

Article

Thermal Safety Analysis of On-Site Emulsion Explosives Mixed with Waste Engine Oil

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Abstract: The study of the thermal safety of emulsion explosives mixed with waste engine oil is very important for the safety of these types of explosives used in mine blasting. In order to study the thermal safety of emulsion explosives mixed with waste engine oil, thermal safety tests were carried out using a Differential Scanning Calorimeter (DSC), non-isothermal kinetics, and the Flynn–Wall–Ozawa method. The results show that the minor particle impurities in the filtered waste engine oil are mainly combustibles; after adding different amounts of waste engine oil, the activation energy of the emulsion matrix decreases from 110.33 kJ/mol to 75.39 kJ/mol, 74.50 kJ/mol, and 82.23 kJ/mol, and the critical temperature for thermal explosion changes from 194.16 °C to 169.73 °C, 227.47 °C, and 208.78 °C. The addition of waste engine oil reduces the activation energy of emulsion explosives. The waste engine oil is negatively correlated with the activation energy and the thermal explosion reaction temperature of emulsion explosives, and the correlation coefficient is -0.686 and -0.333 . The emulsifier is positively correlated with the critical temperature of thermal explosion of emulsion explosives, and the correlation coefficient is 0.251 . The small particles in the waste engine oil create a hot spot in the emulsion explosives, which reduces the thermal safety of the emulsion explosives mixed with waste engine oil. The emulsifier reduces the droplet size of the emulsion explosive, improves the oil-water interface strength, and improves the thermal safety of the emulsion explosives mixed with waste engine oil. The thermal safety of emulsion explosives mixed with waste engine oil can be improved by reducing the proportion of the sensitizer and increasing the proportion of the emulsifier.

Keywords: emulsion explosives; waste engine oil; non-isothermal kinetics; thermal safety



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1. Introduction

Emulsion explosives are widely used in the blasting of mines and the creation of tunnels, water conservancy developments, and hydropower projects [1]. Emulsion explosives are made up of a class of volatile water-in-oil solutions. Generally, the aqueous phase consists chiefly of ammonium nitrate, sodium nitrate, and water; the fuel phase is made up mainly of different kind of mineral oil, usually engine oil, diesel fuel, and emulsifiers [2,3].

The mining production generates a large amount of waste engine oil. If the waste engine oil produced by the mine can be used to produce emulsion explosives, it can solve the problem of the economic utilization of waste engine oil, reduce environmental pollution, and reduce production costs. The Shenhua Zhungeer Co., Ltd. Explosives Factory manufactures ANFO (a widely used bulk industrial explosive) using filtered waste engine oil and diesel fuel, with a 2:1 ratio of waste engine oil to diesel fuel [4]. Waste cooking oil and diesel fuel have been used in a 1:1 ratio to replace the pure diesel fuel for the on-site mixing of ANFO [5]. A porous granular ammonium nitrate explosive was prepared with a 1:1 ratio of waste engine oil to diesel fuel at the Shenhua Zhungeer Factory [6]. Energy and safety are the two most important concerns for emulsion explosives. Since the waste

engine oil contains solid particles, it is necessary to pay attention to the thermal safety of the emulsion explosives mixed with waste engine oil. This is especially important in large mines that carry out their blasting a long time after loading the boreholes.

Currently, there has been little research published on the thermal safety of emulsion explosives mixed with waste engine oil. In order to make extend the understanding of the thermal safety of emulsion explosives mixed with waste engine oil, this study investigates the kinetics of the thermal decomposition of emulsion explosives mixed with various waste engine oil contents using differential scanning calorimetry (DSC) and thermogravimetry (TG), and the activation energy and the critical temperatures of thermal explosion of the emulsion explosives are calculated.

2. Experimental Section

2.1. Materials

The waste engine oil used in this study is the spent lubricant engine oil used in a mine. The type of oil used is SAE 15W40. The physical and chemical data describing the waste engine oil are shown in Table 1.

Table 1. Waste engine oil analysis sheet.

