triglyceride-rich vegetable oil characterised by high oleic and linoleic acid contents, relatively high flash point and good oxidative stability compared with many other plant oils [22, 23]. These attributes suggest that sesame oil may serve as a suitable base stock for the development of bio-based quenching media. Nevertheless, comprehensive baseline data on how sulfate salt additives affect the physicochemical properties, thermal safety characteristics, thermal degradation behaviour and cooling performance of sesame oil are currently lacking.

An explicit understanding of these properties is essential because they collectively determine the safety, stability and heat extraction capability of any prospective quenchant. Physicochemical parameters such as density, viscosity, acid value and iodine value provide insight into fluidity, molecular structure and susceptibility to degradation. Thermal safety characteristics, including smoke point, flash point and fire point, define operational safety limits, while thermogravimetric and differential thermal analyses reveal degradation onset temperatures and maximum mass loss rates. Cooling curve analysis, finally, offers direct evaluation of heat transfer behaviour and quenching severity.

Therefore, this study aims to comprehensively characterize raw sesame oil and sesame oil modified with varying concentrations of potassium sulfate and sodium sulfate through physicochemical analysis, thermal safety testing, thermogravimetric/differential thermal analysis and cooling curve evaluation. The data provides fundamental insight into the suitability of sulfate salt–modified sesame oil as a potential bio-based quenching medium and establishes a scientific foundation for subsequent application-oriented heat treatment studies

## 2. Materials and Methods

### *2.1 Materials*

Commercially available sesame oil without prior chemical modification was procured from a local supplier in Kurmi market, Kano state, Nigeria and was used as the base quenchant for this study. Potassium sulfate ($K_2SO_4$) and sodium sulfate ($Na_2SO_4$) of analytical grade purity were used as additives. All reagents were used as received without further purification. Distilled water was employed for the cleaning of glassware and sample containers.

### *2.2 Preparation of Sulfate Salt–Modified Sesame Oil*

Sesame oil was modified with potassium sulfate and sodium sulfate at concentrations of 0, 1.5 and 3.0 wt. %. The required mass of each salt was weighed using a digital analytical balance and gradually introduced into preheated sesame oil maintained at approximately 60 °C. The mixture was stirred for 30 min using a magnetic stirrer to ensure uniform dispersion of the additives within the oil matrix. The modified oils were then allowed to cool naturally to room temperature and stored in sealed containers before characterisation.

Nine experimental runs were generated by combining the additive concentrations in accordance with the experimental design, as shown in Table 1.

**Table 1**: Taguchi L9 design of experiment for varying concentrations of additives

| Experiment no. | $K_2SO_4$ concentration (%) | $Na_2SO_4$ concentration (%) |
|---|---|---|
| 1 | 0 | 0 |
| 2 | 0 | 1.5 |
| 3 | 0 | 3.0 |
| 4 | 1.5 | 0 |
| 5 | 1.5 | 1.5 |
| 6 | 1.5 | 3.0 |
| 7 | 3.0 | 0 |
| 8 | 3.0 | 1.5 |
| 9 | 3.0 | 3.0 |

### *2.3 Physicochemical Characterisation*

#### *2.3.1 Density*

The density of the oil samples was determined using a laboratory density bottle at 25 °C. The bottle was first cleaned, dried and weighed empty. It was then filled with the oil sample, wiped dry externally and reweighed. Density was calculated from the mass of oil and the known volume of the bottle.

#### *2.3.2 Viscosity*

Viscosity was measured at 40 °C using a capillary viscometer placed in a thermostatically controlled water bath. The time required for the oil to flow between the calibrated marks was recorded and viscosity was calculated using the viscometer constant.

#### *2.3.3 Acid Value*

Acid value was determined by titration of a known mass of oil dissolved in ethanol with standardised potassium hydroxide solution using phenolphthalein as an indicator. Acid value was calculated and expressed in mg KOH/g oil.

#### *2.3.4 Iodine Value*

Iodine value was determined using the Wijs method. The oil sample was reacted with iodine monochloride solution and excess iodine was titrated with standardised sodium thiosulfate solution. Results were expressed as grams of iodine absorbed per 100 g of oil.

### *2.4 Thermal Safety Characteristics*

Smoke point, flash point and fire point were determined using a digital infrared pyrometer. Each oil sample was heated gradually in a stainless-steel container placed on a controlled heating plate. The temperature was continuously monitored with the pyrometer.

The smoke point was recorded as the temperature at which continuous visible smoke first appeared. The flash point was recorded as the lowest temperature at which the vapour above the oil momentarily ignited when exposed to a small flame. The fire point was taken as the temperature at which sustained combustion occurred for at least 5 seconds.

### *2.5 Thermogravimetric and Differential Thermal Analysis (TGA/DTA)*

The thermal degradation behaviour of the oil samples was evaluated using a simultaneous TGA/DTA analyser. Approximately 10 mg of each sample was placed in an alumina crucible and heated from room temperature to 600 °C at a heating rate of 10 °C/min under an inert atmosphere.

From the TGA/DTA curves, the onset temperature of decomposition (Tonset) and the temperature corresponding to maximum mass loss rate (Tmax) were extracted.

### *2.6 Cooling Curve Analysis*

Cooling behaviour of the oil samples was evaluated using temperature–time cooling curve measurements. A standard cylindrical metallic probe fitted with a thermocouple was heated to 850 ºC, held for 15 mins and then immersed in each oil sample. Temperature variation with time during cooling was recorded using a data acquisition system.

Cooling curves were plotted as temperature versus time for each experimental run. The curves were used to compare the cooling behaviour between raw sesame oil and sulfate-modified sesame oils.

### *2.7 Data Analysis*

All experiments were conducted in triplicate. Mean values were calculated and reported. Graphical analyses were performed using Minitab statistical software.

## 3.0 Results and Discussion

### *3.1 Physicochemical Properties of Raw and Sulfate Salt–Modified Sesame Oil*

The measured physicochemical properties of raw sesame oil (R1) and sulfate salt–modified sesame oil samples (R2 – R9) are summarised in Table 2. These properties provide fundamental insight into the flow behaviour, chemical stability and heat transfer potential of the quenchants, which directly influence their suitability for heat treatment applications [5–7].

**Table 2:** Identification of physicochemical properties across all experimental runs

| Sample | Viscosity (cP) | Density (g/mL) | Acid value | Iodine value |
|---|---|---|---|---|
| **R1** | 0.60 | 0.950 | 5.6 | 23.73 |
| **R2** | 0.60 | 0.950 | 7.3 | 20.05 |
| **R3** | 0.50 | 0.945 | 6.6 | 20.30 |
| **R4** | 0.50 | 0.955 | 6.7 | 18.40 |
| **R5** | 0.50 | 0.920 | 7.9 | 18.53 |
| **R6** | 0.70 | 0.940 | 6.1 | 18.28 |
| **R7** | 0.70 | 0.940 | 7.3 | 18.27 |
| **R8** | 0.50 | 0.940 | 6.7 | 17.51 |
| **R9** | 0.80 | 0.945 | 6.7 | 20.93 |

#### *3.1.1 Viscosity*

The viscosity values of the oils ranged from 0.50 to 0.80 cP (Table 2). The raw sesame oil (R1) exhibited a viscosity of 0.60 cP, while modified samples showed both lower and higher values depending on additive concentration. Samples R3, R4, R5 and R8 recorded the lowest viscosity of 0.50 cP, indicating enhanced fluidity relative to the base oil. Conversely, sample R9 exhibited the highest viscosity of 0.80 cP. The reduction in viscosity observed in several modified samples suggests that the incorporation of $K_2SO_4$ and $Na_2SO_4$ can disrupt intermolecular attractions among triglyceride chains, thereby increasing molecular mobility. Lower viscosity favours improved convective heat transfer and faster bubble detachment during quenching, leading to higher cooling rates [9]. Similar viscosity-lowering trends have been reported for vegetable oils modified with inorganic additives and surface-active agents [16, 21]. However, the moderate increase in viscosity observed for sample R9 indicates that higher additive content may promote localised agglomeration or increased internal friction, which can slightly hinder fluid flow. Nevertheless, all measured viscosity values fall within a narrow range suitable for oil quenchants, indicating that sulfate salt modification does not adversely compromise fluidity.

The main effect plot, as shown in Figure 1, reveals a slight increase in viscosity at 1.5% additives concentration for both $K_2SO_4$ and $Na_2SO_4$, followed by a decrease at 3.0% below the baseline. This trend suggests that higher sulfate addition weakens intermolecular cohesion within the triglyceride matrix, improving molecular mobility, whereas moderate salt content increases ionic interactions and microstructural resistance to flow. Lower viscosity at excessive additive levels is desirable for thermal fluids, as it promotes enhanced convection and more efficient heat transport.

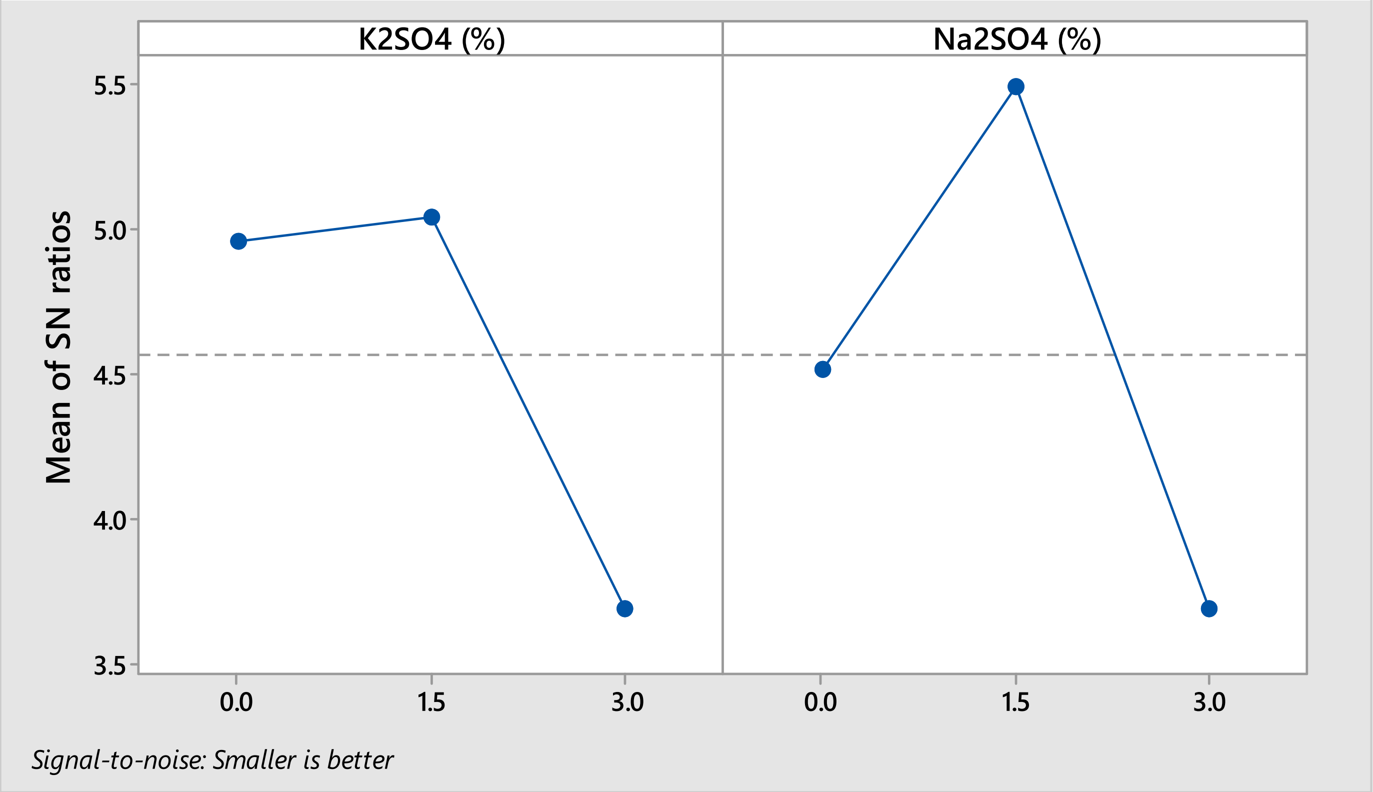


**Figure 1:** Main effect plot for signal-to-noise (S/N) ratio of viscosity of sulfate salt–modified sesame oil. Experimental conditions: base oil = sesame oil; additive concentrations = 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; Taguchi L9 design.

### *3.1.2 Density*

Density values across all samples varied between 0.920 and 0.955 g/mL. Raw sesame oil (R1) exhibited a density of 0.950 g/mL, while modified oils showed minor fluctuations around this value. The lowest density was recorded for R5 (0.920 g/mL), whereas the highest density occurred for R4 (0.955 g/mL). These small variations indicate that sulfate salt addition does not significantly alter the bulk mass–volume relationship of sesame oil. Slight increases in density can be attributed to the higher intrinsic density of inorganic salts dispersed within the oil matrix. Comparable observations have been reported for vegetable oils containing particulate or inorganic modifiers [28]. From a heat transfer standpoint, modest density enhancement may promote improved thermal conductivity and convective heat transport, thereby enhancing heat extraction from hot steel surfaces [13]. The narrow density range observed suggests stable flow behaviour across all samples.

The main effect plot as shown in Figure 2 reveals that density generally decreases from 0% to 1.5% additives concentration for both $K_2SO_4$ and $Na_2SO_4$, then increases slightly at 3.0%. The increase up to 3.0% suggests improved molecular packing caused by sulfate ions occupying interstitial spaces within the oil structure. The slight decline at moderate concentration may be due to agglomeration or incomplete dispersion of salt particles. Comparable density trends have been reported for additive-treated vegetable oils [11]. Higher density contributes to increased volumetric heat capacity, beneficial for thermal applications.

### *3.1.3 Acid Value*

Acid value ranged from 5.6 to 7.9 mg KOH/g. The raw sesame oil (R1) recorded the lowest acid value of 5.6 mg KOH/g, indicating good initial quality. Modified samples exhibited slightly higher acid values, with the maximum observed for R5 (7.9 mg KOH/g).

The modest increase in acid value following salt incorporation may be attributed to interactions between salt species and polar functional groups in the oil, as well as limited catalytic effects during heating and mixing. Importantly, all values remain within acceptable limits reported for industrial vegetable oils, indicating that sulfate salt modification does not induce severe hydrolytic or oxidative degradation [4]. Low acid value is beneficial for quenchant longevity and minimises the risk of corrosive attack on heat-treated components and equipment [15]. The observed acid values, therefore, confirm that the modified oils retain acceptable chemical stability.

The main effect plot as shown in Figure 3 indicates a decrease at 1.5% additive concentration for both $K_2SO_4$ and $Na_2SO_4$, followed by stabilisation or slight reduction at 3.0% $K_2SO_4$ and an increase at 3.0% $Na_2SO_4$. The small rise suggests limited hydrolysis or interaction between salts and ester groups, while the absence of sharp increases indicates that sulfate additives do not severely promote oil degradation. Similar observations have been reported for chemically stabilised vegetable oils [9]. The relatively low acid values across all samples confirm acceptable chemical stability for thermal-fluid usage.

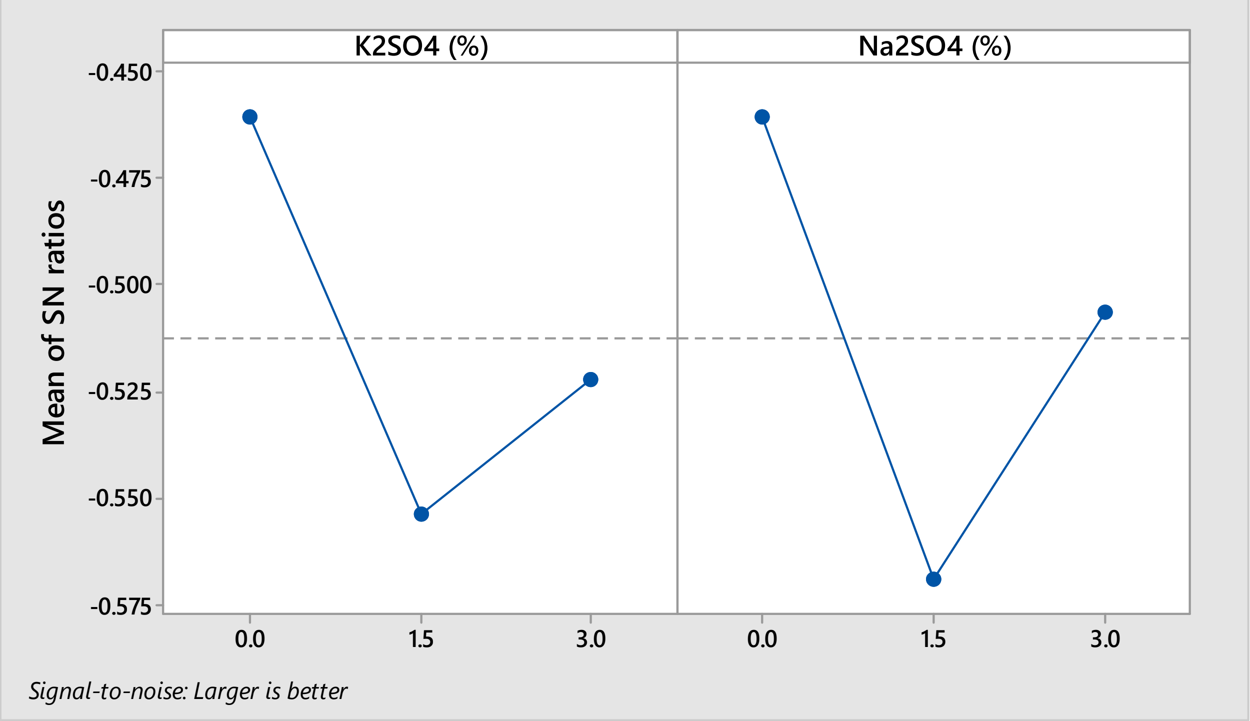


**Figure 2:** Main effect plot for signal-to-noise (S/N) ratio of density of sulfate salt–modified sesame oil. Experimental conditions: base oil = sesame oil; additive concentrations = 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; Taguchi L9 design.

### *3.1.4 Iodine Value*

The iodine value of the samples ranged from 17.51 to 23.73 g $I_2$/100 g oil. Raw sesame oil (R1) exhibited the highest iodine value (23.73 g $I_2$/100 g), indicating a relatively high level of unsaturation. Modified samples generally showed slightly reduced iodine values, with the lowest recorded for R8 (17.51 g $I_2$/100 g).

The slight reduction in iodine value suggests limited interaction between salt additives and unsaturated bonds, possibly due to adsorption or partial shielding effects. Nevertheless, the iodine values remain within the range characteristic of unsaturated vegetable oils, indicating preservation of the fundamental fatty acid structure. Unsaturated fatty acids contribute to lower viscosity and improved low-temperature flow behaviour, which are advantageous for quenching operations [11].

Furthermore, sesame oil contains natural antioxidants, such as sesamol and sesamin, that enhance oxidative stability despite its relatively high unsaturation [12, 13]. The combined effect of preserved unsaturation and inherent antioxidants supports the suitability of sesame oil as a base quenchant.

The main effect plot, as shown in Figure 4, demonstrates a decreasing trend with increasing additive concentration, particularly at 3.0%, indicating reduced availability of reactive double bonds. Lower iodine values correspond to improved oxidative stability, which is advantageous for high-temperature operation [15].

### *3.2 Thermal Safety Characteristics*

The thermal safety characteristics of raw sesame oil (R1) and sesame oil modified with salt-based additives (R2 – R9) were evaluated using smoke point, flash point and fire point measurements, as presented in Table 3.

These parameters are critical for assessing the ignition tendency, volatility and operational safety of quenching oils under high-temperature conditions (ASTM International, 2012).

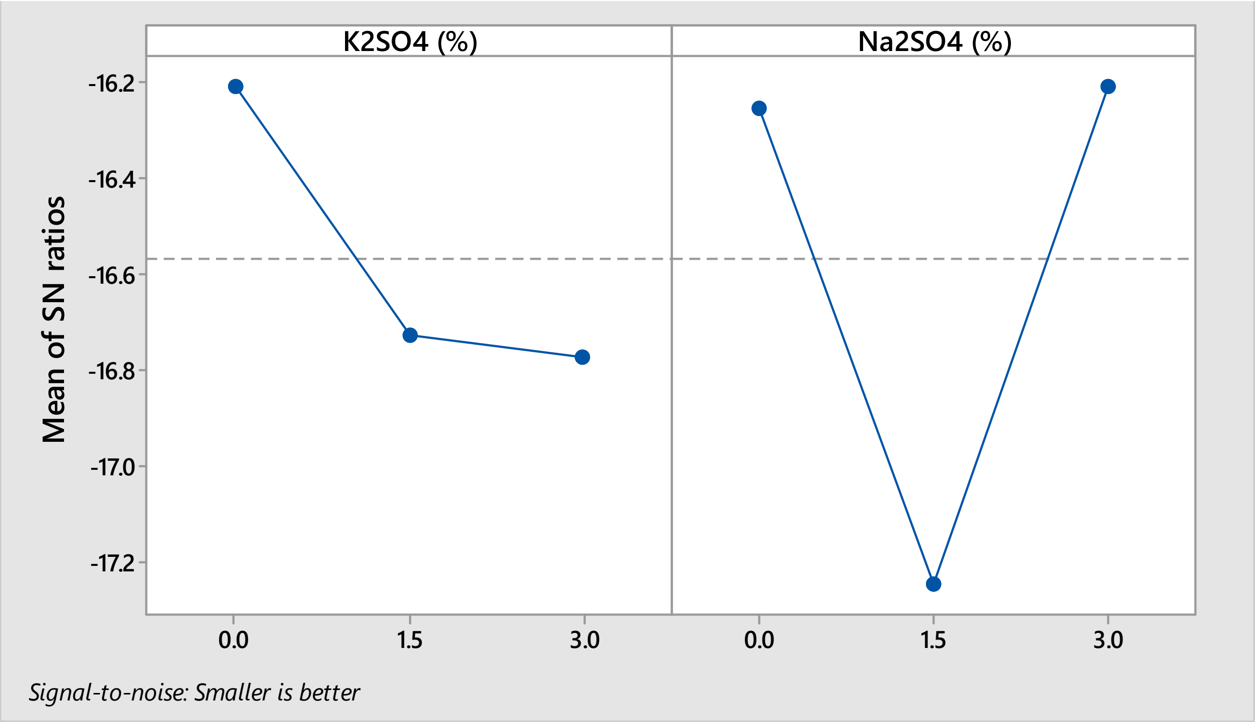


**Figure 3:** Main effect plot for signal-to-noise (S/N) ratio of acid value of sulfate salt–modified sesame oil. Experimental conditions: base oil = sesame oil; additive concentrations = 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; Taguchi L9 design.

