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PROPELLANT DEVELOPMENT USING LOCAL SOURCES OF NITRATE COMPOUNDS

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Abstract

Currently in Indonesia, propellant research is still rarely carried out due to bureaucratic and budgetary problems. This study aimed to determine the optimum composition of propellant using local sources of nitrate compounds based on its combustion heat value and to study the effect of the composition on its combustion heat value. The propellant composition used in this study consists of oxidizing agents (local nitrate compounds), fuel (Aluminium), binder (polyester-based resin), and additive (catalyst). A bomb calorimetry method (ASTM D5865/5865-19) was used to determine the combustion heat value of the propellant. The results showed that the heat of combustion of local content nitrate compound-based propellants was high (> 1500 cal/g), adding binder to the propellant composition increases the heat of combustion. Ammonium nitrate-based propellant has the highest heat of combustion value of 3,788 cal/g. The optimum binder composition in the propellant was 33% (w/w). Based on this study, local source of nitrate compounds has potential to be used for development of propellant, especially in Indonesia. Therefore, it can encourage rocket research in Indonesia as a capital for the development of defense equipment to be less expensive.

INTRODUCTION

In modern warfare, the use of rockets has become the backbone of every battle and is an important factor in winning a battle. in fact, the development of our rocket technology is still not as expected. Rockets and the basic materials for making propellants as rocket motors still have to be imported directly from abroad so costs increase. In rocket research, the propellant is a single-use rocket component that is needed in large quantities. This is because to determine the best conditions for rocket performance, a lot of rocket launch trials are needed, this is what causes research to be expensive, not to mention that import activities are vulnerable to global conditions such as the Covid-19 pandemic that we experienced recently. To reduce prices, it is necessary to find a solution to make the manufacture of propellants cheaper which will lead to the manufacture of rockets independently.

In this study, an alternative for making propellant using cheap raw materials, especially nitrate fertilizer, was investigated. Nitrate fertilizer as an oxidizing agent is easily obtained in the local market and is quite cheap with high purity. When viewed from the prospect of propellants in the future, nitrate compounds have advantages compared to perchlorate compounds which are still widely used when viewed from the environmental impact [1-5]. Perchlorate compounds are known to release chloride gas which is a high pollutant in addition to a large amount of smoke produced. Other basic materials are also used as cheap and widely marketed materials such as aluminum powder as propellant fuel and polyester resin as a binder [6-10].

The study tested the combustion energy of several nitrate compounds to determine their value to know whether the combustion energy derived from several nitrate fertilizer materials on the market has a value that meets the requirements as a propellant. The combustion energy requirements refer to Herve Austruy (Solid Rocket Propulsion Technology, 1993) which states a high-energy propellant if it has a combustion energy value of 1500 cal/g or higher [7]. In addition, it will be seen that nitrate compounds have combustion energy and the effect of polyester resin on combustion energy. Combustion energy is the parameter studied because this quantity is the basic parameter for further propellant research. If the combustion energy is below the specified requirements according to the Herve Austruy limit, the propellant mixture automatically is not suitable for use as propellant-making material.

EXPERIMENT

Materials

The chemicals used are the basic ingredients of the propellant consisting of an oxidizing agent, fuel, and binder. The nitrate compounds used are ammonium nitrate (NH_4NO_3), potassium nitrate (KNO_3), and sodium nitrate ($NaNO_3$) derived from nitrate fertilizers on the market. These three compounds have been famously used as a mixture of propellants and explosives [1,8-11]. From the packaging data, the purity of nitrate is quite high, namely at least 98%.

The oxidizing agents used are potassium nitrate and sodium nitrate in the form of white solids, especially ammonium nitrate which is green because it is given a dye that is useful for distinguishing from other chemicals and as a safety factor. All ingredients are in granular form except sodium nitrate which is in powder form [12-14]. The odorless material indicates the absence of additional compounds or active impurities that can affect the basic properties of the nitrate material. The fuel consists of aluminum metal [15-17] while the binder is polyester using MEKPo (methyl ethyl ketone peroxide) as a curing catalyst [6,18].

Procedures

Pretest. The study begins with pre-testing to determine the initial conditions before proceeding to test to obtain data. Pre-testing is carried out to save time and research costs. The aim is to obtain data on the initial conditions of the process, to find out the obstacles that will be found in the process of making propellant, the composition of the compound roughly as a reference for the actual composition, and to see the combustion properties of the propellant.

