Manuscript Details

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Title	Calorimetric study on electrolytic decomposition of hydroxylammonium nitrate (HAN) ternary mixtures
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Abstract

Electrolytic decomposition of hydroxylammonium nitrate (HAN) is appealing for development of chemical micropropulsion system due to its effectiveness in thermal management. In this paper we present the decomposition characteristics and behaviour of various HAN ternary mixtures prepared according to 0 Oxygen Balance (0 OB). There are multiple stages of decomposition depending on the type of fuels added into the HAN solution. While concentrated HAN solution (73 wt%) has only single stage of decomposition, the saccharides-based HAN ternary mixtures has three stages reaction with increased energy release. The addition of nitrogen-rich compounds has sustained the electrolytic decomposition process into the second stage of reaction, which produced the highest decomposition temperature. The study also reveals a linear relationship between the electrical resistivity of HAN ternary mixture and reaction rate in the first stage of reaction, indicating the presence of Joule heating in the process. The influence of electrical resistivity of the ternary mixture became negligible in the second stage of reaction. This work concludes the importance of combined electrical and thermal energy in the first stage decomposition of HAN ternary mixtures.

Keywords	hydroxylammonium nitrate (HAN), green propellant, electrolytic decomposition, micropropulsion
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Table 1.docx [Table]

Table 2.docx [Table]

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Submission of a Manuscript for Evaluation

Dear Editor-in-Chief,

Enclosed is a manuscript of original research article entitled “*Calorimetric study on electrolytic decomposition of hydroxylammonium nitrate (HAN) ternary mixture*” to be considered for publication in Acta Astronautica.

The article is based on our research project collaboration with Propulsion Unit, National Space Agency Malaysia (ANGKASA).

In this manuscript, we evaluated the electrolytic decomposition characteristics of HAN solution added with different commercially available fuel components (known as HAN ternary mixture). Previous literature has demonstrated that electrolytic technique is a promising alternative for ignition of HAN green propellant at microscale.

This study reveals a linear relationship between the electrical resistivity of HAN ternary mixture and reaction rate in the first stage of reaction, indicating the presence of Joule heating in the process. The addition of nitrogen-rich compounds has sustained the electrolytic decomposition process into the second stage of reaction, which produced the highest decomposition temperature. These findings are expected to have significant impact to the space community, in particular those who are working on in-space chemical micropropulsion system.

Thank you for your time and consideration. Hope to hear from you soon.

Sincerely,

Kean How CHEAH

The authors appreciate the constructive comments given by the reviewer. Addressing the comments has significantly enhanced the overall quality of this manuscript.

The minor issues have been revised accordingly. They are highlighted in yellow colour for the ease of tracing.

Outline:

In this study, electrolytic decomposition of HAN (hydroxylammonium nitrate) ternary mixtures were studied using calorimetric technique. The mixtures considered can be grouped in three categories: HAN-alcohols (Methanol and Propanol), HAN-carbohydrates (Dextrose and Sucrose) and HAN-nitrogen compounds (Urea and Ammonia).

Comments by reviewers. No revision is required.

Results:

Multiple stages of decomposition of HAN ternary mixtures are identified. Particularly, the authors show that the decomposition of these mixtures occurs in two stages.

The study shows that the behavior of electrolytic decomposition is dependent on the type of fuel component in the HAN ternary mixtures. Indeed, alcohols reduce the reaction rate in the first stage of decomposition because of part of the energy released from the decomposition of HAN molecules was absorbed by the alcohols; the electrolytic decomposition of the ternary mixture occurs in three stages if the the saccharides are used as fuel component because, during the second stage, the mixture accumulates sufficient thermal energy to cause the decomposition of saccharides and then a further rise of the temperature (third stage); the use of nitrogen compounds (urea and ammonia) causes, during the second stage, the production of additional electrons from the electrolysis that promote the decomposition reaction and, hence, leads to higher decomposition temperature.

A linear relationship between the electrical resistivity of HAN ternary mixture and reaction rate in the first stage of reaction (the influence of electrical resistivity of the ternary mixture is negligible in the second stage of reaction) is identified; the results demonstrate that the Joule effect affects significantly the process in this stage.

Comments by reviewers. No revision is required.