Item	Unit	Value
TBN	mg KOH/g	9.42
TAN	mg KOH/g	1.68
Viscosity (at 40 °C)	cSt	143.75

The waste engine oil is filtered twice before its use using a 10 µm filter cloth. The solid particle pollutants in the filtered waste engine oil are measured using a laser particle sizer, and according to ISO4406 standards, the resulting measurement is 28/25/14. The code signifies that there are 250,000 to 1,300,000 particles equal to or larger than 4 µm per milliliter, and 160,000 to 320,000 particles equal to or larger than 6 µm per milliliter. There are 80 to 160 particles equal to or larger than 14 µm per milliliter. The element content of new engine oil and waste engine oil is analyzed using an infrared spectrometer, and the measurement results are shown in Table 2. According to the comparison between new engine oil and waste engine oil, the elements B, Na, Si, Fe, Cu, and Al all increase in waste engine oil, and the pollutants are mainly small particles below 14 µm.

Table 2. The element contents of new engine oil and waste engine oil (unit: µg/g).

Item	B	Si	Na	Ca	P	Zn	Mg	Mo	Fe	Pb	Cu	Al
new	0.2	3	1	824	729	646	11.3	86	1	1	0	1
waste	0.5	13.4	2.7	1459	646	776	10.4	64.7	5.4	1.8	1.1	1.5

Other materials included in the study are Lubrizol's LZ2820 emulsifier, diesel fuel, ammonium nitrate, and water (Lubrizol, Cleveland, OH, USA).

Four different formulations were designed to analyze the thermal safety of the emulsion explosives mixed with waste engine oil. The aqueous phases of the four formulations were identical, and the oil phase fractions are shown in Table 3. The samples were stored for one month prior to testing in order to simulate the conditions of emulsions fired a long time after being loaded into the blastholes.

Table 3. The formulations of emulsion explosive mixed with waste engine oil.

No.	Emulsifier of Emulsion Explosives (wt%)	Engine Oil (wt): Diesel Fuel (wt)	Proportion of Waste Engine Oil in Engine Oil (wt%)	Waste Engine Oil in Emulsion Explosives (wt%)
000	1.2	6:4	0	0
001	1.2	6:4	100	3.18
002	1.2	5:5	33	0.87
003	1.5	7:3	100	3.50

2.2. Thermal Decomposition Conditions

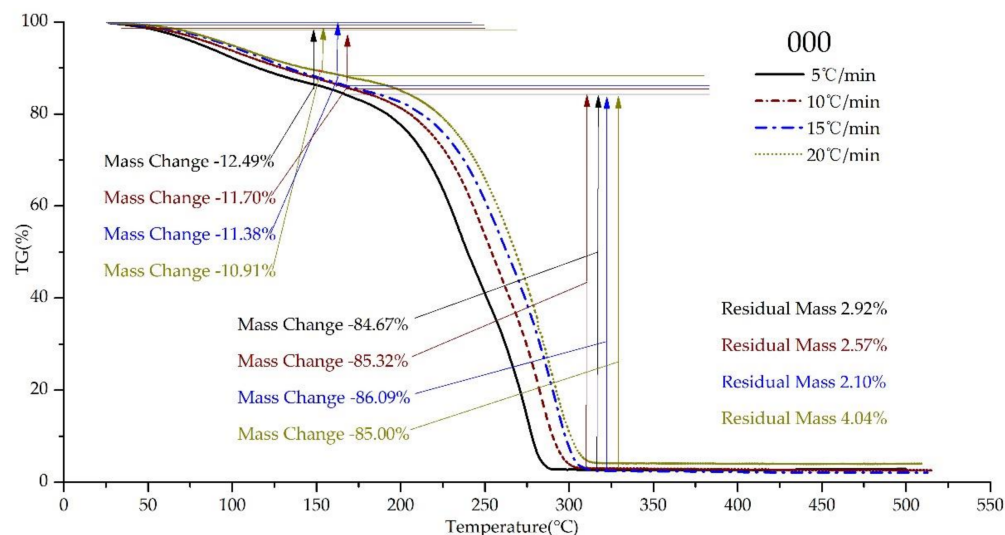
The TG-DSC analysis of the emulsion explosives matrix was carried out using a simultaneous thermal analyzer model STA 449 (NETZSCH, Selb, Germany). Open-lid aluminum sample vessels were used. A nitrogen atmosphere was applied during the analysis (flow rate of 100 mL/min) at ambient pressure. For a kinetic study of the reactions, thermal analysis experiments were performed at heating rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. In each experiment, approximately 10 mg of the emulsion explosives matrix sample was obtained and heated from 25 °C to 500 °C. The precision of the temperature was within ± 0.01 °C and the precision of mass was within ± 0.1 mg.

3. Results and Discussion

3.1. Thermal Behavior

The TG curves of the four samples of the emulsion explosives matrix tested at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min are shown in Figure 1.

The TG curves of the four samples show an obvious weight loss in the temperature range of 45 °C to 150 °C. The weight loss is 10.15% to 15.34%. This is mainly caused by the evaporation of minor amounts of water dispersed in the oil phase and the demulsified portion of the matrix, plus the evaporation of water in the water-to-oil interface. Given the water content of the samples, the weight loss at 150 °C means that most of the water is evaporated at this temperature.

**Figure 1.** Cont.

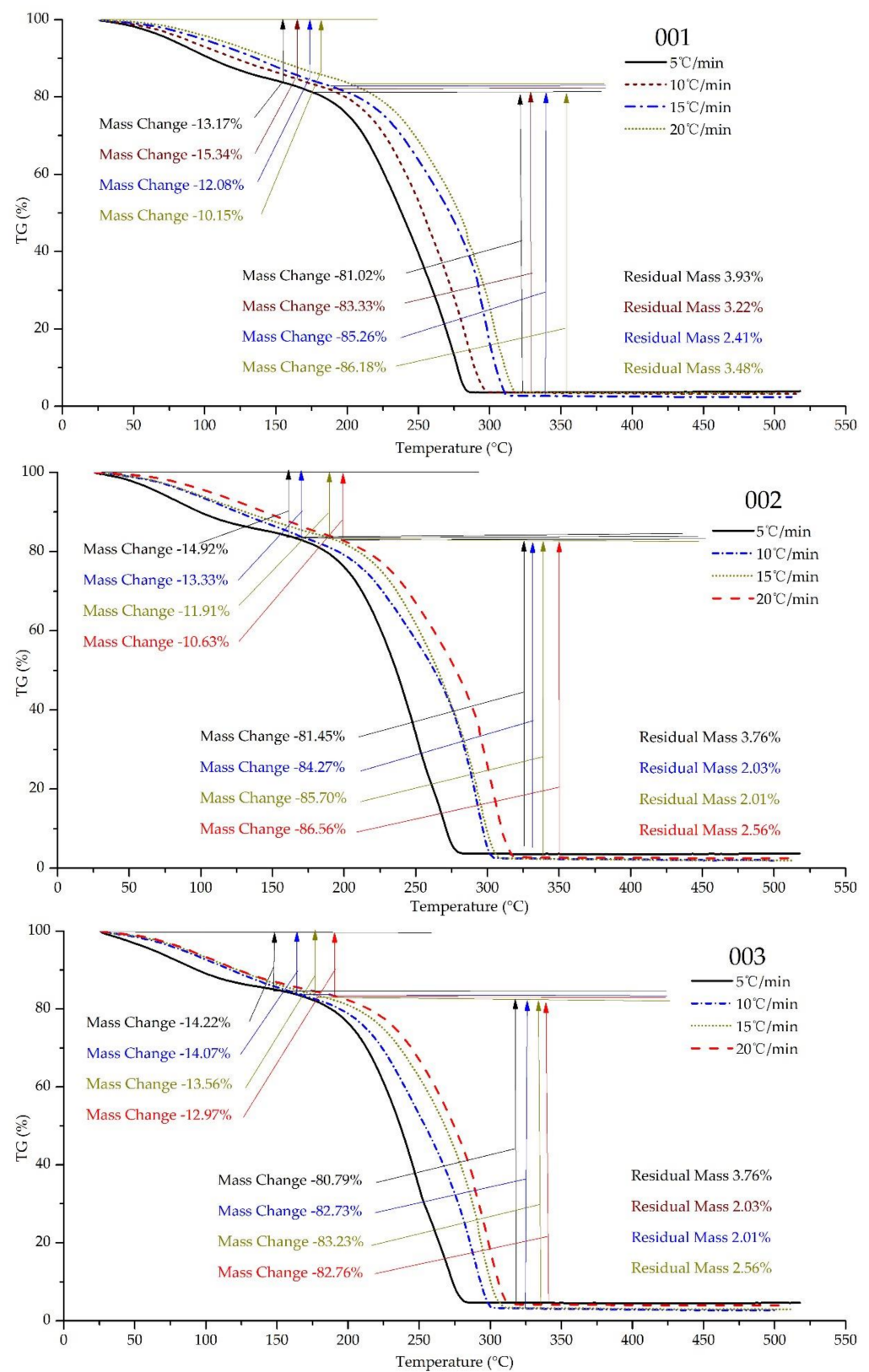


Figure 1. The TG curves of the emulsion explosives matrix samples 000 to 003 at different heating rates under a nitrogen atmosphere.

The initial dehydration stage is followed by the stagnation phase, after which, in the temperature range of 175–200 °C to 270–310 °C, the weight loss rate and the weight loss amount are the highest. This is mainly because the oil phase material is thermally

decomposed by the ammonium nitrate, a reaction accelerated by its exothermic nature. After this rapid decomposition and weight loss phase, samples show a slow weight loss as the temperature further increases, mainly caused by the thermal decomposition of some impurities in the ammonium nitrate oil phase materials. It is observed that the proportion of the residual mass of each sample remains the same indicating that the impurities in the waste engine oil are mainly combustible particles, and the proportion of non-combustible materials is very small.

The DSC curve in Figure 2 shows that, in the low temperature zone (100–200 °C), there are two small exothermic peaks indicating the presence of impurities, and the exothermic reaction occurs in the low temperature zone. For sample No. 000 without waste engine oil, the exothermic peak is small and the curve is flat, indicating that there are fewer impurities involved in the exothermic reaction. For the sample with waste engine oil, the exothermic peak is high and the curve fluctuates greatly, indicating that there are more impurities involved in the exothermic reaction. In the high-temperature area (200–350 °C), the radiation band of sample No. 000 without waste engine oil is narrow, and the radiation band of the sample with waste engine oil is large, indicating that there are many impurities, and impurities participate in the exothermic reaction. At the same time, we can see that the peak exothermic temperature of each sample increases with the increase in the heating rate. At low heating rates (5 °C/min, 10 °C/min), the peak exothermic temperature does not change much. At a high heating rate (15 °C/min, 20 °C/min), the peak exothermic temperature of the emulsion explosives matrix without waste engine oil is close to that exhibited at the low heating rate, and the peak exothermic temperature of the emulsion explosives matrix with waste engine oil is significantly increased. At a heating rate of 20 °C/min, the peak exothermic temperature of the emulsion explosives matrix with waste engine oil is higher than the peak exothermic temperature of the emulsion explosives matrix without waste engine oil. This indicates that the influence of the heating rate on the peak exothermic temperature of the emulsion explosives matrix is significant, and a higher heating rate will increase the peak exothermic temperature point.

The addition of waste engine oil affects the response of the emulsion explosives matrix to the heating rate. At a low heating rate, there is more time available for heat to penetrate by diffusion into the bulk of the sample, and the impurities in the waste engine oil have more time to react, thereby influencing the thermal safety of the emulsion explosives matrix. Conversely, at higher heating rates, there is less time for the impurities to react, so the reaction must take place at higher temperatures, which increases the peak exothermic temperature.

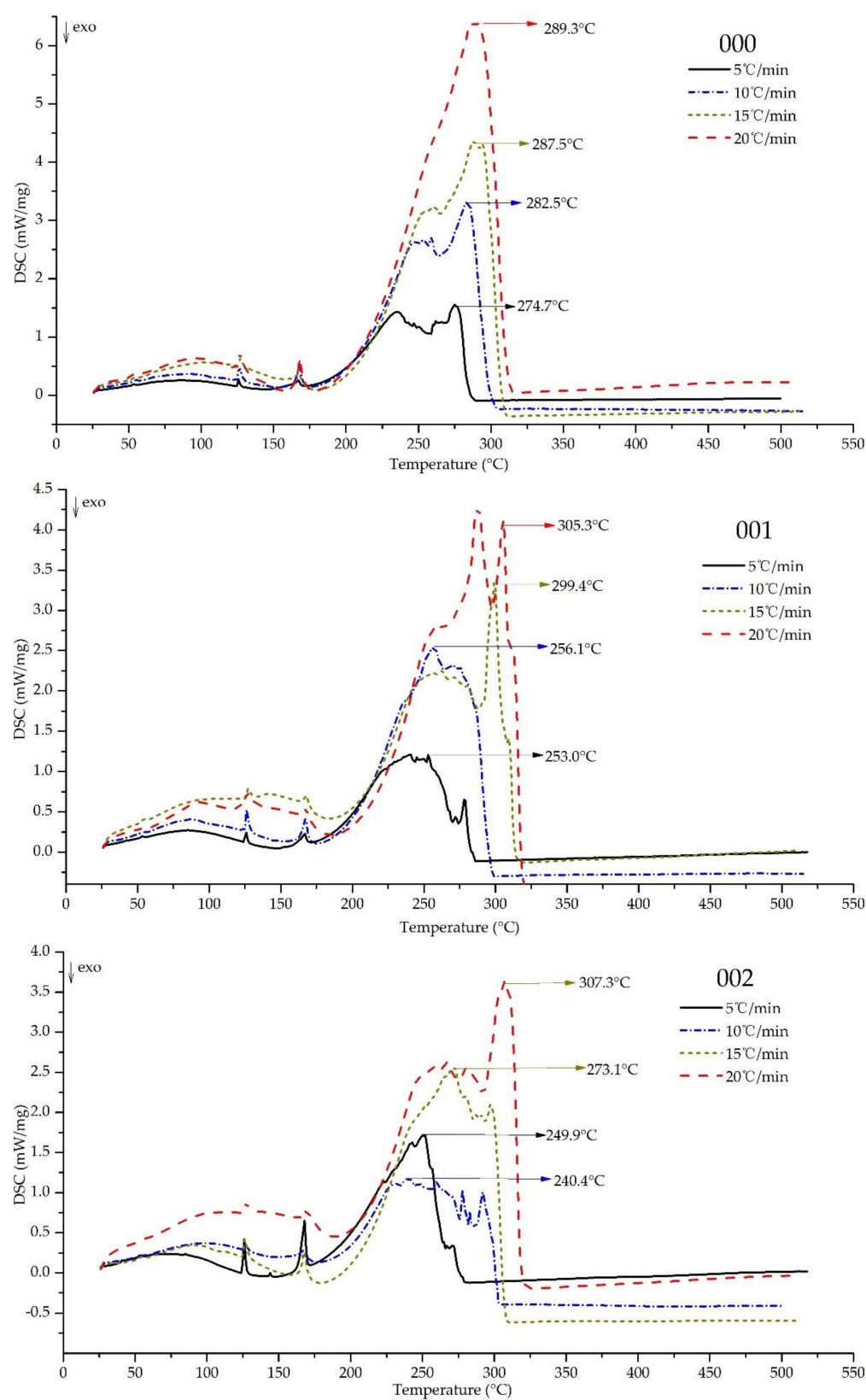


Figure 2. Cont.

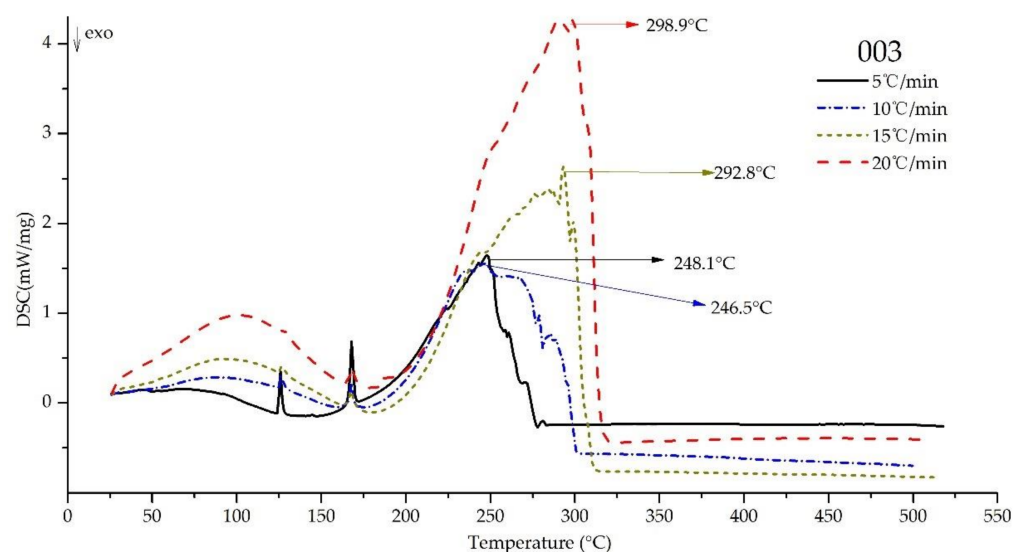


Figure 2. The DSC of the emulsion explosives matrix samples 000 to 003 at different heating rates under a nitrogen atmosphere.

3.2. Non-Isothermal Reaction Kinetics

In order to explore the reaction mechanism of the intense exothermic decomposition process of emulsion explosives and to obtain the apparent activation energy, the rate of the kinetics of decomposition was determined.

The process rate in thermal analysis is generally described by [7–9]:

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (1)$$

where α is the conversion fraction, T is temperature (K), A (1/min) is the pre-exponential factor, E is the activation energy (kJ/mol), R is the gas constant (8.314 J·mol^{−1}/K), β is the heating rate (K/min), and $f(\alpha)$ is the reaction model function, depending on the particular decomposition mechanism [10–12].

The values of activation energies were obtained from the DSC curves using the Flynn–Wall–Ozawa method at the heating rates of 5 °C/min, 10 °C/min, 15 °C/min, and 20 °C/min. This method can be expressed by [10,13–16]:

$$\lg \beta = \lg\left(\frac{AE}{RG(\alpha)}\right) - 2.315 - 0.4567 \frac{E}{RT} \quad (2)$$

where $G(\alpha)$ is the kinetic model function. The activation energy can be obtained from plots of $\ln(\beta)$ versus $1/T$ at different extents of conversion; α , can be obtained by linear regression using the least-squares method [17,18].

The activation energies of all samples in the range of 0.1–0.9 are presented in Figure 3.

From Figure 3, using the conversion factor, it can be seen that the activation energies show a general growing trend. For samples 001 to 003 (with waste engine oil), the energies remain fairly constant (even with some local decrease) using the conversion factors of 0.2 to about 0.7. This indicates that the addition of waste engine oil reduces the activation energy of the emulsion explosives matrix, but the correlation between the amount added and the activation energy is not high.

The average of activation energies (conversion factors of 0.1 to 0.9) is given in Table 4; the means of the adjusted r-squares (R^2) and of the residual sums of squares (RSS) are also listed in Table 4.

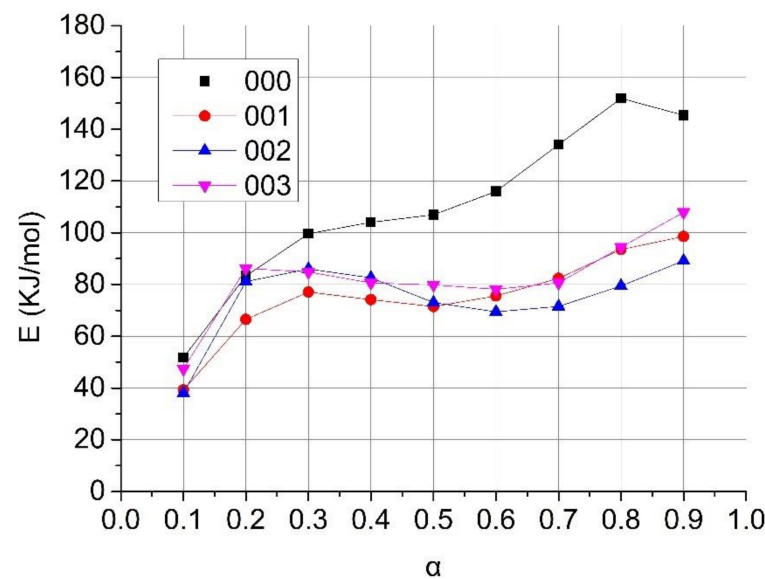


Figure 3. The E vs. α curve of the samples of emulsion matrix using the Flynn–Wall–Ozawa method.

Table 4. The average of activation energies and their adjusted r-square and residual sum of squares calculated using the Flynn–Wall–Ozawa method at a value of 0.1–0.9 for the thermal decomposition of the emulsion explosives matrix using the DSC data.

NO.	E (kJ/mol)	Adj. R^2	RSS
000	110.33 ± 31.38	0.988	0.0017
001	75.39 ± 17.01	0.965	0.0047
002	74.50 ± 15.20	0.933	0.0091
003	82.23 ± 16.10	0.960	0.0054

The correlation coefficient between the activation energy and the amount of waste engine oil is -0.686 . The increase in the amount of waste engine oil will reduce the activation energy.

The small particles in the waste engine oil act as a hot spot in the emulsion explosives, increasing the sensitivity and reducing the thermal safety of the emulsion explosives mixed with waste engine oil.

3.3. Thermal Safety Studies

The reaction model function of the exothermic decomposition process for the emulsion explosives matrix can use $f(\alpha) = 1$ [12,19]. Using this formula, the critical temperature of thermal explosion (T_b) is:

$$T_b = \frac{E - \sqrt{E^2 - 4ERT_{e0}}}{2R} \quad (3)$$

where T_{e0} is the onset temperature when $\beta \rightarrow 0$, it can be determined by a fit of the onset temperature with β of the type:

$$T_{ei} = T_{e0} + a\beta_i + b\beta_i^2 + c\beta_i^3 \quad (4)$$

where T_{ei} is onset temperature and β_i is heating rate, a , b , and c are polynomial coefficients. The T_{e0} values obtained and the corresponding T_b from Equation (3) for the different formulations are given in Table 5. The polynomial coefficients in Equation (4) are also listed.

Table 5. The critical temperature of thermal explosion of emulsion explosives matrix.

No.	T_{e0} (°C)	a	b	c	T_b (°C)
000	177.7	2.477	0.034	−0.0027	194.16
001	148.1	11.6	−0.724	0.0152	169.73
002	199.5	−1.6	0.274	−0.0076	227.47
003	185.3	3.39	−0.236	0.0076	208.78

The same formulation of No. 000 and No. 001 samples, the critical temperature of thermal explosion was reduced by 12.58% after replacing the engine oil with waste engine oil. When the ratio of engine oil (including waste engine oil) in the oil phase material was reduced (No. 002), the critical temperature of thermal explosion increased by 17.15%. The critical temperature of thermal explosion of No. 003 increased by 7.53% when the proportion of emulsifier in the oil phase material was increased.

The correlation coefficient between the critical temperature of thermal explosion and the amount of waste engine oil, the critical temperature of thermal explosion and the amount of new engine oil and the critical temperature of thermal explosion and the amount of emulsifier are −0.333, 0.271 and 0.251. These indicate that the addition of waste engine oil will lower the critical temperature of thermal explosion of the emulsion explosives matrix and reduce the thermal safety of the emulsion explosives. However, this can be compensated by increasing the proportion of emulsifier that has been observed to increase the critical temperature of thermal explosion of the emulsion explosives matrix, this increasing thermal safety of the emulsion explosives.

4. Conclusions

TG and DSC methods were used to study the thermal behavior of the emulsion explosives matrix mixed with waste engine oil under non-isothermal conditions.

The addition of waste engine oil affects the process of thermal decomposition of the emulsion explosives. The addition of waste engine oil causes the weight loss curve to slightly shift towards a lower temperature.

The activation energy of the sample without waste engine oil is 110.33 ± 31.38 kJ/mol, and the activation energy of the sample containing waste engine oil is significantly lower, 75.39 ± 17.01 kJ/mol, 74.50 ± 15.20 kJ/mol, and 82.23 ± 16.10 kJ/mol. The amount of the emulsifier added also affects the activation energy of the sample. An increase in the content of the waste engine oil reduces the activation energy of the emulsion explosives, and an increase in the amount of the emulsifier increases the activation energy of the emulsion explosives.

The critical temperature of thermal explosion of the sample without waste engine oil is 194.16 °C, and the critical temperature of thermal explosion of the samples with waste engine oil is 169.73 °C, 227.47 °C, and 208.78 °C. The correlation coefficient indicates that the higher the proportion of waste engine oil in the oil phase material, the lower the critical temperature of the thermal explosion of the emulsion explosives. The higher the proportion of the emulsifier in the oil phase material, the higher the critical temperature of thermal explosion of the emulsion explosives. According to theoretical analysis, the loss of thermal safety caused by the addition of the waste engine oil can be compensated by reasonably reducing the proportion of the sensitizer and increasing the proportion of the emulsifier.

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