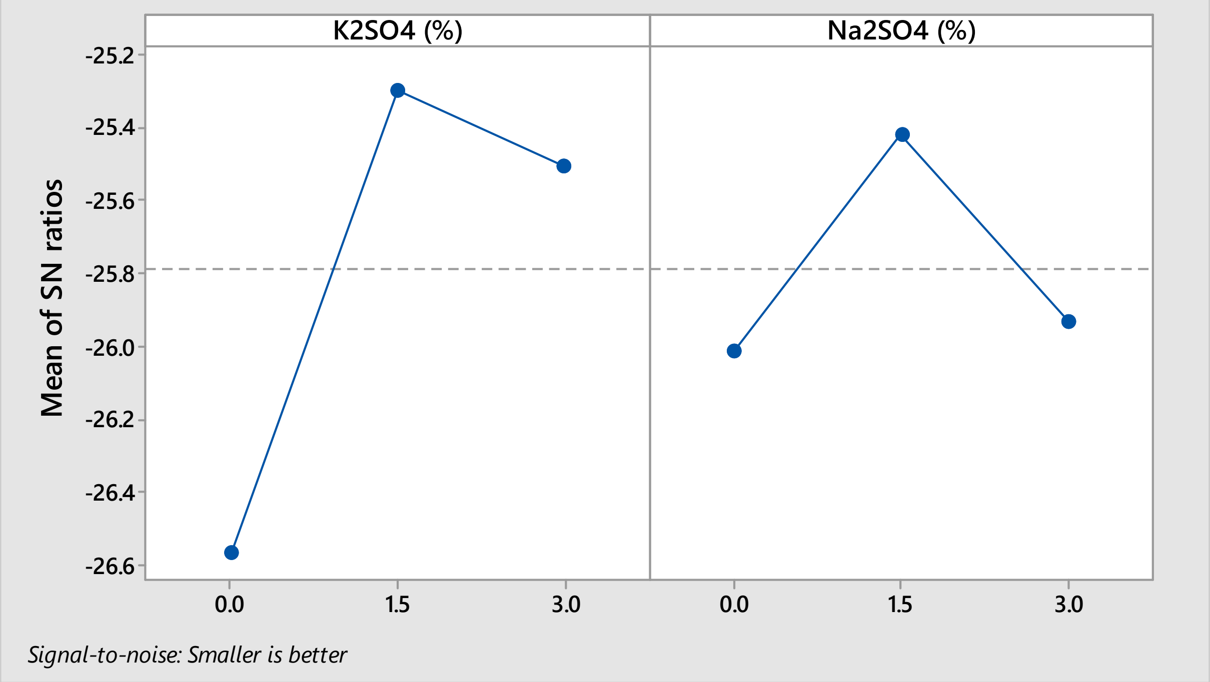


**Figure 4:** Main effect plot for signal-to-noise (S/N) ratio of iodine value of sulfate salt–modified sesame oil. Experimental conditions: base oil = sesame oil; additive concentrations = 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; Taguchi L9 design.

**Table 3:** Identification of thermal safety characteristics across all experimental runs

| Sample | Smoke Point (°C) | Flash Point (°C) | Fire Point (°C) |
|---|---|---|---|
| R1 | 140 | 350 | 385 |
| R2 | 180 | 370 | 380 |
| R3 | 152 | 360 | 370 |
| R4 | 185 | 340 | 345 |
| R5 | 161 | 340 | 375 |
| R6 | 146 | 350 | 392 |
| R7 | 142 | 354 | 357 |
| R8 | 147 | 363 | 364 |
| R9 | 181 | 335 | 343 |

### *3.2.1 Smoke Point*

Smoke point values ranged from 140 to 185 °C. Raw sesame oil (R1) exhibited a smoke point of 140 °C, while modified samples such as R2 and R9 showed elevated values of 180 °C and 181 °C, respectively.

Main effect plots shown in Figure 5 indicate a notable increase at 1.5% additive concentration, followed by a decline at 3.0%. The increase indicates suppression of volatile decomposition products by sulfate additives. Higher smoke point reflects improved resistance to early thermal breakdown [21].

### *3.2.2 Flash Point*

Flash points ranged from 335 to 370 °C. Raw sesame oil recorded 350 °C, whereas R2 exhibited the highest value (370 °C). Several modified samples (R3, R6, R8) maintained values ≥ 360 °C. Main effect plots shown in Figure 6 indicate at moderate additive levels of $K_2SO_4$ and $Na_2SO_4$ a decrease and an increase, and vice versa for higher concentrations. Higher flash point implies reduced flammability and safer handling during elevated-temperature service [28].

### *3.2.3 Fire Point*

Fire points ranged from 343 to 392 °C. Raw sesame oil showed 385 °C, while R6 exhibited the highest fire point (392 °C). The upward shift in fire point confirms that sulfate modification improves thermal ignition resistance. Main effect plots shown in Figure 7 reveal that fire point decreases with increasing additive levels of $K_2SO_4$, while it increases at moderate additive levels of $Na_2SO_4$, with a slight decline at higher additive concentrations.

### *3.3 TGA/DTA Thermal Stability*

Each of the TGA and DTA curves (Figures 8 - 16) corresponds to different combinations of potassium sulfate and sodium sulfate concentrations in the oil (R1 – R9). The red and blue curves represent the TGA and DTA curves, respectively.

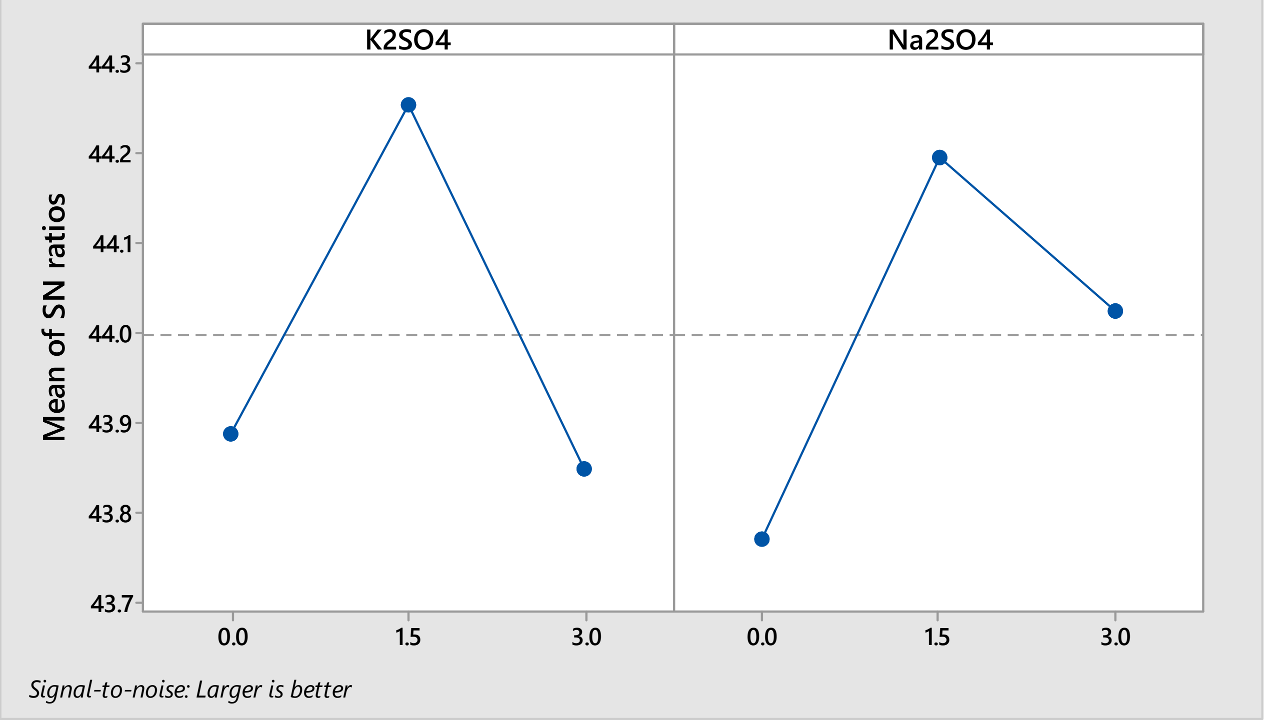


**Figure 5:** Main effect plot for signal-to-noise (S/N) ratio of smoke point of sulfate salt–modified sesame oil. Experimental conditions: base oil = sesame oil; additive concentrations = 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; Taguchi L9 design.

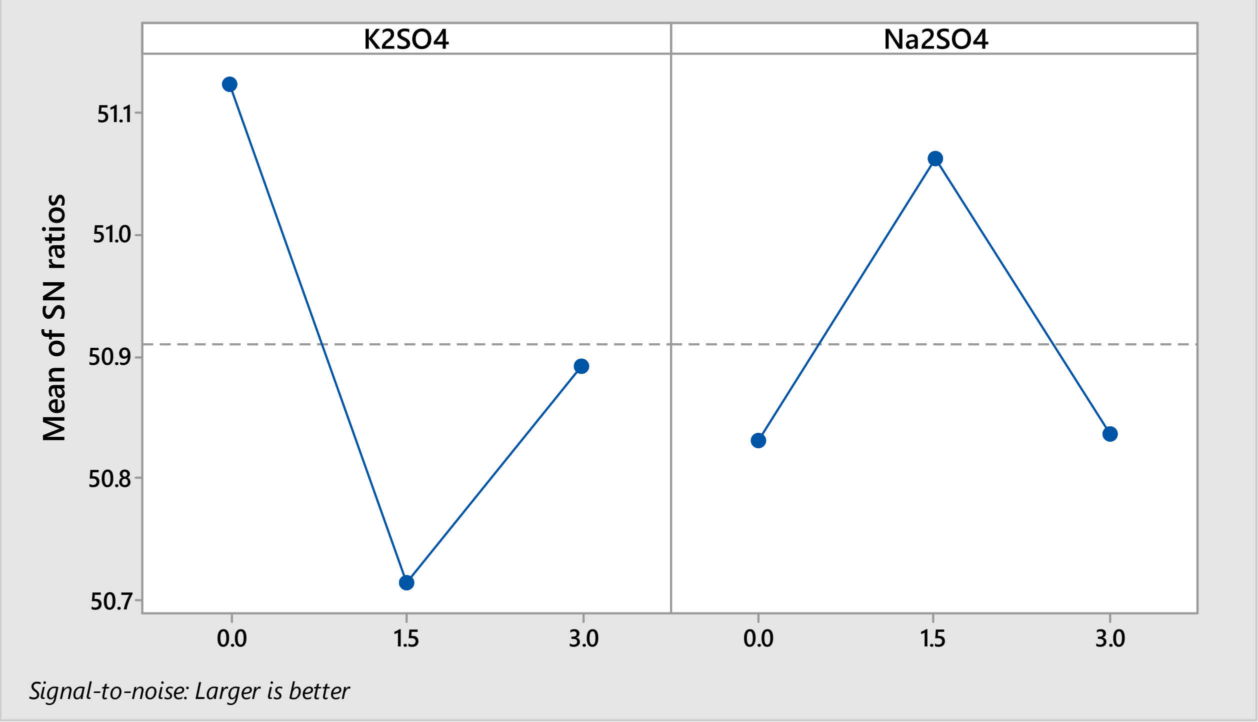


**Figure 6:** Main effect plot for signal-to-noise (S/N) ratio of flash point of sulfate salt–modified sesame oil. Experimental conditions: base oil = sesame oil; additive concentrations = 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; Taguchi L9 design.

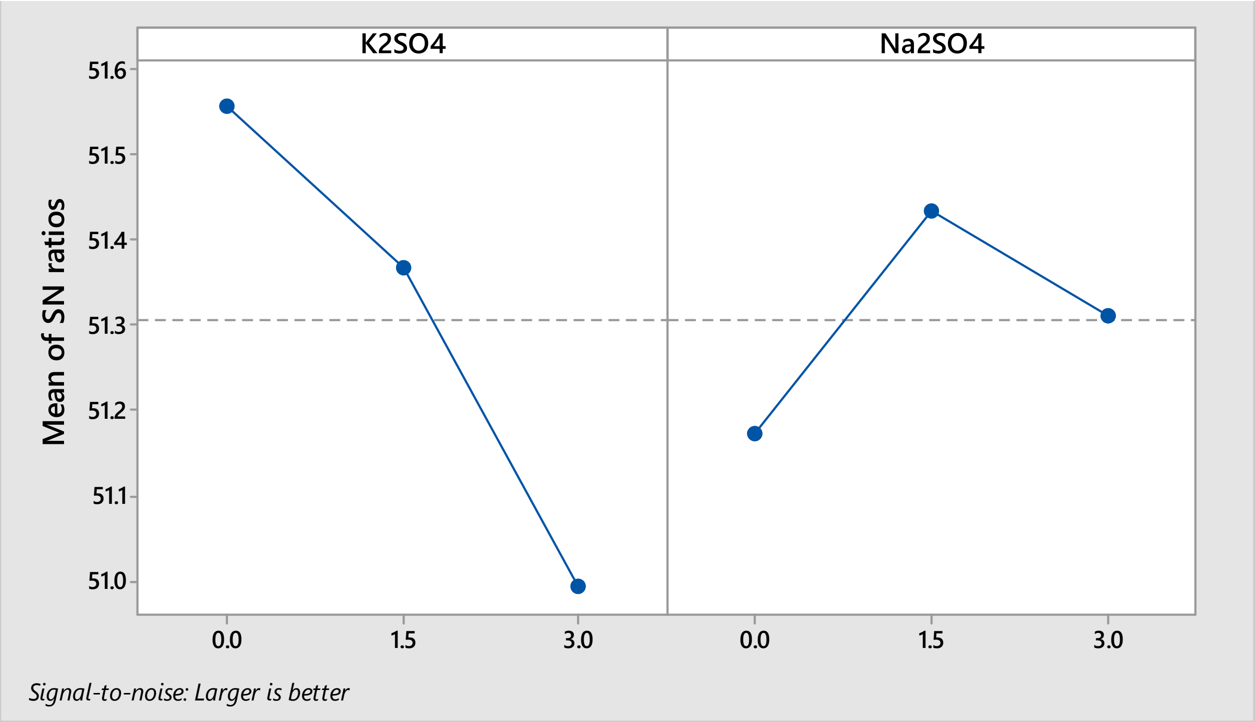


**Figure 7:** Main effect plot for signal-to-noise (S/N) ratio of fire point of sulfate salt–modified sesame oil. Experimental conditions: base oil = sesame oil; additive concentrations = 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; Taguchi L9 design.

**Table 4:** Thermal stability under nitrogen atmosphere (onset and maximum mass loss rate temperatures) extracted from Figures 8 – 16

| Runs | Tonset (°C) | Tmax (°C) |
|---|---|---|
| R1 | 160 | 275 |
| R2 | 180 | 265 |
| R3 | 175 | 270 |
| R4 | 200 | 275 |
| R5 | 170 | 265 |
| R6 | 195 | 285 |
| R7 | 195 | 280 |
| R8 | 180 | 275 |
| R9 | 190 | 290 |

Raw sesame oil (R1) exhibited a decomposition onset temperature (Tonset) of 160 °C and a maximum mass loss rate (Tmax) of 275 °C. The most stable runs were R6, R7 and R9, which exhibited significantly higher onset temperatures of 190 - 195 °C and peak decomposition temperatures of 280 - 290 °C. Tmax increased to 290 °C in R9. The delayed Tonset and Tmax confirm stronger resistance to pyrolytic breakdown. R7 showed overlapping peaks, indicating multiple decomposition pathways. The overlapping signals suggest that additive interactions introduced heterogeneity in the pyrolysis process, a phenomenon recently reported in vegetable oil systems subjected to inert thermal analysis [13]. These results demonstrate that higher concentrations of $Na_2SO_4$ and $K_2SO_4$ improve thermal stability under nitrogen by delaying volatilisation and moderating decomposition kinetics.

Main effect plots (Figures 17 and 18) represent the main effect of each additive on decomposition onset temperature and maximum mass loss rate temperature respectively. The figures revealed that an increase in $K_2SO_4$ and $Na_2SO_4$ concentrations increases decomposition onset temperature and maximum mass loss rate temperature, with an optimum at 3.0 % respectively, but 1.5 % $Na_2SO_4$ additive concentration shows a decrease in both decomposition onset temperature and maximum mass loss rate temperature. This indicates enhanced resistance to thermal degradation due to restricted molecular mobility and improved heat absorption pathways introduced by sulfate ions [8]. Higher Tonset and Tmax values signify longer service life and better thermal endurance

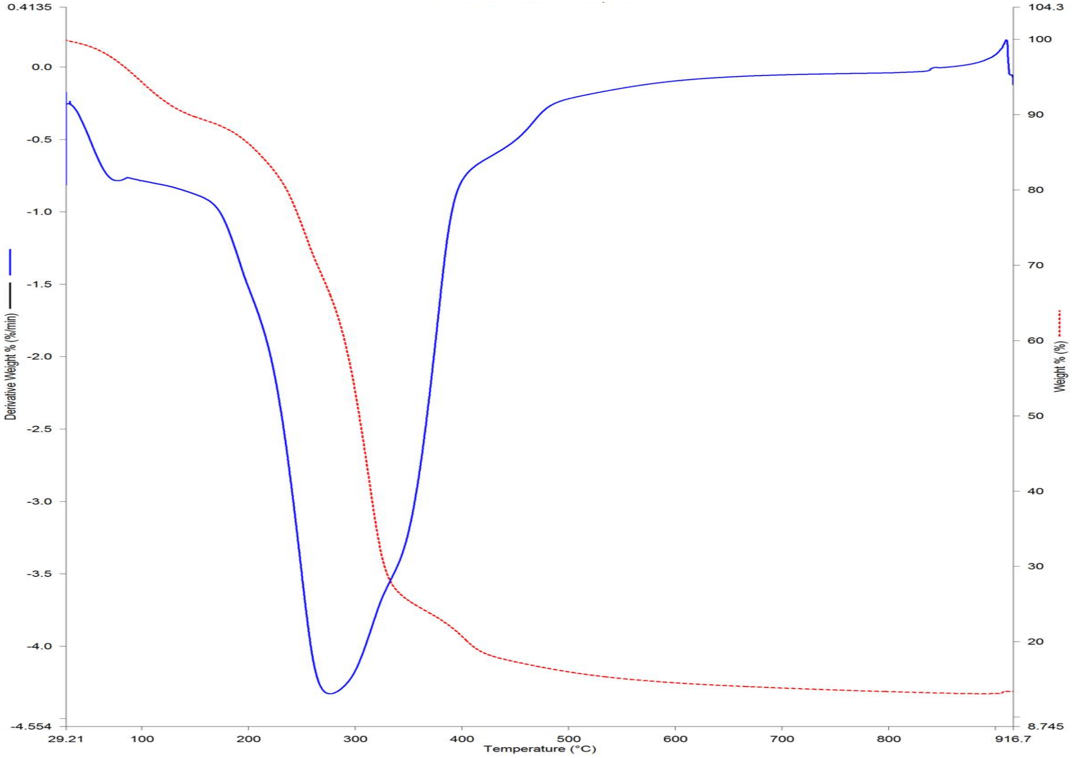


**Figure 8**: TGA/DTA curves of raw sesame oil (R1). Experimental conditions: sample mass ≈ 12 mg; temperature range = 30 – 900 °C; heating rate = 10 °C/min; atmosphere = nitrogen.

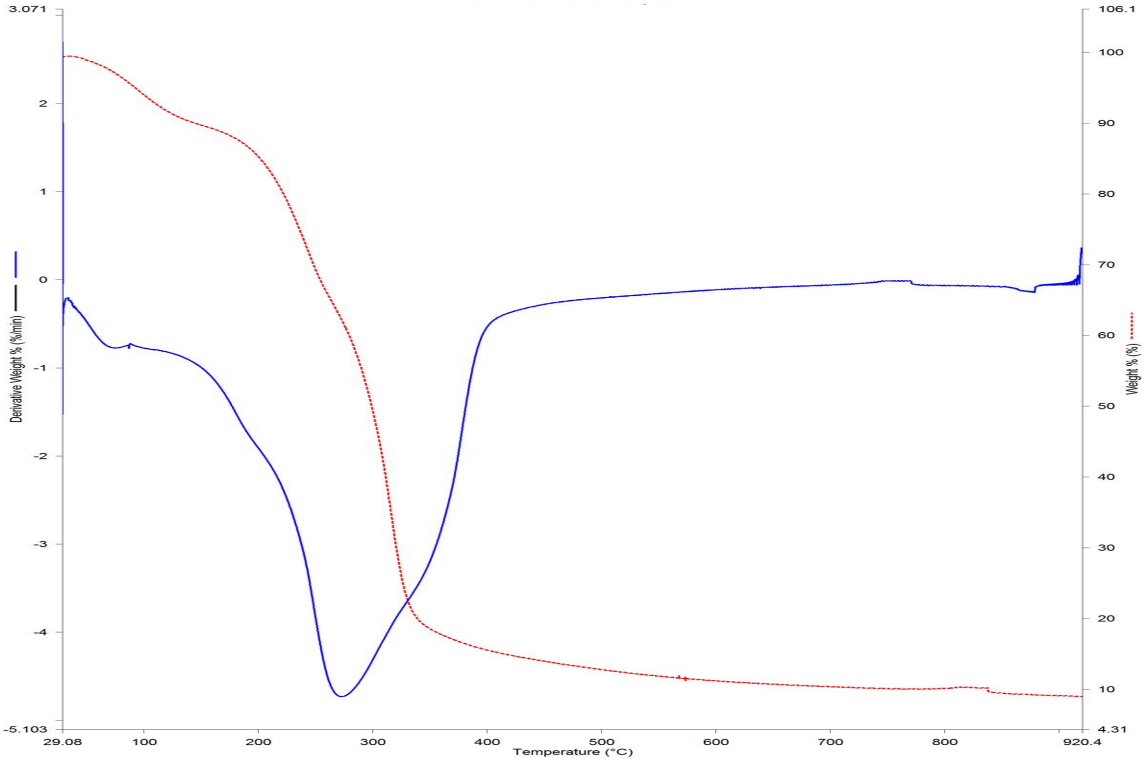


**Figure 9**: TGA/DTA curves of sulfate salt–modified sesame oil (R2). Experimental conditions: base oil = sesame oil; additives = 0 wt. % $K_2SO_4$ and 1.5 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.

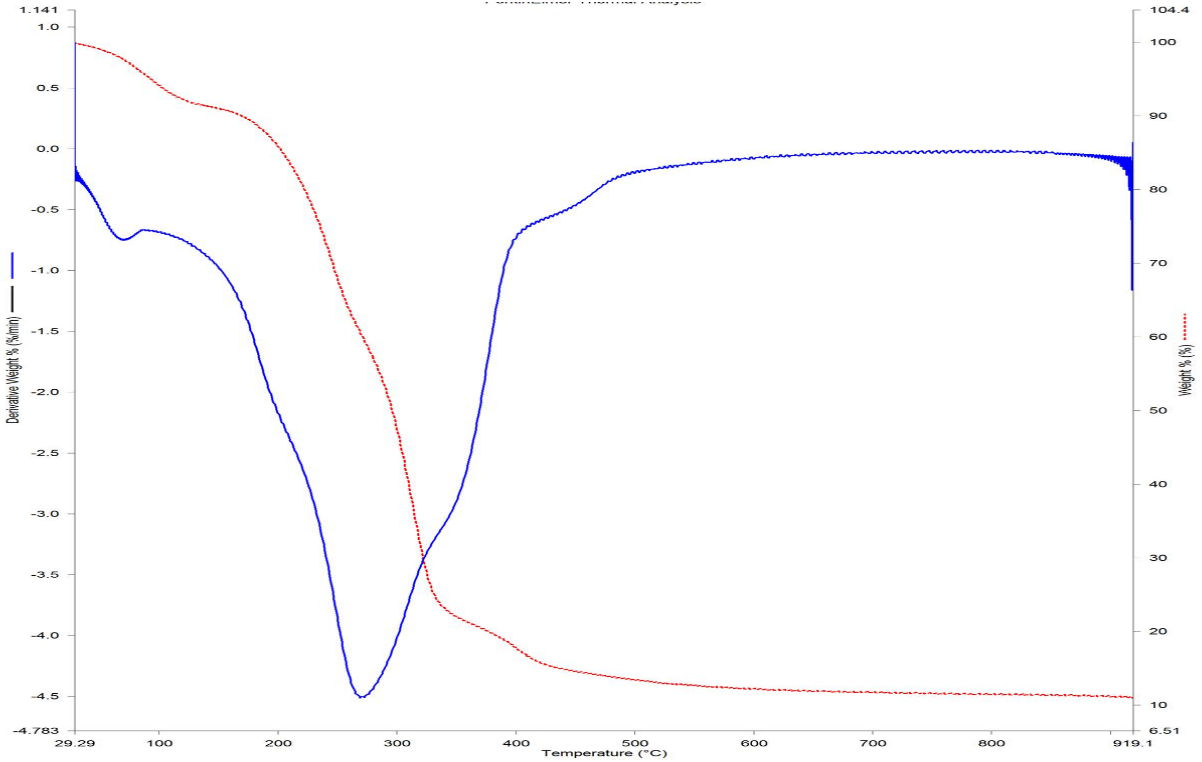


**Figure 10:** TGA/DTA curves of sulfate salt–modified sesame oil (R3). Experimental conditions: base oil = sesame oil; additives = 0 wt. % $K_2SO_4$ and 3.0 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.

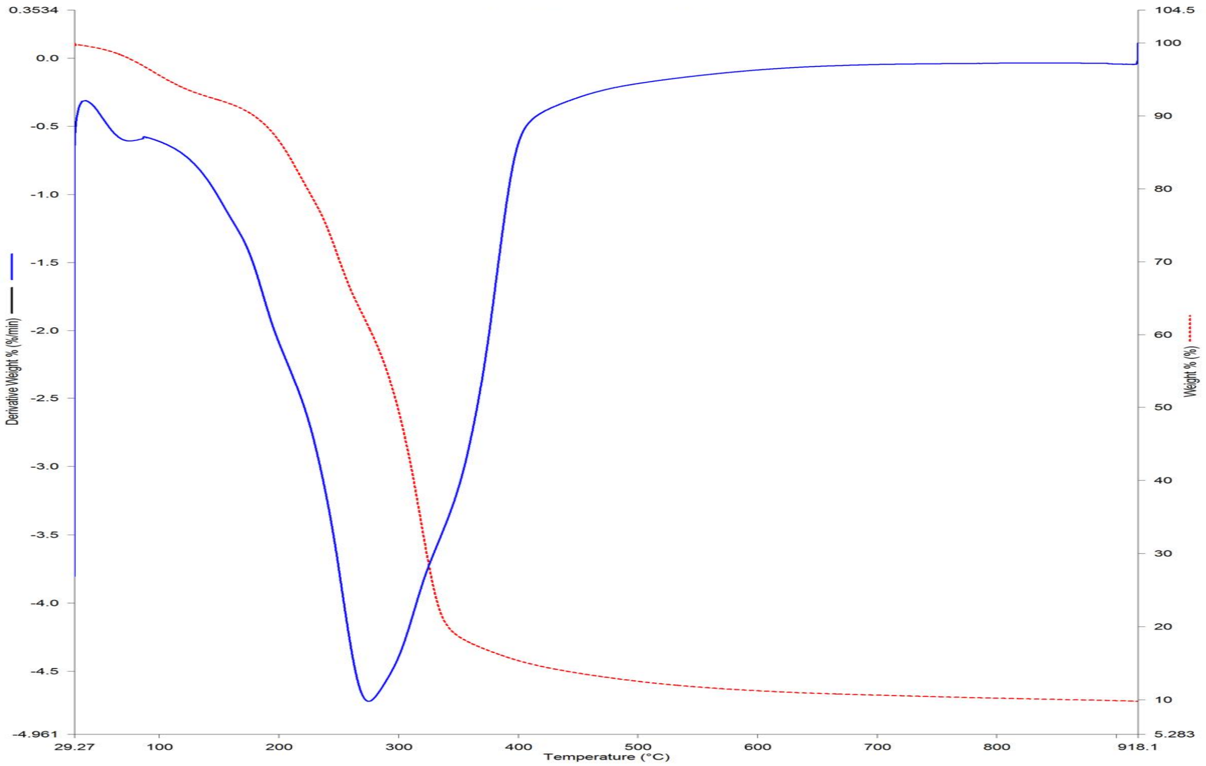


**Figure 11:** TGA/DTA curves of sulfate salt–modified sesame oil (R4). Experimental conditions: base oil = sesame oil; additives = 1.5 wt. % $K_2SO_4$ and 0 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.

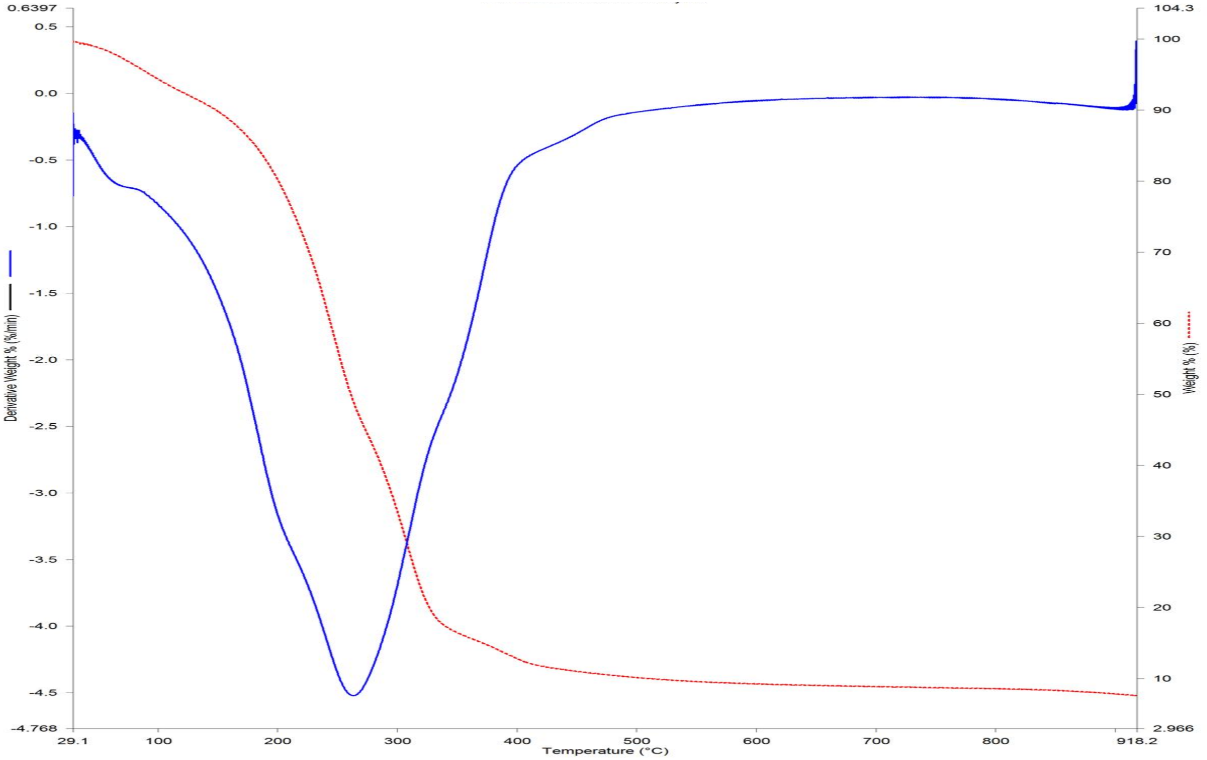


**Figure 12:** TGA/DTA curves of sulfate salt–modified sesame oil (R5). Experimental conditions: base oil = sesame oil; additives = 1.5 wt. % $K_2SO_4$ and 1.5 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.

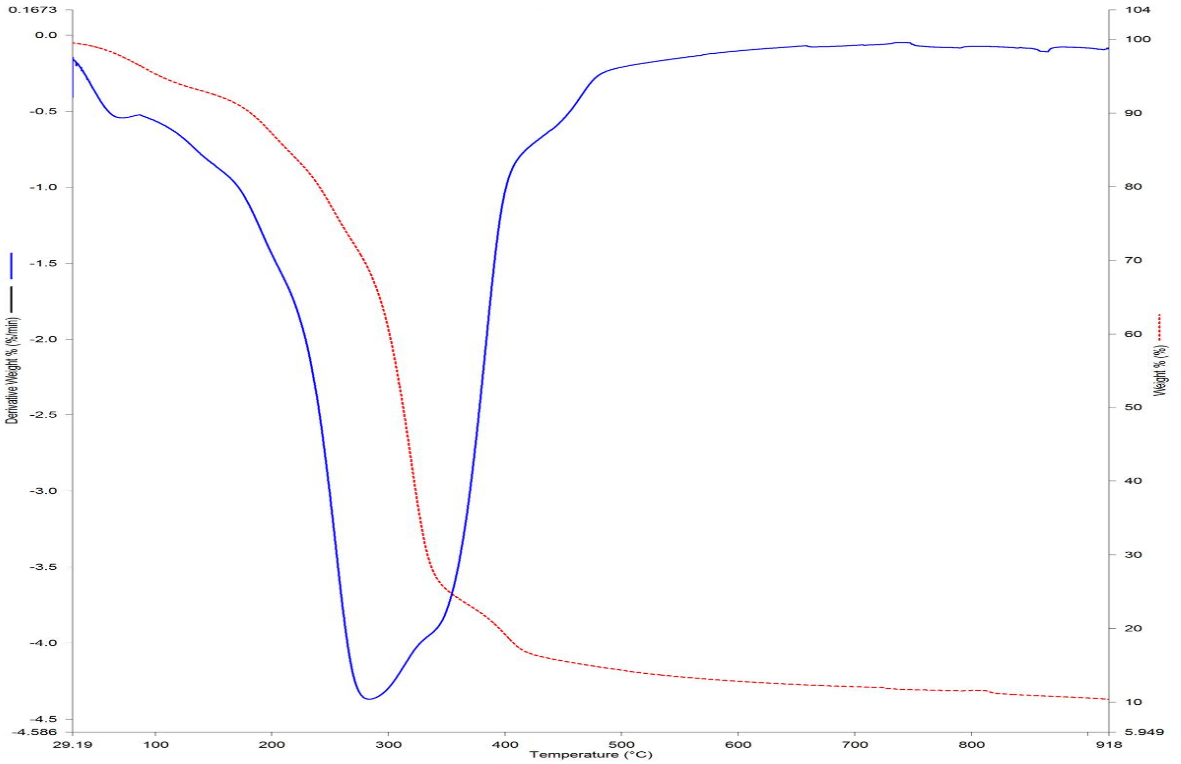


**Figure 13:** TGA/DTA curves of sulfate salt–modified sesame oil (R6). Experimental conditions: base oil = sesame oil; additives = 1.5 wt. % $K_2SO_4$ and 3.0 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.

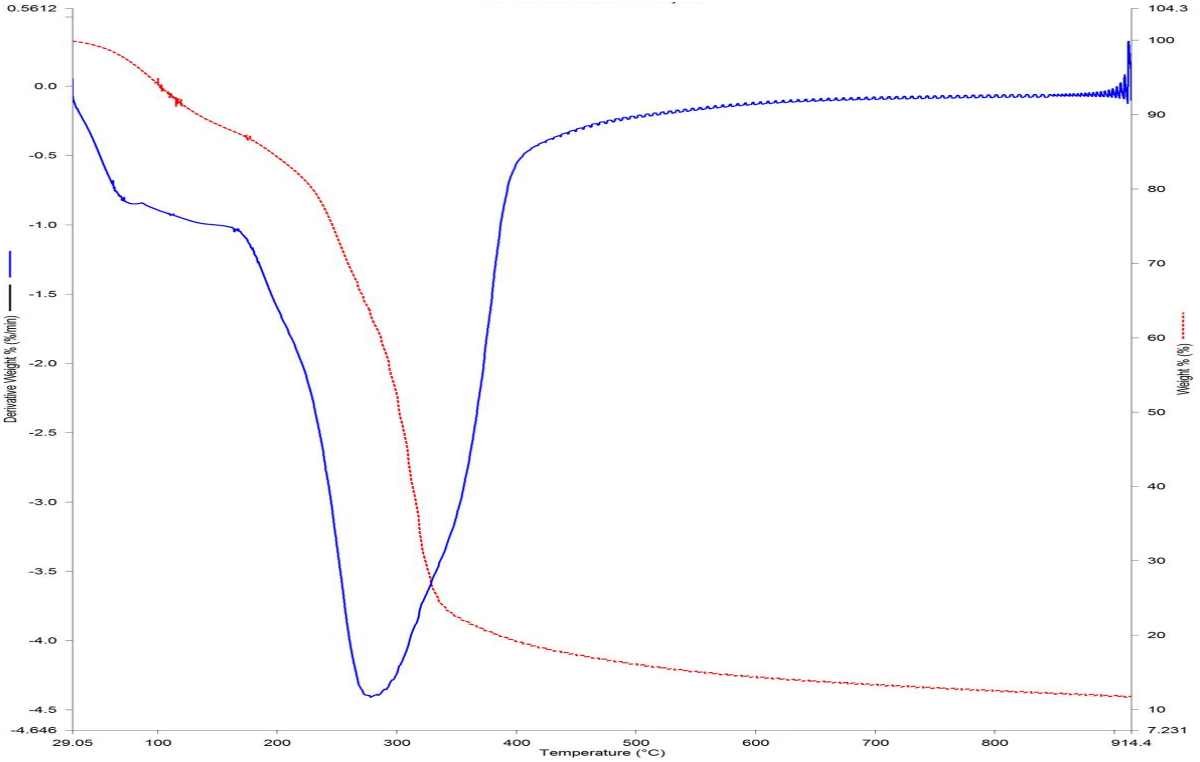


**Figure 14:** TGA/DTA curves of sulfate salt–modified sesame oil (R7). Experimental conditions: base oil = sesame oil; additives = 3.0 wt. % $K_2SO_4$ and 0 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.

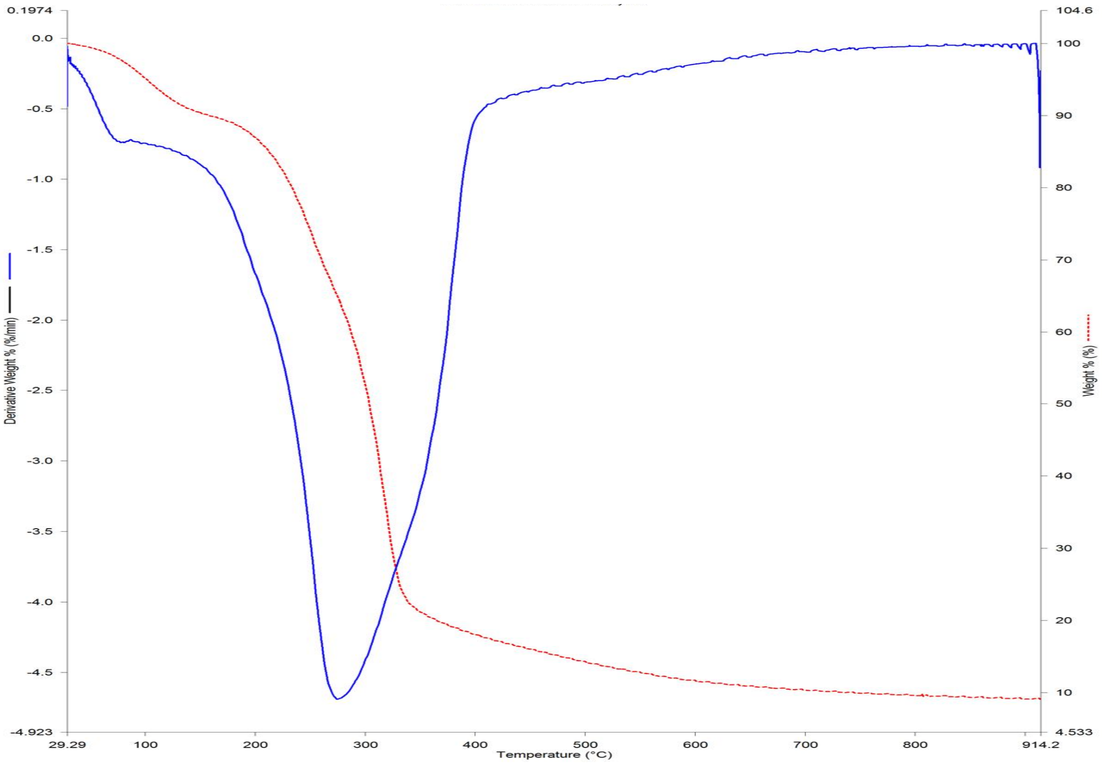


**Figure 15:** TGA/DTA curves of sulfate salt–modified sesame oil (R8). Experimental conditions: base oil = sesame oil; additives = 3.0 wt. % $K_2SO_4$ and 1.5 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.

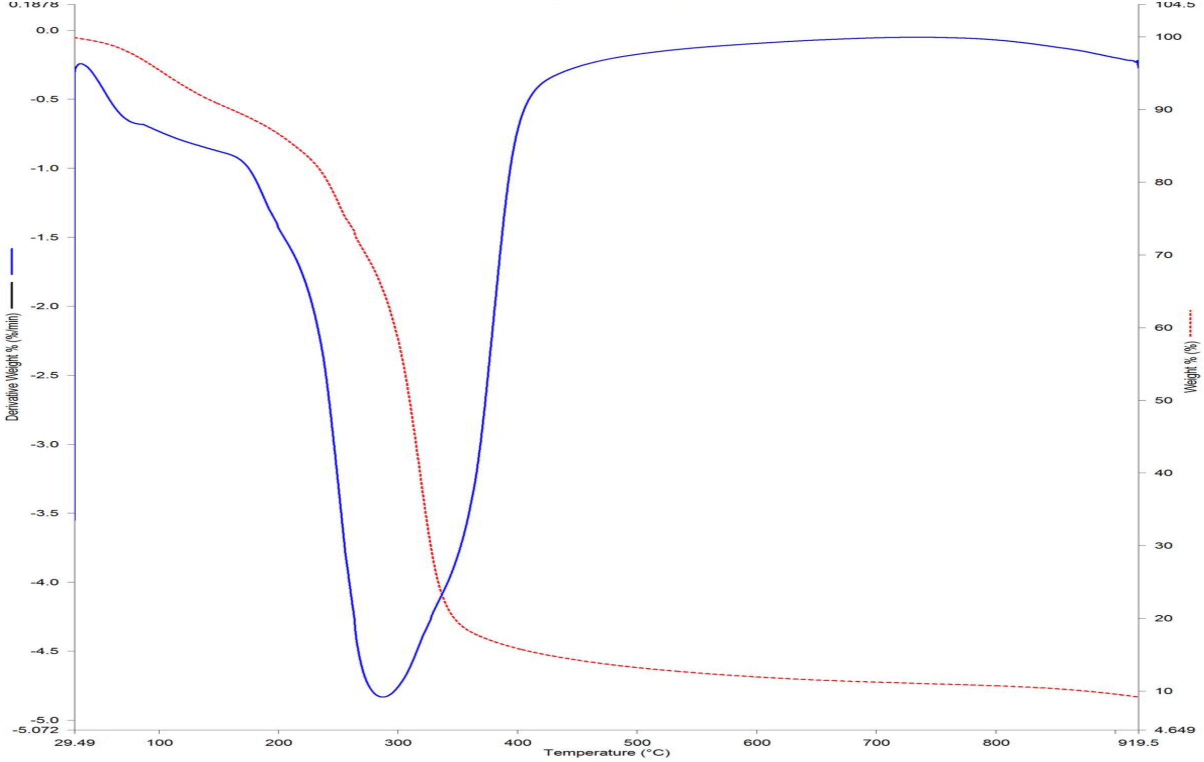
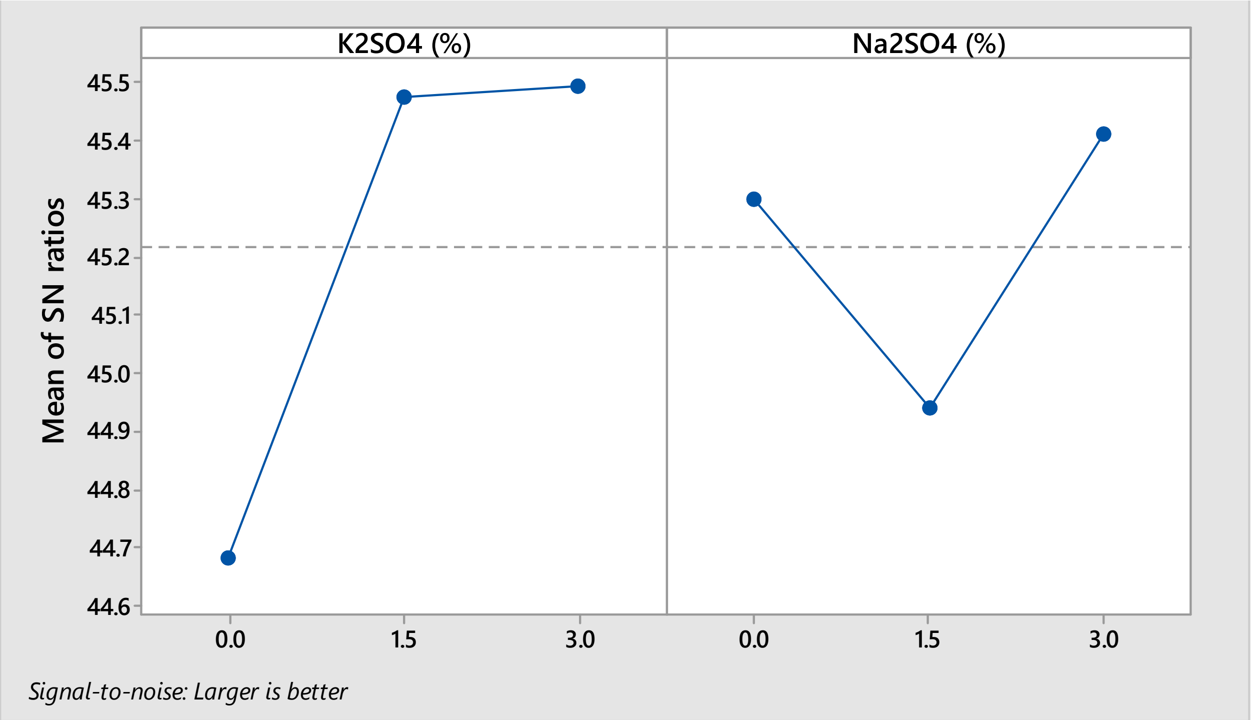


**Figure 16:** TGA/DTA curves of sulfate salt–modified sesame oil (R9). Experimental conditions: base oil = sesame oil; additives = 3.0 wt. % $K_2SO_4$ and 3.0 wt. % $Na_2SO_4$; heating rate = 10 °C/min; temperature range = 30 – 900 °C; atmosphere = nitrogen.



*Signal-to-noise: Larger is better*

**Figure 17:** Main effect plot for signal-to-noise (S/N) ratio of decomposition onset temperature (Tonset) of sulfate salt–modified sesame oil. Experimental conditions: TGA performed under nitrogen atmosphere; heating rate = 10 °C/min; additive concentrations = 0 – 3.0 wt.% $K_2SO_4$ and $Na_2SO_4$.

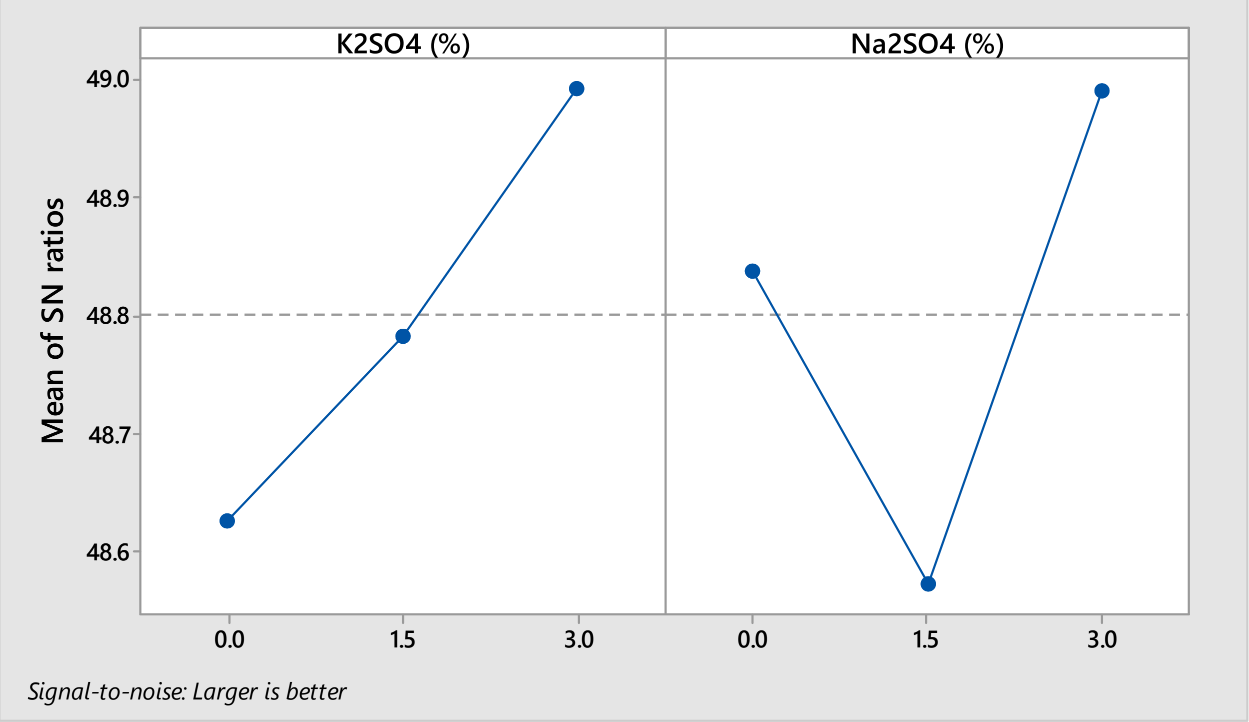


**Figure 18:** Main effect plot for signal-to-noise (S/N) ratio of maximum mass loss rate temperature (Tmax) of sulfate salt–modified sesame oil. Experimental conditions: TGA performed under nitrogen atmosphere; heating rate = 10 °C/min; additive concentrations = 0 – 3.0 wt.% $K_2SO_4$ and $Na_2SO_4$.

### *3.4 Cooling Curve Characteristics (Temperature–Time Response)*

Representative cooling curves for raw sesame oil (R1) and sulfate-modified sesame oil (R2 – R9) formulations recorded over 70 seconds are shown in Figure 19. The curves describe the transient temperature evolution of a heated probe immersed in the oil samples and reflect the intrinsic heat extraction capability of each formulation. Quenching behaviour typically proceeds through three stages: vapour blanket formation, nucleate boiling and convective cooling. The efficiency of these stages determines the resulting microstructure and mechanical properties of the steel [24].

During the stage I (0 – 5 s), samples R5, R8 and R9 exhibited the highest cooling rates, indicating rapid vapour blanket breakdown and efficient nucleate boiling. The enhanced thermal response of modified oils is attributed to the presence of sulfate ions, which improve surface wetting and destabilise the vapour film. Improved wetting promotes direct liquid–surface contact, accelerating heat transfer through nucleate boiling. Similar effects have been reported for additive-modified vegetable oils and nanofluid quenchants, where surface-active species reduce vapour blanket stability and enhance heat extraction [36]. In contrast, raw sesame oil (R1) demonstrated the slowest initial cooling rate, consistent with its higher volatility and delayed bubble collapse.

In the intermediate cooling (stage II), Runs R4 and R5 reached approximately 210 °C at 13 seconds, demonstrating superior heat extraction efficiency. This temperature range coincides with the bainitic transformation window for high alloy steels, confirming that these oil formulations are suitable for promoting bainite formation during austempering [24].

During the final convective cooling stage, all samples showed comparable gradual temperature reduction, suggesting that additive modification primarily influences early and intermediate cooling behaviour rather than late-stage natural convection. Similar trends have been reported in salt-modified quenching oils, where additives improve nucleate boiling but slightly reduce convective heat transfer at extended durations [1].

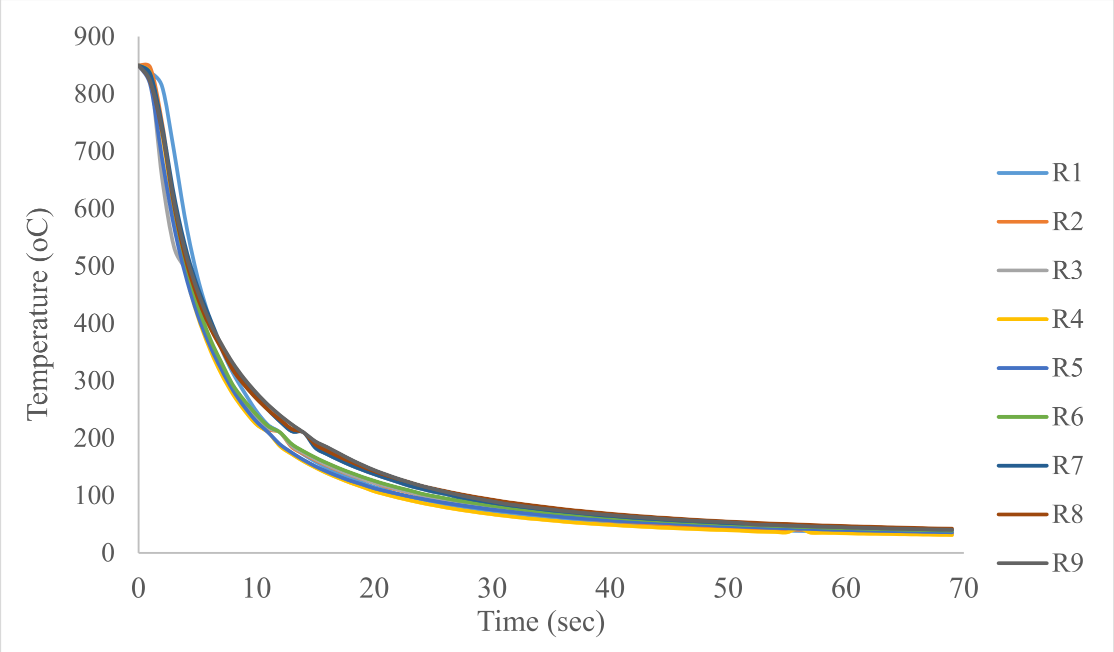


**Figure 19:** Cooling curves of high carbon steel probe quenched in raw (R1) and sulfate salt–modified sesame oils (R2 – R9). Experimental conditions: probe material = high carbon steel; austenitizing temperature = 850 °C; holding time = 15 min; quenching media = sesame oil with 0 – 3.0 wt. % $K_2SO_4$ and $Na_2SO_4$; temperature recorded using embedded thermocouple and data acquisition system.

### *3.5 Limitations and Future Work*

Despite the promising findings obtained in this study, certain limitations should be acknowledged. The present investigation was conducted at a laboratory scale and the scalability of sulfate salt modification of sesame oil for industrial heat treatment applications remains to be established. In particular, challenges related to large-scale dispersion of inorganic salts, process cost and operational consistency require further evaluation.

Additionally, the long-term thermal and oxidative stability of the modified oils under repeated quenching cycles was not investigated. Prolonged service conditions may influence degradation behaviour, additive stability and overall quenchant performance. The potential effects of sulfate salt additives on equipment corrosion and environmental impact were also beyond the scope of this study.

Future research should therefore focus on cyclic durability testing, large-scale validation, corrosion assessment and techno-economic analysis to fully establish the industrial applicability of sulfate salt–modified sesame oil as a bio-based quenching medium.

## 4.0 Conclusion

i. Thermal analysis using TGA/DTA confirmed that the incorporation of sulfate salt additives significantly improved the thermal stability of sesame oil. Raw sesame oil (R1) exhibited an onset decomposition temperature (Tonset) of 160 °C and a maximum mass loss rate temperature (Tmax) of 275 °C, indicating early thermal degradation. In contrast, salt-modified oils recorded elevated Tonset values ranging from 175 °C to 200 °C and Tmax values up to 290 °C, with Run R9 exhibiting the highest Tmax. These increases demonstrate delayed thermal degradation and improved resistance to high-temperature exposure, validating the suitability of salt-modified sesame oil for austempering applications.
ii. Thermal safety test demonstrates that harmonising sesame oil with salt-based additives (R2 – R9) lead to measurable improvement of the oil's smoke point. While raw sesame oil (R1) already exhibits acceptable flash and fire points, its lower smoke point limits its performance under prolonged high-temperature exposure.
iii. Physicochemical analysis showed that the addition of $K_2SO_4$ and $Na_2SO_4$ caused only marginal variations in density, viscosity, acid

value and iodine value. While slight increases in iodine value and limited reductions in acid value were observed, these changes remained within acceptable limits and did not indicate severe oxidative degradation.

iv. Cooling curve analysis revealed that salt-modified sesame oils significantly improved stage I heat extraction. At the critical 0 – 5 s interval, Runs R3, R4 and R5 recorded temperatures of 423 °C, 414 °C and 416 °C, respectively, compared to 481 °C for raw sesame oil (R1). This enhanced early-stage cooling reflects accelerated vapour blanket breakdown and intensified nucleate boiling, which are essential for effective austempering and controlled phase transformation.

## References

1. Totten, G. E. (2006). Steel heat treatment: metallurgy and technologies. CRC Press.
2. Bhadeshia, H. K. D. H. (2015). Bainite in steels: Theory and practice (3rd ed.). Maney Publishing.
3. Zhou, J. H., Chen, J. S., & Shen, Y. F. (2019). Heat Treatment of Metals, 100–103.
4. Totten, G. E. (2019). Investigation of quenchants based on sodium aqueous ionic solutions. In Heat Treat 2019: Proceedings of the 30th ASM Heat Treating Society Conference (pp. 253–259)
5. Fox, N. J., & Stachowiak, G. W. (2007). Vegetable oil-based lubricants—A review of oxidation. Tribology International, 40(7), 1035–1046.
6. Saka, A., Abor, T. K., Okafor, A. C., & Okoronkwo, M. U. (2025). Thermo-rheological and tribological properties of low- and high-oleic vegetable oils as sustainable bio-based lubricants. RSC Sustainability, 3, 1461-1476.
7. Stachowiak, G. W., & Batchelor, A. W. (2025). Engineering tribology (4th ed.). Butterworth-Heinemann.
8. Owuna, F. J. (2020). Stability of vegetable based oils used in the formulation of ecofriendly lubricants – A review. Egyptian Journal of Petroleum, 29(3), 251–256.
9. Ribeiro, D. C. M., Ramalho, A., Serra, A. C., & Coelho, J. (2025). Biolubricants based on epoxidized vegetable oils: A review on chemical modifications, tribological properties and sustainability. Lubricants, 13, 510.
10. Sarker, M. I., Mainali, K., & Sharma, B. K. (2025). Investigations on the thermal stability and kinetics of biolubricants synthesized from different types of vegetable oils. Lubricants, 13, 105.
11. Adekunle, A. S., Adeleke, A. A., Gbadamosi, T. A., Nwosu, F. O., Odusote, J. K., Omoniyi, P. O., Popoola, T. O., & Adebiyi, K. A. (2020). A cooling potential of formulated bio-quenchant oils on a cast aluminium alloy material. Journal of Chemical Technology and Metallurgy, 55 (5), 1140-1149.
12. Singh, T., & Chhibber, R. (2018). Vegetable oil-based quenchants: A review. Materials Performance and Characterization, 7(3), 20180040.
13. Morsy, M.K., Sami, R., Algarni, E., Al-Mushhin, A. A. M., Benajiba, N. A. A., Almasoudi, A.G., & Mekawi, E. (2022). Phytochemical profile and antioxidant activity of sesame seed (sesamum indicum) by-products for stability and shelf life improvement of refined olive oil. Antioxidants, 11, 338.
14. Sabarinath, S., Kumarapillai, P., & Perikinalil, R. (2017). Evaluation of physicochemical, thermal and tribological properties of sesame oil (Sesamum indicum L.): A potential agricultural crop base stock for eco-friendly industrial lubricants. International Journal of Agricultural Resources, Governance and Ecology (IJARGE), 13(1), 77–90.
15. Gunstone, F. D. (2011). Vegetable oils in food technology: Composition, properties and uses (2nd ed.). Oxford, UK: Wiley-Blackwell.
16. Chabni A, Bañares C. & Torres C. F. (2024). Study of the oxidative stability via Oxitest and Rancimat of phenolic-rich olive oils obtained by a sequential process of dehydration, expeller and supercritical $CO_2$ extractions. Front. Nutr. 11:1494091.
17. Gharby, S., Asbbane, A., Hallouch, O., Ibourki, M., Oubannin, S., Nid Ahmed, M., Bijla, L., Gagour, J., Goh, K. W., & Bouyahya, A. (2025). Vegetable oil oxidation: Mechanisms, impacts on quality and approaches to enhance shelf life. Food Chemistry: X, 28, 102541.
18. Astrid, A. E. C., Delgado-Tobón, A. E., & Aperador Chaparro, W. A. (2019). Comparative study of the thermal properties of sesame oil and two mineral oils of different viscosity. INGE CUC, 15(2), 99 – 109.
19. Gharby, S., Harhar, H., Bouzoubaa, Z., Asdabi, A., El Yadini, A., & Charrouf, Z. (2017). Chemical characterization and oxidative stability of seeds and oil of sesame grown in Morocco. Journal of the Saudi Society of Agricultural Sciences, 16(2), 105–111.
20. Mobarak, H. M., (2014). The prospects of biolubricants as alternatives to mineral-based

lubricants. Renewable and Sustainable Energy Reviews, 33, 34–43.

21. Simêncio, O. R. L., Canale, L. C. F., Totten, G. E., & Meekisho, L. (2017). Vegetable oils as metal quenchants: A comprehensive review. Materials Performance and Characterization, 6(1), 174-250
22. Kheirati, R. S., Akrami, M. F., Moshtaghi, B. H., Pourramezani, F., Jambarsang, S., Kiani, H., & Khalili, S. E. (2021). The chemical composition and heavy metal content of sesame oil produced by different methods: A risk assessment study. Food Science & Nutrition, 9(6), 2886-2893.
23. Kurt, C. (2018). Variation in oil content and fatty acid composition of sesame accessions from different origins. Grasas Aceites 69(1), e 241
24. Bhadeshia, H. K. D. H., & Honeycombe, R. (2017). Steels: Microstructure and properties (4th ed.). Oxford, UK: Butterworth-Heinemann.
25. Sujay, K. D., & Yakshil, B. C. (2020). Basic concepts of iron and steel making.
26. Totten, G. E., & Howes, M. A. H. (1997). Steel heat treatment handbook. New York, NY: Marcel Dekker.
27. Bhadeshia, H., & Honeycombe, R. (2017). Steels: Microstructure and properties (4th ed.). Butterworth-Heinemann.
28. Rudnick, L. R. (2017). Lubricant additives: Chemistry and applications (2nd ed.). Boca Raton, FL: CRC Press.
29. Shelke, S. D., Sangale, M. D., & Pondhe, G. M. (2024). Effect of additives in vegetable lubricating oil. International Journal of Research Publication and Reviews, 5(3), 1469-1477.
30. Aabid, A., Quadros, J. D., Khan, S. A., Mohin, M., Mogul, Y. I., Baig, M., & Ahmed, O. S. (2024). Heat transfer of $Ca(NO_3)_2$-$KNO_3$ molten salt mixtures for austempering and martempering processes of steels. ACS Omega
31. Ramesh, G., & Prabhu, K. N. (2016). Wetting and cooling performance of vegetable oils during quench hardening. Heat Transfer—Asian Research, 45(4), 321–333.
32. Das, S. K., Choi, S. U. S., & Patel, H. E. (2006). Heat transfer in nanofluids—A review. Heat Transfer Engineering, 27(10), 3–19.
33. Kobasco, N. I. (2022). Basics of quench process hardening of powder materials and irons in liquid media. European Journal of Applied Physics, 4 (3).
34. Greenwood, N. N., & Earnshaw, A. (1997). Chemistry of the elements (2nd ed.). Oxford, UK: Butterworth-Heinemann.
35. Totten, G. E., Bates, C. E., & Clinton, N. A. (2011). Handbook of quenchants and quenching technology (pp. 138–147). ASM International.
36. Liscic, B., Tensi, H. M., Canale, L. C. F., & Totten, G. E. (2010). Quenching theory and technology (2nd ed.). CRC Press.