Sample preparation. The preparation stage is carried out by drying and refining the chemical. with 80 mesh sieve. Preparation of the binder solution, by pouring the polyester resin solution into the container and adding the curing catalyst in a ratio of 20:1. Mixing. The raw materials that have been prepared (nitrate compounds and aluminum) are put into a container and stirred until evenly distributed. Add the binder solution little by little and stir (mixing). The mixing process takes place at room temperature. After the mixing process is complete, the homogeneous mixture is placed in a container, and then curing is done. After the curing time is complete, the sample is re-smoothed. The propellant sample is ready to be tested with a bomb calorimeter [19-22].

Performance test. Experiments in the study were carried out in several stages as follows: (1) Determine the value of the combustion energy of a mixture of propellants without a binder to determine how the effect of the binder on the mixture of materials. (2) The determination of the propellant combustion energy value of the nitrate compound was used to determine whether the propellant combustion energy of the nitrate compound can match the propellant combustion energy requirements and to determine the type of nitrate compound that has the highest combustion energy and its composition. (3) Determining the value of the combustion energy of the propellant mixture with various weights of binders to determine the effect of the binder in the propellant. Measurement of combustion energy was carried out at the Mineral and Coal Laboratory, Bandung, West Java, using a Bomb calorimeter with measurement conditions, room temperature 25ºC, humidity 78%, and the method using ASTM D 5865/5865M-19 [19-21].

RESULTS AND DISCUSSION

Physical Properties of Propellant

The propellant resulting from the mixing will solidify in an average of 3 hours according to the composition of the mixture. The propellant material that has been finished is in the form of a metal-colored solid from aluminum. Physical properties of the mixture, odorless and hard. The mixture is stable and non-flammable/explosive. In general, there is no difference in the physical form of the various propellant compositions. thehardness of the propellant will depend on the composition of the mixture **(Figure 1** dan **Figure 2**).

Figure 1. The physical appearance of one of the obtained propellant.

Figure 2. Photo of propellant combustion test.

Combustion Heat Value of Propellant

The measurement of combustion heat was carried out at the Mineral and Coal Technology Laboratory, Bandung. The tested material consisted of three parts, namely (1) a mixture of oxidizing agent and fuel without a binder; (2) a mixture of oxidizing agents and fuel with a binder; and (3) variations of polyester resin in a fixed mixture of oxidizing agent and fuel. The results obtained are shown in **Table 1-5**.

Part 1: Propellant without binder

Propellant without binder was carried out for a mixture of Ammonium nitrate and Aluminum metal with the results according to **Table 1**.

Table 1. Test results without binder.

No	NH_4NO_3/Al (% w/w)	Combustion Heat (cal/g)
1	65/35	1788
2	80/20	1034

Part 2: Propellant with binder and a variety of local nitrate

Propellant with a binder consists of three kinds of oxidizing agents, namely ammonium nitrate, potassium nitrate, and sodium nitrate. The test was carried out by varying the oxidizing agent according to the weight percent of the mixture. The results were listed in **Table 2-4**.

Table 2. Combustion heat of sodium nitrate-based propellant.

No	$NaNO_3$/Al (% w/w)	Combustion Heat (cal/g)
1	50/50	3130
2	65/35	2152
3	80/20	1688

Table 3. Combustion heat of potassium nitrate-based propellant.

No	KNO_3/Al (% w/w)	Combustion Heat (cal/g)
1	50/50	3596
2	55/45	3558
3	65/35	2095
4	80/20	1921

Table 4. Combustion heat of ammonium nitrate-based propellant.

No	NH_4NO_3/Al (% w/w)	Combustion Heat (cal/g)
1	50/50	3788
2	55/45	3630
3	65/35	3293
4	80/20	3140
5	85/15	2336

Part 3: Propellant with a variety of %w/w binder

Table 5. Combustion Heat of Propellant with different %w/w binder.

No	Binder (% w/w)	Combustion Heat (cal/g)
1	26	2378
2	29	3140
3	31	3169
4	33	2970

The test results (**Table 1-5**) show that the combustion energy values vary. The combustion energy of the sample without binder has a value of about 1000 cal/g. While the energy of combustion of mixed materials using a binder has a higher yield, which is above 1500 cal/g. The highest combustion energy is in the mixture with the binder for the ammonium nitrate oxidizing agent. When viewed from the test results in general, the energy value of the propellant combustion of nitrate fertilizer materials obtained from the market has a value that meets the requirements according to the provisions of Herve Austruy, All the results obtained except for the mixture without binder can achieve sufficiently high combustion energy so that the propellant mixture made is categorized as a high energy propellant. When compared with the experimental results by LAPAN using an ammonium perchlorate oxidizing agent, the results are shown in **Table 6**.

Table 6. Combustion heat of ammonium perchlorate-based propellant obtained by LAPAN.

Propellants composition	Heat of Combustion (cal/g)
80%AP/20%PES+urethane	1575.07
80%AP/20%PES+urethane	1837.44
80%AP/20%PES+urethane	2217.71
80%AP/20%PES+urethane	2376,15
80%AP/20%PES+urethane	2966.61
80%AP/20%PES+urethane	3524.70

The value of combustion heat of AP-based propellant was also not far adrift with the obtained propellant combustion heat. In addition, the experimental results was also higher when compared to the propellant test using PES organic fuel listed in **Table 7**.

Table 7. Combustion heat of propellant with aluminium content variations [8].

Al Content	Combustion Heat (cal/g)
8%	2885
10%	3001
12%	3151
14%	3237
16%	3750
18%	3496

Chemically, the difference in combustion energy is due to the different types of chemical compounds used as propellants. Thus, oxidizing compounds such as nitrate compounds, as long as they are of the same type and composition, will obtain the same combustion energy from any source, be it imported materials or from the local market, while the impurities present only have little effect because high combustion energy causes high heat and burns the impurities. . The difference in combustion energy is more influenced by the physical properties of the mixture such as particle size and composition of the propellant mixture [23].

Effect of binder

Tests to find out how much the polyester binder affects the combustion energy. By knowing the difference in combustion energy, it will be known how the effect of the polyester binder is on the chemical or physical properties of the mixture. The experimental yield curve for this mixture is given in **Table 1**.

The test results show the value of combustion energy without binder gives the lowest results compared to other mixed groups. Lower yields can occur in the absence of a binder so there is no adhesion between the oxidizing agent and the fuel, so that in the mixture there is a possibility of separation of the oxidizing chemical and fuel both during mixing and during testing. As a result, the mixture occurs in conditions where there are parts that lack fuel and other parts have excess fuel. In the combustion process, oxidizing compounds are compounds that are reactive to heat, so the oxidizing agent is the trigger for the fuel to burn. Fuel is a chemical compound that absorbs and disperses heat [23-25]. Lack of fuel causes the thermal energy of the oxidizing compound not to spread because the function of the fuel as a spreader and increases the heat is reduced while the composition of excess fuel causes the impact of energy generated from the decomposition of the oxidizing agent to be not large enough to react with the fuel.

A mixture with a lower oxidizing weight content turned out to provide a higher combustion energy value. The difference occurs in the composition of 65/35 which is a better composition than 80/20. This shows that the 65/35 composition of the fuel is quite balanced to increase the combustion energy compared to the 80/20 composition. Thus the oxidizing compound and fuel must be in the combustion reaction in the same place with a balanced composition because a single compound, either oxidizing agent or fuel alone will not be able to cause combustion.

Propellant with binder

In general, mixing using a binder provides a higher combustion energy value. The effect of the binder on the mixture gives a significant meaning to the increase in combustion energy. The function of the binder is to maintain the position of the oxidizing chemical compound and the fuel in the mixture, this means covering the weaknesses that occur in the mixture without a binder related to the spread of chemicals. In the presence of a binder, the mixture will be evenly distributed depending on the stirring process. After the binder solidifies, the composition of the mixture will not change, it is strongly bound by the binder so that the combustion reaction becomes more complete.

The combustion energy curve (**Figure 3**) for each oxidizing compound shows the difference in combustion energy but the shape of the combustion energy curve does not differ as shown in the curve. Sodium nitrate has the lowest combustion energy. In the oxidizing mixture of potassium nitrate or with ammonium nitrate, the combustion energy value is quite high, namely between 3596 cal/g for potassium nitrate and 3788 cal/g for ammonium nitrate, a difference of 192 cal/g, but both are high-energy mixtures. Thus, theoretically, these two oxidizing chemicals can be used as a mixture of propellants.

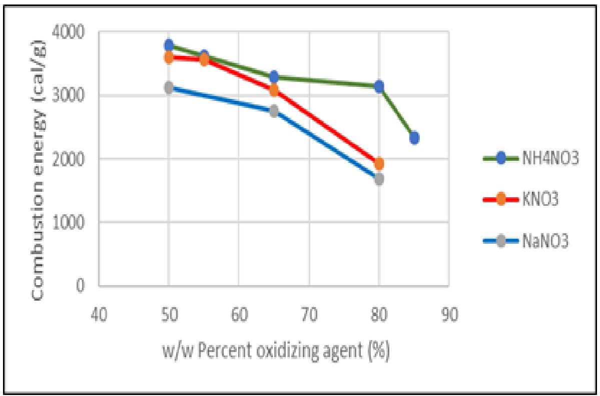

Figure 3. