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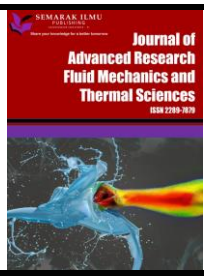

Application of Mixture Design for Optimization of Smoke Signal Formulation: A Comparative Study of $KClO_3$ and KNO_3 as Oxidizers

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ABSTRACT

Smoke signals are traditionally used in military contexts, but in recent times, they have gained popularity among civilians. The M18 smoke grenade was designed with a highly reactive oxidizer, $KClO_3$, and substituting it with a safer oxidizer, notably KNO_3, is one way that helps provide a safer choice for civilian use. However, providing optimal formulations for both formulations helps in deciding whether KNO_3 can be substituted for the traditional $KClO_3$ oxidizer. One of the techniques for enhancing smoke formulation is the Design of Experiments (DOE). Many researchers these days are focusing on substituting the smoke chemicals for a safer option using a trial-and-error process. However, from the standpoint of environmental contamination, numerical testing to identify the most significant output causes air pollution and chemical waste, which is not only costly but also endangers sea life if not properly disposed of. Therefore, it is crucial to optimize the smoke formulation in order to decrease waste and air pollution as well as enable future mass production of the product for both military and civilian use. The purpose of this paper is to implement the mixture design tool of the DOE approach to determine the optimal formulation of smoke signals using $KClO_3$-based formulations, as well as to provide a comparative analysis of substituting KNO_3 to optimize $KClO_3$-based formulations in terms of time and smoke emission. From the $KClO_3$-based formulation (28.68 wt.% $KClO_3$, 23.47 wt.% $C_{12}H_{22}O_{11}$, 34.39 wt.% dye, and 13.46 wt.% $MgCO_3$) with an average time of 73.43 seconds, an acceptable formulation with a data means of 73.43, substituting with KNO_3 oxidizer gave an average of 80.18 seconds, in which the smoke emission was slightly thinner compared to $KClO_3$. As a result, KNO_3 can be used as an alternative oxidizer to $KClO_3$, and the $KClO_3$-optimized formulation can be considered a baseline for smoke formulation for future research.

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1. Introduction

Smoke signal is a pyrotechnic device that has traditionally been employed in military contexts [1]. However, in recent times, it has gained popularity among civilians for various purposes, such as weddings or photography sessions, particularly when utilizing coloured smoke-based variants [1]. As the use of smoke signals has expanded to civilian purposes, many researchers have been focusing on replacing the chemical, especially the oxidizer, with a safer and more environmentally friendly option. Changing chemicals becomes difficult since shifting one chemical in the smoke signal necessitates modifying the weight percentages of all other chemicals. As a result, having an optimized formulation from the typical smoke formulation before changing to safer chemical is critical to avoid chemical waste. One approach that a researcher may employ to achieve an optimized ratio of chemical formulations is to replicate the experimental procedure. However, this method may lead to a significant amount of chemical waste due to potential errors, such as the occurrence of fire during testing and the absence of smoke emission upon combustion [2]. Frequently, the optimization process is conducted through a trial-and-error methodology, wherein one factor is varied at a time. However, this approach often fails to identify the "optimal" conditions for a specific process when multiple factors are simultaneously present [2].

The statistical technique known as "Design of Experiment" (DOE), which is used to plan and optimize studies, is recognized as a high-quality technology for creating remarkable products [3]. The unique DOE features that aid in formulation performance prediction and the capability to locate errors through route cause analysis by comprehending interactions and impacts among the factors [4]. Screening and optimization designs are two distinct types of DOE experimental layouts [4]. Fractional factorial, Taguchi, and Plackett-Burman designs are some examples of screening designs that are commonly used for discovering high-risk variables [4]. A few typical optimization design types are central composite, Box-Behnken, optimal response surface, and mixture design, which concentrate on determining the response's ideal values [4]. The optimization formulation is the emphasis of this study; hence, the optimal mixture designs were used for the DOE experimental design. In mixture design, two or more components are combined in a variety of ratios, and the responses are determined solely by the ratios of the substances present in the mixtures, regardless of the physical states [3]. The response data from the parameters for each chemical analysis preparation can be used to produce the most effective formulation [5]. The model chosen depends on a number of factors, including the model's significance and expected r-square during the ANOVA analysis of the materials utilized [5]. The experimental research suggested by the design expert is then carried out, and actual outcomes are produced [6].

In past years, the military scope of smoke signal, M18-colored smoke grenades were used due to their efficiency and high performance, and they employed potassium chlorate as an oxidizer in the smoke signal composition [7]. In general, potassium chlorate was employed as an oxidizer, sugar as fuel, and colour dye, with the addition of magnesium carbonate as a coolant in the M18 smoke composition [8]. The use of potassium chlorate is a popular oxidizer and is commonly used in pyrotechnic smoke formulations due to its low reaction temperatures [9]. As further asserted by Zeman *et al.,* [10], the conventional smoke signal analysis utilized in commercially available smoke devices includes potassium chlorate ($KClO_3$), sugar ($C_{12}H_{22}O_{11}$), and colour dye. Adding a coolant helps to prevent excessive dye degradation and also acts as a buffer for $KClO_3$ [8]. Therefore, further investigation to discover the optimal formulation of $KClO_3$-based formulations is performed based on the smoke emission time using the DOE tool based on the composition range of the M18 smoke signal. As mentioned by Diviacchi *et al.,* [8], the permissible burn period for M18 smoke and newly synthesized smoke must be between 50 and 90 seconds. As a consequence, this is the optimization

parameter of the Design Expert numerical optimization criteria for the measured time. This DOE was the first phase in developing smoke signal devices, with the goal of determining the ideal composition before moving on to other variables such as thermal characteristics and ignition mechanisms. As illustrated in Table 1, the $KClO_3$ oxidizer formulation of the smoke signal, M18 smoke grenade, was used as a reference point for identifying the optimal formulation for this analysis.

Table 1
Chemical Formulation of Typical Smoke Signal [8]

Materials	Percent by Weight (in dry state), %
Potassium Chlorate, $KClO_3$	18 to 35
Sugar, $C_{12}H_{22}O_{11}$	20 to 50
Dye	27 to 50
Magnesium Carbonate, $MgCO_3$	8 to 25

However, several problems with $KClO_3$, a highly reactive chemical, have been reported, including an unintentional ignition combination with combustible, low-melting fuel [11]. Since then, other researchers have discovered more smoke signal formulations, which Astika *et al.,* [12], made intriguing by utilizing potassium nitrate, KNO_3, as an oxidizer. When KNO_3 is added, the flame temperature is significantly lower than when chlorate or perchlorate are used [13]. This is advantageous since the result of the ignition of the smoke signal formulation must only be smoke, with no fire present during the reaction. Maintaining lower combustion temperatures throughout the reaction is essential; otherwise, the colour dye will burn rather than sublime [11]. As a result, design experts are employed to observe the optimal formulations derived from the $KClO_3$-based formulation as the weight percent range from the M18 smoke composition is utilized as a guideline. Then, from the optimized $KClO_3$ formulation, substitute a safer KNO_3 oxidizer while keeping other chemical constants to investigate differences in time for smoke emission when changing the oxidizer.

Before changing the smoke chemical to a safer and more environmentally friendly option, it is important to find the optimal formulation of the smoke signal using typical formulations, which include $KClO_3$, $C_{12}H_{22}O_{11}$, dye, and $MgCO_3$ [14]. This is not only particularly helps in terms of environmental contamination, numerical testing to determine the greatest output leads to air pollution and chemical waste that is not only costly but also endangers sea life if not properly disposed of. Therefore, it is important to optimize the smoke signal composition since doing so not only helps to decrease waste and air pollution but also makes it possible to produce the product in massive quantities in the future for use by the military and civilians. The purpose of this paper is to implement the mixture design tool of the DOE approach to determine the optimal formulation of smoke signals using $KClO_3$-based formulations, as well as to provide a comparative analysis of substituting KNO_3 to optimize $KClO_3$-based formulations in terms of time and smoke emission.

2. Methodology

2.1 Mixture Design Applications

Using the Design Expert Version 13 software, a total of 24 experimental runs were designed and executed in a systematic manner. The formulation was optimized through the implementation of these experiments, and the optimal formulation will then go through three replications to verify the accuracy and consistency of the results.