Opinion:

Undoubtedly, the electrolytic decomposition of HAN-based propellant appears to be a promising and interesting research topic in micro-propulsion systems field. However, the study appears to lack originality. Particularly, the effects of alcohols, carbohydrates and nitrogen compounds on the behavior of electrolytic decomposition appear to be expected by considering the studies to which reference is made in the text. For example, the importance of the production of additional electrons from the electrolysis in the promotion of the decomposition reaction is discussed also in Chai et al. "Parametric Studies of Electrolytic Decomposition of Hydroxylammonium Nitrate (HAN) Energetic Ionic Liquid in Microreactor Using Image Processing Technique," Chemical Engineering Journal, Vol. 296, 2016, pp.19-27 DOI: 10.1016/j.cej.2016.03.094.

The additional electrons which promotes the decomposition reaction in Chai et al. (2016) originates from the copper electrodes. In contrast, the origin of additional electrons is electrolysis of the nitrogen compounds in this study.

A statement was added to clarify this point specifically:

'Our previous work demonstrated the additional electrons from copper electrodes has facilitated the electrolytic decomposition of HAN solution [9]. In this study, we explore the additional source of electrons from the fuel component in order to validate the role of electrons in electrolytic decomposition of HAN solution. The additional electrons are anticipated to originate from the electrolysis of nitrogen-rich compounds.'

Furthermore, in my opinion, this study lacks results interesting from an engineering point of view. For example, the electrochemical kinetics is not deepened in contrast to other studies (e.g. Khare et al., "Thermal and Electrolytic Decomposition and Ignition of HAN-Water Solutions," Combustion Science and Technology, Vol. 187, No. 7, 2015, pp.1065-1078). Indeed, a reaction mechanism describing electrochemical kinetics can be very useful for numerical/modeling investigation.

Finally, I suggest to accept the work only after major revisions. I suggest to:

- 1) emphasize strongly the innovative aspects of the study by underlying the differences with previous studies on this topic;

The major innovative aspects of this study are the adding of saccharides-based and nitrogen-rich compounds as fuel components. The rationale to add these two classes of fuel component has been included and elaborated. This can be found in Section 3C and summarized in Section 4 Conclusion.

For example:

Saccharides are widely used as fuel component in candy rocket (amateur rocketry) as they are commercially available and safe to handle. In this study, we examine the characteristics of electrolytic decomposition using the combination of this cost effective fuel and HAN solution, which has not been reported.

2) deepen the electrochemical kinetics by suggesting a reaction mechanism suitable for numerical investigations.

The relevant electrochemical kinetics have been included, i.e. R6, R7, R10, R11, R12 and R13, along with the elaboration.

P/S:

All the major revisions were highlighted in grey to differentiate themselves from minor issues.

Highlights

- Alcohol, saccharides and nitrogen rich compounds were added to HAN solution to form HAN ternary mixtures.
- Electrolytic decomposition characteristics and behaviours of the HAN ternary mixtures were investigated.
- Presence of Joule heating in the first stage of reaction was discovered.
- Saccharides-based HAN ternary mixtures has three stages reaction with increased energy release.
- Addition of nitrogen-rich compounds has sustained the electrolytic decomposition and produced the highest decomposition temperature.

Calorimetric study on electrolytic decomposition of hydroxylammonium nitrate (HAN) ternary mixtures

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Abstract

Electrolytic decomposition of hydroxylammonium nitrate (HAN) is appealing for development of chemical micropropulsion system due to its effectiveness in thermal management. In this paper we present the decomposition characteristics and behaviour of various HAN ternary mixtures prepared according to 0 Oxygen Balance (0 OB). There are multiple stages of decomposition depending on the type of fuels added into the HAN solution. While concentrated HAN solution (73 wt%) has only **single** stage of decomposition, the saccharides-based HAN ternary mixtures has three stages reaction with increased energy release. The addition of nitrogen-rich compounds has sustained the electrolytic decomposition process into the second stage of reaction, which produced the highest decomposition temperature. The study also reveals a linear relationship between the electrical resistivity of HAN ternary mixture and reaction rate in the first stage of reaction, indicating the presence of Joule heating in the process. The influence of electrical resistivity of the ternary mixture became negligible in the second stage of reaction. This work concludes the importance of combined electrical and thermal energy in the first stage decomposition of HAN ternary mixtures.

Keywords: **hydroxylammonium** nitrate (HAN), green propellant, electrolytic decomposition, micropropulsion

1. Introduction

Hydroxylammonium nitrate (HAN) is a green chemical propellant with much lower toxicity than the traditional propellants such as hydrazine and nitrogen oxides [1]. Its relatively high energy density, low freezing point, ease to store and handling properties, are appealing for application in micropropulsion system since complicated and costly handling procedures are not required, resulting in significant reduction in overall cost for a satellite mission [2].

Thermal and catalytic decomposition techniques are commonly **proved to be effective** in the macroscale decomposition of HAN-based propellants. Thermal decomposition, being the simplest technique, is widely used in various studies to understand mechanisms in the decomposition of HAN-based propellants. A series of simplified global reaction model and kinetic equations on the thermal

decomposition of HAN solution were deduced [3, 4]. On the other hand, catalytic decomposition technique produces a rapid reaction by lowering the activation energy and catalytic metal of iridium (Ir) was found to achieve an optimum decomposition for HAN-based propellant [5, 6]. The difference in species of gas products obtained from thermal and catalytic decomposition was not obvious, which implies that the decomposition mechanisms are rather similar [6]. However, pre-heating of catalyst bed is always required for the occurrence of complete decomposition. In addition, the associated heat loss is significantly enhanced at microscale due to high surface area to volume ratio, leading to reduced efficiency in the micropropulsion systems [7].

Recently, a new technique based on electrolysis was successfully demonstrated in the decomposition of HAN-based propellant in different forms, such as high electrical voltage [8], continuous flowing of HAN solution [9], static testing of HAN-based propellant droplet [10]. External parameters that affect the electrolytic decomposition, e.g. input voltage, electrodes surface area, etc. were also investigated [11]. There is only one type of HAN ternary mixture, LP 1846 (60.8 % HAN, 19.2 % triethylammonium nitrate (TEAN), and 20 % water) being studied extensively to date [3, 12]. Despite proven to be feasible, further studies on electrolytic decomposition were still required for the understanding of complicated reaction kinetics and additional reaction mechanisms in the process. In particular, the combining effects of chemical interaction and electrochemical properties towards electrolytic decomposition of HAN ternary mixture are still not fully understood.

This paper investigates the electrolytic decomposition of different HAN ternary mixtures, prepared with three different classes of fuel components using calorimetric technique. The temperature profile of each ternary mixture was analysed to study the influence of different fuel components on the electrolytic decomposition process. In addition, the influence of electrical resistivity on the reaction rates of electrolytic decomposition was studied by evaluating the rate of temperature elevation ($\dot{T}$), which is equivalent to the rate of reaction. Better understanding of the role of fuel components, especially those common and commercially available, in the electrolytic decomposition of HAN ternary mixtures, is beneficial in identifying the suitable HAN-based propellant for a specific micropropulsion system in the future. In addition, electrolytic decomposition of HAN ternary mixture is an efficient way for 'thrust on-demand' for production of gas from liquid, with potential applications in many microscale devices, e.g. micro-gas generator [13], microreactor [14] and microthruster [15-17].

2. Experimental setup

a. Preparation of zero OB HAN-based ternary mixtures

HAN was synthesized in house by titration of nitric acid and hydroxylamine solution, as shown in Figure 1(a). The end product is a diluted HAN solution which was then further concentrated to 73 wt% in a rotary evaporator [18]. The low toxicity of HAN allows its storage in a normal vial, as shown in Figure 1(b), for later experimental studies.

Figure 1: (a) Schematic of experimental setup for synthesis of HAN solution. (b) Concentrated 73wt% HAN stored in a glass vial

In this study, three (3) highly negative Oxygen Balance (OB) chemical compounds, i.e. alcohols, saccharides and nitrogen-rich compounds, were selected as the fuel component and mixed with concentrated HAN solution to form zero Oxygen Balance (0 OB) ternary mixture. The OB of a chemical component can be calculated using equation (1).

$$OB\% = \frac{-1600}{MW}(2X + 0.5Y - Z) \quad (1)$$

Oxygen balance is defined as the weight percentage of oxygen which remains after the oxidation of hydrogen (X), carbon (Y) and metal (Z) to produce the by-products of H₂O, CO₂ and metallic oxide [19]. A zero oxygen balance mixture refers to the ideal chemical propellant commonly used in thermal decomposition as it releases the maximum amount of thermal energy during the combustion. Based on equation (1), the amount of chemical compound added to 5.00 g of HAN solution to achieve 0 OB ternary mixture was determined and summarized in Table 1.

Table 1 Amount of fuel component added to achieve zero OB ternary mixtures

Number	Component	OB, %	Mass of fuel added, g
	HAN ^a	33.30	-
1	Propanol	-239.64	0.51
2	Methanol	-149.83	0.81
3	Sucrose	-112.20	1.08
4	Dextrose	-96.90	1.26
5	Urea	-79.93	1.52
6	Ammonia ^b	-68.49	5.07

^a 73 wt% HAN solution in water

^b 35 wt% ammonium hydroxide in water solution

The electrical properties of the mixtures are critical as the decomposition of HAN-based ternary mixtures will be initiated via electrolysis. The electrical conductivity of the prepared ternary mixtures was measured using a conductivity meter (Eutech, CON 2700, Singapore). The electrical resistivity, ρ_M , of the mixture, is then taken as the reciprocal of the electrical conductivity. Based on the instrument specifications, the accuracy of electrical resistivity measurements is $\pm 0.0015 \Omega\text{m}$ and all experiments were carried out under standard condition.

b. Experimental setup for electrolytic decomposition of HAN ternary mixtures

Schematic diagram of the experimental setup is illustrated in Figure 2. A 0 OB HAN ternary mixture was poured into a beaker and covered with a custom-made lid. A pair of commercial-grade copper wire (Element14, BS 6362, UK) was used as electrodes. Electrolytic decomposition of the ternary mixture was initiated through a DC power supply unit (Elektro-Automatik, PS 8080-120 2U, Germany), in which the voltage was set to 60 V and current was capped at 5 A. The change in temperature of the ternary mixture was measured at 1 Hz using a K-type thermocouple connected to a data logger (Cole Parmer, 37953-20, US). The temperature measurement was stopped when the current flow from the power supply has dropped to zero, indicating complete consumption of the HAN ternary mixture. Simultaneously, the event of electrolytic decomposition of the ternary mixture was recorded using a camcorder. Each experiment was repeated at least 3 times for repeatability purpose.

Figure 2: Schematic of experimental setup for electrolytic decomposition of HAN-based ternary mixture in a thermally insulated beaker.

3. Results and Discussion

a. Temperature profile for electrolytic decomposition of HAN-based ternary mixtures

Temperature of the HAN-propanol ternary mixture, as shown in Figure 3, remained constant at room temperature, T_0 , for approximately 2 seconds after the power supply was switched on. This implies a delay, t_i , in the electrolytic decomposition, which is due to the induction time for the electrolysis to occur [15, 20].

Once the decomposition was initiated, a rapid rise in temperature was observed as the initial HAN-propanol mixture contains large amount of ions in aqueous form, its electrolysis yields a higher reaction rate at the beginning of decomposition. This is consistent with previous study that the initial stage of electrolytic decomposition of HAN mixture is dominated by electrolysis of water at low

temperature [21]. The rate of temperature elevation decreases after reaching 100 °C. At this stage, the effect of electrochemical reactions diminished and the decomposition of concentrated HAN is promoted by the protons produced from electrolysis of water [20], further reaction of the mixture is dependent on thermal decomposition thereafter.

In general, the temperature profile for electrolytic decomposition of HAN ternary mixtures can be divided into two distinctive stages. The slopes of these two stages, $\dot{T}_1$ and $\dot{T}_2$, represent the rate of reaction and are evaluated as

$$\dot{T}_1 = (100\text{ }^{\circ}\text{C} - T_0)/(t_1 - t_i) \quad (2)$$

$$\dot{T}_2 = (T_{max} - 100\text{ }^{\circ}\text{C})/(t_2 - t_1) \quad (3)$$

$\dot{T}_1$ and $\dot{T}_2$ are illustrated as dotted and dashed line, respectively in Figure 3. They are the indication of rate of reactions at first and second stage of decomposition respectively, as well as performance indicators of electrolytic decomposition of HAN ternary mixtures. The peak temperature during the entire electrolytic decomposition, T_{max} , indicates the degree of completion of reaction. During experiment, the HAN ternary mixtures turned from colourless (inset A) to blue (inset B) as copper wire decomposed into Cu^{2+} in the solution.