2.2 Experimental Setup for Smoke Signal Analysis

The smoke signal formulation was prepared following the data generated by Design Expert Version 13. From the Mixture Design Optimization in Design Expert Version 13 software application, the smoke signal was analysed to find the optimal formulation. Further analysis of the smoke signal formulation was done to obtain the time taken for the emission of smoke.

The chemicals used in this study were potassium chlorate ($KClO_3$) potassium nitrate (KNO_3) sugar ($C_{12}H_{22}O_{11}$), magnesium carbonate ($MgCO_3$), and dye (Take It Global, Malaysia brand). The chemicals prepared were shaken thoroughly in a closed container for 2 minutes for each run, a total of 29 testing. The mixture was weighed accordingly. The prepared smoke composition was then ignited, and the time taken, recorded using stopwatch during smoke emission was recorded at the same distance, 150 cm from the smoke device to the recording place using Samsung A31 camera for all testing. The result of the smoke emission was observed during ignition.

2.3 Data Collection and Statistical Analysis

The acquired data was then inputted into the Design Expert software, which generated the analysis of variance testing (ANOVA) that established the significance [15]. The data were reported as mean ± standard error [15]. The software used to observe chemical reactions was able to generate every required model, including an interactive contour plot graph. The optimized $KClO_3$-based formulation was then replaced with KNO_3 oxidizer to observe the time the smoke took to emit.

3. Results and Discussion

3.1 Analysing the $KClO_3$-based Formulation using Mixture Design Expert

A significant amount of gas was released as a result of the interaction between $KClO_3$ and $C_{12}H_{22}O_{11}$, which lifts the dye into the air to provide a colourful effect [9]. According to Young [16], $KClO_3$ is a very strong oxidizing agent in that it evolves oxygen when heated to decomposition temperatures. It is a suitable oxidizing agent for ensuring the optimal temperature range for dye sublimation [11]. The results from the testing of the smoke signal formulation are shown in Table 2.

As previously indicated, the smoke signal mixture can be divided into four components to generate decent smoke: an oxidizer, fuel, coolant, and colour [17,18]. Each chemical had a significant impact on smoke output. As the smoke mixture supplies enough energy to sublime the dye, which then condenses into small particles [11]. In order to prevent the dye from being burned instead of sublimed, the combustion temperature is kept lower by not adding too much or too little of these four chemicals. All the figures provided of the ignition of the smoke signal at 30 seconds, as it was the peak time of smoke emission, gave a better observation for analysing the data.

According to observations made from all testing, as shown in Table 2, test number 16 resulted in the presence of fire, as shown in Figure 1. This might be due to the fact that using too much $C_{12}H_{22}O_{11}$ caused an excessively strong reaction with $KClO_3$, which degraded the dye molecules at an elevated temperature instead of at a sublimated temperature [14]. The complex dye molecules would theoretically disintegrate, producing black soot rather than coloured smoke, if smoke mixtures were to react with high flame temperatures [13]. This is demonstrated by adding two times as much fuel as oxidizer with only 8% $MgCO_3$, which raises the temperature of the mixture and causes the dye to burn rather than sublime.

Table 2
Smoke Signal Analysis based on DOE software generated formulation

Number of testing	$KClO_3$ (wt. %)	$C_{12}H_{22}O_{11}$ (wt. %)	Dye (wt %)	$MgCO_3$ (wt%)	Time taken of Smoke Emission (sec)
1	25.60	28.20	38.20	8.00	69.98
2	35.00	23.33	30.34	11.33	74.49
3	26.00	20.00	38.00	16.00	67.21
4	21.92	23.22	42.95	11.91	72.00
5	26.00	20.00	38.00	16.00	65.11
6	19.33	20.00	50.00	10.67	61.63
7	18.00	31.67	42.33	8.00	66.06
8	18.00	39.33	34.67	8.00	71.00
9	22.91	24.22	33.12	19.75	59.62
10	30.67	20.00	41.33	8.00	81.00
11	35.00	23.33	30.34	11.33	70.50
12	18.00	20.00	43.50	18.50	65.69
13	29.33	35.67	27.00	8.00	72.80
14	18.00	28.20	38.20	15.60	67.54
15	18.00	32.34	30.33	19.33	63.56
16	18.00	47.00	27.00	8.00	72.43
17	18.00	20.00	37.00	25.00	65.90
18	25.60	28.20	38.20	8.00	74.89
19	26.80	29.40	27.00	16.80	66.78
20	18.00	28.20	38.20	15.60	69.12
21	32.67	20.00	27.00	20.33	68.98
22	26.80	29.40	27.00	16.80	67.93
23	23.00	25.00	27.00	25.00	65.91
24	18.00	41.33	27.00	13.67	63.98

Fig. 1. Testing 16 at 30 seconds Smoke Emission

Adding too much oxidizer to a small amount of fuel in the formulation also caused fire in between smoke emissions, as shown in Figure 2 with formulation number 11. Theoretically, the temperature at which $KClO_3$ decomposed was 400^{o}C [9]. The $KClO_3$ was especially reactive at this decomposition rate since the reaction is exothermic. This accelerates the dye-$KClO_3$-$C_{12}H_{22}O_{11}$ sublimation process [13]. As time passes, the combustion temperature rises due to the large amount of $KClO_3$. As the time passes, the exothermic energy release between the $KClO_3$ and $C_{12}H_{22}O_{11}$ passes the decomposition

temperature, resulting in the presence of fire in the middle of testing as the amount of $MgCO_3$ added as a cooling agent was insufficient to control the smoke emission temperature of the reaction.

Fig. 2. Testing 11 at 30 seconds smoke emission

Next, as for test 23, adding too much $MgCO_3$ to the $C_{12}H_{22}O_{11}$-$KClO_3$ reaction caused the dispersion of smoke in a smaller quantity, as illustrated in Figure 3. This purpose of using $MgCO_3$ as a stabilizer and coolant is to lower the reaction temperature through endothermic decomposition [13].

Fig. 3. Testing 11 at 30 seconds smoke emission

Therefore, adding a moderate amount of oxidizer, fuel, and cooling agent to the dye particles was needed to make sure the oxidizer-fuel reaction was provided with enough energy in order for the dye to sublime and obtain the desired colour output [7]. These were proven in tests 4 and 10, as observed in Figure 4. By utilizing an adequate amount of oxidizer for the reaction with fuels, resulting in a reaction temperature that was sufficient to overcome the dye's comparatively low boiling point and sublimate from the solid to gas phase [19]. This provides enough exothermic reaction to sublime the dye particles to recondense as small particles in the air, providing smoke instead of fire [11].

(a) (b)

Fig. 4. Smoke Emission $KClO_3$-based formulation (a) Testing Number 4 and (b) Testing Number 11 at 30 seconds

The analysis of the 24 tests conducted can be further observed from the ANOVA data of the linear model in Table 3 generated by the software, as it shows that the model was significant to its p-value ($p = 0.0030$). The significance p-value is less than 0.01 ($p<0.01$), indicating that the formula was very significant and fit the model. This meant that the model was separated into individual terms and tested independently. However, the lack of fit of the p-value in the residual was not significant, at slightly more than 0.1, as it might be due to environmental aspects or other noises.

Table 3
The ANOVA Analysis of Smoke Formulation

Source	Sum of Squares	df	Mean Square	F-Value	P-Value	
Model						
i. Linear Mixture	250.66	3	83.55	6.50	0.0030	Significant
Residual	257.10	20	12.86			
i. Linear Mixture	232.98	15	15.53	3.22	0.1011	Not Significant

However, the value of predicted R^2 compared to the adjusted R^2 was not close to a difference of 0.2, as illustrated in Table 4. This might be due to the 24 runs of smoke analysis, which cause a varied response due to many trials and are also affected by environmental aspects and other noises, as graphed in Figure 5. However, the adequate precision that measures the signal to the noise ratio was 8.095, which was greater than 4, indicating that the ratio is desirable.

Table 4
The statistical data of smoke signal

Data		Data	
Std. Dev.	3.59	R^2	0.4937
Mean	68.50	Adjusted R^2	0.4177
C.V. %	5.23	Predicted R^2	0.2168
		Adeq Precision	8.0953

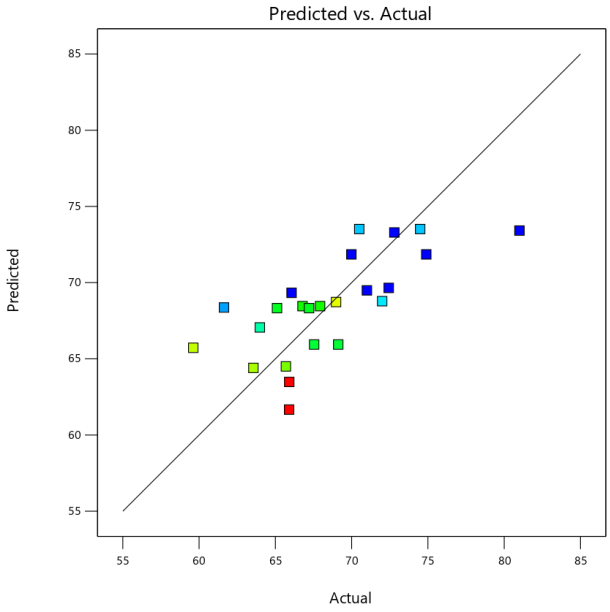

Fig. 5. The Predicted Versus Actual Graph

3.2 Verification of the Model Formulation

The contour graph of both desirability and time taken showed that the optimized formulas generated from the software were 28.68 wt.% $KClO_3$, 23.47 wt.% $C_{12}H_{22}O_{11}$, 34.39 wt.% Dye, and 13.46 wt.% $MgCO_3$. The interpreted data from the desirability contour graph shows the dimensionless desirability value (d), which ranges between d = 0, which indicates that the response is utterly unacceptable, and d = 1, which indicates that the response is more desired [20]. As shown in Figure 6, the predicted values were observed to obtain the time taken for smoke emission in the range of the military scope, in which each response was translated to a dimensionless desirability value (d).

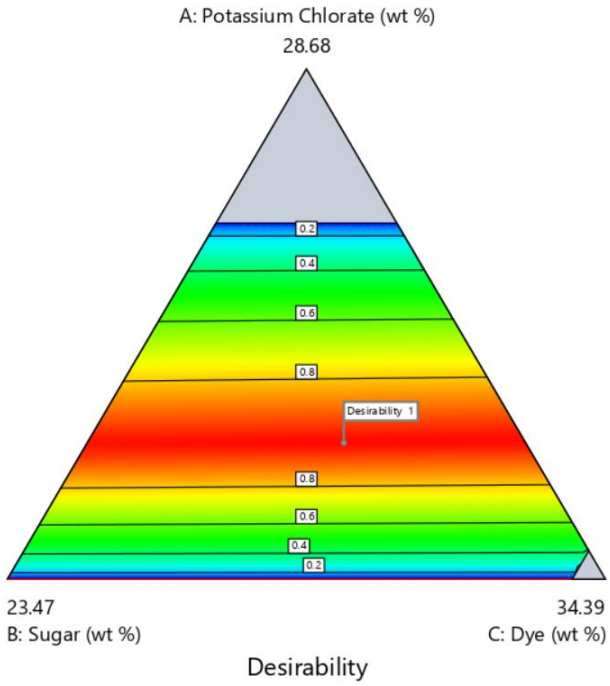

Fig. 6. The contour graph of desirability

In order to achieve desirability =1, the generated optimized formulation of $KClO_3$, $C_{12}H_{22}O_{11}$, dye, and $MgCO_3$ was needed for further analysis. This is observed in the formulation based on the estimated time taken for the emission of smoke, as illustrated in Figure 7 of the contour graph.

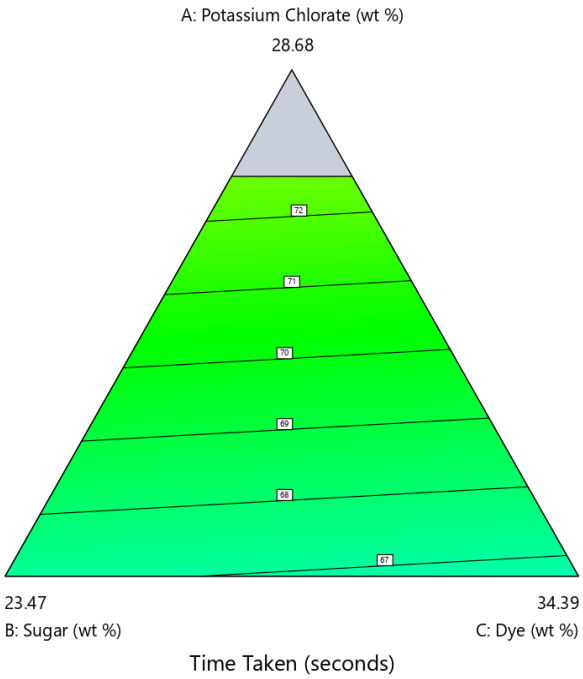

Fig. 7. The contour graph generated of time taken of smoke emission

From Figure 7, A is $KClO_3$, B is $C_{12}H_{22}O_{11}$, and C is dye. As for D for $MgCO_3$, it was not plotted in the graph; however, the weight percent given is 13.46 wt.%. From the estimated time taken, the range of significance time taken value of smoke emission for the given formulation should be in the range of 67 to 72 seconds, and the predicted mean time was around 70.43 seconds. The post-analysis was further experimentally conducted by testing the formulation three times to verify the formulation as in Table 5.

Table 5
The Post Analysis of Smoke Formulation

Number of Testing	$KClO_3$ (wt. %)	$C_{12}H_{22}O_{11}$ (wt %)	Dye (wt%)	$MgCO_3$ (wt%)	Time taken of Smoke Emission (sec)
1	28.68	23.47	34.39	13.46	72.00
2	28.68	23.47	34.39	13.46	74.00
3	28.68	23.47	34.39	13.46	74.30

From the testing conducted, the time taken for the smoke emission was around 72 to 74.3 seconds, with an estimated mean time taken of 73.43 seconds as generated by the software shown in Table 6. The result was higher than their estimated mean in Table 5 and slightly higher than the range of time taken on the contour graph in Figure 6. However, the formulation was still accepted as it was still in the range between the percentage of prediction intervals of low and high 95% confidence levels generated from the analysis done by 24 tests. It is also still within the acceptable range of the military specification. This showed that the desirableness of the formulation was 1, indicating that the formulation was more desirable. Hence, the formulation generated by both contour graphs was accepted.

Table 6
The predicted mean time of smoke emissions with the actual data mean time

Analysis	Predicted Mean	Predicted Median	Std Dev	n	SE Pred	95% PI low	Actual Data Mean	95% PI high
Time taken	70.43	70.43	3.59	3	2.30	65.64	73.43	75.22

3.3 Effect of Substitution of KNO_3 Oxidizer to Optimize $KClO_3$-based Formulation

The optimized $KClO_3$ formulation was further analysed by substituting the $KClO_3$ oxidizer with KNO_3 oxidizer while the other chemicals were kept constant. According to Tang *et al.,* [21], although $KClO_3$-$C_{12}H_{22}O_{11}$ was a typical binary pyrotechnic system, its application had been restricted in various places due to safety concerns. The substitution of $KClO_3$ for the KNO_3 oxidizer supports the Strategic Environmental Research and Development (SERDP) claim of producing "next-generation pyrotechnics" with lower environmental and health impacts [11]. As observed from Table 7, the time taken for smoke emission by KNO_3 oxidizers was longer compared to $KClO_3$ oxidizers.

Table 7
The KNO_3-based Formulation

Number of Testing	KNO_3 (wt. %)	$C_{12}H_{22}O_{11}$ (wt %)	Dye (wt%)	$MgCO_3$ (wt%)	Time taken of Smoke Emission (sec)
1	28.68	23.47	34.39	13.46	81.00
2	28.68	23.47	34.39	13.46	80.50
3	28.68	23.47	34.39	13.46	83.89

Averagely, using the KNO_3-based oxidizer, the time taken for smoke emission was 81.80 seconds compared to the $KClO_3$-based formulation, which was 73.43 seconds. Although the smoke emission time with KNO_3 was significantly longer than with $KClO_3$, the thickness of the smoke indicated otherwise. The overview of both formulations can be illustrated as shown in Figure 8. However, if the used $KClO_3$ was still implemented as an oxidizer, it could increase environmental compliance due to the presence of chloride in the future [22]. Hence, using KNO_3 was one of the choices of oxidizer that should be used in formulating safer smoke signals.

(a) (b)

Fig. 8. Smoke Emission of (a) $KClO_3$-based formulation and (b) KNO_3-based formulation at 30 seconds

A deeper knowledge of the chemical reaction between oxidizer and fuel can be gained through studying the formulation Eq. (1) between $KClO_3$ and $C_{12}H_{22}O_{11}$.

$$8\ KClO_3 + C_{12}H_{22}O_{11} \rightarrow 12CO_2 + 11H_2O + 8KCl \quad (1)$$

From the chemical reaction between $KClO_3$ and $C_{12}H_{22}O_{11}$, which ignited as soon as chloric acid was produced [23]. As a result, it was necessary to use a cooling agent, specifically $MgCO_3$, to reduce the presence of fire throughout the reaction [23]. As mentioned previously, using $KClO_3$ can cause harm to both human and aquatic life over a long period of time, and the low decomposition temperature of $KClO_3$ could lead to accidental ignition of the formulation without safe storage, especially if it is in contact with an acidic component such as sulphur [13]. As mentioned by Mocella and Conkling [13], a number of serious accidents involving $KClO_3$ oxidizer in fireworks manufacturing plants occurred. Hence, substituting KNO_3 was one of the safest choices to work with.

The reaction of nitrate and sugar as oxidizer-fuel reaction, involving a heating process that made the two compounds homogenous and gave the chemical reaction shown Eq. (2).

$$9.6\ KNO_3 + C_{12}H_{22}O_{11} \rightarrow 4.8K_2CO_3 + 7.2CO_2 + 11H_2O + 4.8N_2 \quad (2)$$

The released nitrogen gas from nitrogen-rich components reduces smoke volume, as indicated in Figure 4(b), the thickness of smoke emission was thinner compared to Figure 4(a) [24]. These oxygen-rich ionic solids decompose at moderate-high temperatures, liberating oxygen gas [17]. However, implementing this KNO_3 oxidizer not only allows for the use of less hazardous chemicals, but the nitrogen gas also consumes heat, allowing the flame temperature to be controlled [24]. This is visible when there is no flame visible during testing when using KNO_3-based formulation. Low heat and temperature are necessary during the sublimation-recondensation process to obtain the desired smoke production [25]. When KNO_3 is utilized as the oxidizer instead of chlorate, the flame created is very clear [25]. The organic dye is subsequently vaporized by a sublimation-recondensation mechanism [26].

As a result, even though the KNO_3-smoke formulation had a thinner smoke emission than $KClO_3$, the opacity could still be used for civil applications. A smoke device might be employed for rescue operations for a longer period of time since the smoke it produced could better draw attention to their location. This provided civilians with a better and safer option because utilizing $KClO_3$ might in the future harm human health and endanger aquatic life [11].

4. Conclusions

The optimized formula from the $KClO_3$-baesd formulation (28.68 wt.% $KClO_3$, 23.47 wt.% $C_{12}H_{22}O_{11}$, 34.39 wt.% Dye, and 13.46 wt.% $MgCO_3$) with an average mean time of 73.43 seconds that was within the acceptable range of military specification was verified in its formulation using Design of Experiment, in which the significance p-value was less than 0.1 ($p<0.1$) as it were fit to the model. The optimized $KClO_3$-based formulation was further optimized by substituting its oxidizer for a safer option, KNO_3, while keeping other chemicals constant. The result indicates that KNO_3 can be an alternative oxidizer to $KClO_3$, and the $KClO_3$ optimized formulation can be used as a baseline for smoke formulation for further observation. Both $KClO_3$ and KNO_3-based formulations can be further analysed for their thermal properties to get a better view of their decomposition temperatures and exothermic fuel-oxidizer reactions.

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