Figure 3: Temperature-time profile for decomposition of HAN-propanol mixture. Note that the thermal insulation was removed in the inset photographs for the better clarity in demonstration.

b. Effect of electrical resistivity on electrolytic decomposition

Electrical resistivity reflects the rate of electron transfer in a solution, which is a key process in electrolytic decomposition of HAN ternary mixtures. The measured electrical resistivity for different HAN ternary mixtures is listed in Table 2. This study reveals that the electrical resistivity has no significant effect on the maximum temperature obtained from the electrolytic decomposition of HAN ternary mixture. Instead, the maximum temperature obtained is influenced by the type of fuel component added.

Table 2 Electrical resistivity of different HAN ternary mixtures and the maximum temperature achieved from the decomposition

Number	Component	Resistivity of mixture, $\Omega \cdot m$	T_{max} , $^{\circ}C$
1	Propanol	0.0913	137.3
2	Methanol	0.0858	165.4
3	Sucrose	0.1361	170.5
4	Dextrose	0.1609	159.4
5	Urea	0.1453	233.4
6	Ammonia	0.0387	269.1

It was observed that Joule heating phenomenon was present in the first stage of the electrolytic decomposition of HAN ternary mixtures, evidenced by the linear relationship between $\dot{T}_1$ and the electrical resistivity of the mixture, as shown in Figure 4. The graph indicates that the temperature elevation throughout the experiment is not only contributed by electrolysis of HAN but Joule heating too.

Figure 4: Plot of rate of reaction of various HAN ternary mixtures against electrical resistivity of the respective mixture. The line is correlated to Joule heating with the slope of the graph equivalent to square of electrical current.

Low mixture resistivity of HAN-methanol results in lower Joule heating during the electrolytic decomposition. This justifies the lower rate of decomposition reaction of HAN-methanol ternary mixture. Since the heating of methanol suppresses the reaction rate, alcohol-based HAN ternary mixtures demonstrate moderate rate of decomposition reaction which agrees well with the findings from previous studies on thermal and catalytic decomposition of HAN mixtures [22, 23].

On the other hand, the electrical resistivity of the HAN ternary mixtures has negligible influence on the rate of reaction in the second stage of electrolytic decomposition, $\dot{T}_2$. As such, it could be deduced

that the second stage of electrolytic decomposition in HAN ternary mixture is driven by chemical reactions between the remaining fuel components and the HAN oxidizer.

c. Effect of fuel component on electrolytic decomposition

Temperature profile of HAN binary solution and a few selected HAN ternary mixtures during the electrolytic decomposition is shown in Figure 5. In contrary to HAN ternary mixture, the electrolytic decomposition of HAN binary solution occurs in a single stage. Once the decomposition was initiated, the temperature of HAN binary solution raised steadily to the maximum temperature of approximately 185 °C at a mere 16 seconds.

Figure 5: Temperature profile of selected HAN-based ternary mixtures during electrolytic decomposition

The inset photographs in Figure 3 depict the gaseous species evolution (bubbles) during electrolytic decomposition of HAN-propanol ternary mixture. The reactions occur at anode and cathode are stated as below:

At anode:

At cathode:

As the colour of solution turned blue and sustained throughout the reaction, the Cu^{2+} ions released into the solution were in excess, causing R3 to be more dominant than R5.

Thus, the overall electrochemical reaction using the copper electrodes can be postulated as

A thin layer of brown gas (NO_x) was observed in the later stage of thermal decomposition, as shown in inset (b). The formation and bursting of bubbles has interrupted the heat transfer which is typically constant in single phase fluid, as evidenced by the fluctuation in temperature readings. Such observations was supported by the chemical kinetics as proposed by Lee and Litzinger [4, 20], implying that the second stage of electrolytic decomposition is dominated by thermal decomposition.

Since alcohols are highly volatile, part of the energy released from the decomposition of HAN molecules was absorbed by the alcohols. More thermal energy was required to vaporize methanol (0.97 kJ) than propanol (0.40 kJ). Thus, the $\dot{T}_1$ for electrolytic decomposition of HAN-methanol ternary mixture is noticeably lower in comparing to its counterpart of HAN-propanol ternary mixture. However, the measured T_{max} for HAN-methanol (165.4 °C) is higher than that of HAN-propanol ternary mixtures (137.3 °C). This is attributed to the higher theoretical heat of combustion of methanol (-18.08 kJ) during the second stage of electrolytic decomposition than propanol (-17.15 kJ). Nevertheless, both T_{max} are lower than that of the HAN binary solution (185.5 °C).

Saccharides are widely used as fuel component in candy rocket (amateur rocketry) as they are commercially available and safe to handle. In this study, we examine the characteristics of electrolytic decomposition using the combination of this cost effective fuel and HAN solution, which has not been reported. As shown in Figure 5, the electrolytic decomposition reaction of saccharide-based HAN ternary mixture has 3 distinctive stages. The first and second stages are similar to that of alcohol-based HAN ternary mixtures. However, the temperature rise is marginal in the second stage but risen abruptly thereafter in the third stage of reaction. In the second stage, the mixture is accumulating sufficient thermal energy for the decomposition of saccharide, an exothermic process, to occur. Decomposition of sucrose solution was first carried out by hydrolysis reaction [24]:

As carbon residue was observed during experiment, decomposition of sucrose can be represented in the following reaction:

The T_{max} achieved in the electrolytic decomposition of HAN-dextrose and HAN-sucrose ternary mixtures is 159.4 °C and 170.5 °C, respectively. Heat of reaction from the decomposition of dextrose (-16.88 kJ) is slightly lower than that of sucrose (-17.03 kJ). Dextrose is less thermally stable and

possesses lower melting temperature than sucrose. Therefore, dextrose tends to caramelize at elevated temperature and degrading its effectiveness as fuel component [25]. This results in lower T_{max} in HAN-dextrose mixture. The reaction time in the second stage of decomposition of HAN-sucrose (43 s) is notably longer than that of HAN-dextrose (24 s). This is due to the fact that sucrose is the more complex form of saccharide, in which longer time is required to break down, as compared to dextrose.

Our previous work demonstrated the additional electrons from copper electrodes has facilitated the electrolytic decomposition of HAN solution [9]. In this study, we explore the additional source of electrons from the fuel component in order to validate the role of electrons in electrolytic decomposition of HAN solution. The additional electrons are anticipated to originate from the electrolysis of nitrogen-rich compounds. Anodic electrolytic reactions of urea [26] and ammonia [27] are given in R10 and R11:

At the first glance, the temperature profile of electrolytic decomposition of HAN-urea ternary mixture is rather similar to the HAN-alcohol mixtures in which two stages of reaction were observed. A closer inspection by comparing the reaction rates of different HAN ternary mixtures at the first and second stage of electrolytic decomposition is shown in Figure 6. The reaction rate at the second stage of electrolytic decomposition of HAN-urea ternary mixture is notably higher than that of the other mixtures due to the dissolution of urea into water.

Figure 6: Comparison of reaction rates of different HAN ternary mixtures at the first and second stages of electrolytic decomposition

The production of ammonia from hydrolysis of urea has facilitated the decomposition of HAN at second stage, according to R12 [28]:

(R12)

However, carbon dioxide, a side product from the electrolysis of urea, has quenching effect on the overall electrolytic decomposition process. This is evidenced by the relatively lower T_{max} of 233.4 °C, which is 12.73 % lower than HAN-ammonia ternary mixture but higher than the other mixtures studied.

Of all the cases studied, the electrolytic decomposition of HAN-ammonia ternary mixture took place as if a near single stage reaction, instead of multiple stage reaction as observed previously. While all HAN ternary mixtures have lower reaction rate at the second stage of decomposition reaction as compared to the first stage of reaction, the electrolytic decomposition of HAN-ammonia ternary mixture has higher reaction rate at the second stage, in which the difference in reaction rates between the two stages is a mere 7.41 %.

One of the main reactants of the thermal decomposition of HAN as proposed by Lee and Litzinger [4], hydroxylamine (NH_2OH), was formed during the electrolysis of ammonia solution [29], according to R13. Therefore, ammonia has played a rather similar role to the NH_3OH^+ component in HAN solution to promote the decomposition of concentrated HAN solution in the second stage. Coupling with the absence of CO_2 , T_{max} for electrolytic decomposition of HAN-ammonia ternary mixture is the highest at 269.1 °C.

(R13)

Although HAN-ammonia achieved highest T_{max} , the safety issues in handling ammonia mixture (LD50 oral 350 mg/kg) as compared to HAN-urea (LD50 oral 8471 mg/kg) should be considered when an appropriate fuel component is chosen.

4. Conclusion

In this study, electrolytic decomposition of HAN ternary mixtures prepared with alcohols, carbohydrates and nitrogen-rich compounds were systematically studied using calorimetric technique. The combining effects of chemical interaction and electrochemical properties towards electrolytic decomposition of HAN ternary mixtures were investigated. In general, the decomposition of the HAN ternary mixtures occurs in two stages. The rate of reaction in the first stage of decomposition is correlated to a linear relationship with the electrical resistivity of the HAN ternary mixture tested, showing that Joule heating effect is present in the first stage of reaction. After attaining the boiling temperature of water, the rate of reaction is independent of electrical resistivity of the HAN ternary mixture. Thus, the second stage of reaction in the electrolytic decomposition of HAN ternary mixtures is a redox process of oxidizer and fuel component.

The behaviour of electrolytic decomposition was experimentally proven to be dependent on the type of fuel component in the HAN ternary mixtures. The adding of alcohols suppressing the reaction rate in the first stage of decomposition while three-stage reaction evolved with the addition of saccharides as fuel component. Saccharides could be considered for applications, which require prolonged energy release time. The production of additional electrons from the electrolysis of ammonia and hydrolysis of urea has facilitated the electrolytic decomposition reaction further as evidenced by the higher T_{max} . Such results suggest that the sacrificial copper electrodes could be replaced with inert materials, e.g. graphite, for prolonged operation without compromising the electrolytic decomposition reaction.

Acknowledgment

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Figure 1: (a) Schematic of experimental setup for synthesis of HAN solution. (b) Concentrated 73wt% HAN stored in a glass vial

Figure 2: Schematic of experimental setup for electrolytic decomposition of HAN-based ternary mixture in a thermally insulated beaker.

Figure 3: Temperature-time profile for decomposition of HAN-propanol mixture. Note that the thermal insulation was removed in the inset photographs for the better clarity in demonstration.

Figure 4: Plot of rate of reaction of various HAN ternary mixtures against electrical resistivity of the respective mixture. The line is correlated to Joule heating with the slope of the graph equivalent to square of electrical current.

Figure 5: Plot of rate of reaction of various HAN ternary mixtures against electrical resistivity of the respective mixture. The line is correlated to Joule heating with the slope of the graph equivalent to square of electrical current.

Figure 6: Comparison of reaction rates of different HAN ternary mixtures at the first and second stages of electrolytic decomposition

Table 1 Amount of fuel component added to achieve zero OB ternary mixtures

Number	Component	OB, %	Mass of fuel added, g
	HAN ^a	33.30	-
1	Propanol	-239.64	0.51
2	Methanol	-149.83	0.81
3	Sucrose	-112.20	1.08
4	Dextrose	-96.90	1.26
5	Urea	-79.93	1.52
6	Ammonia ^b	-68.49	5.07

^a 73 wt% HAN solution in water

^b 35 wt% ammonium hydroxide in water solution

Table 2 Electrical resistivity of different HAN ternary mixtures and the maximum temperature achieved from the decomposition

Number	Component	Resistivity of mixture, $\Omega \text{ m}$	T_{max} , °C
1	Propanol	0.0913	137.3
2	Methanol	0.0858	165.4
3	Sucrose	0.1361	170.5
4	Dextrose	0.1609	159.4
5	Urea	0.1453	233.4
6	Ammonia	0.0387	269.1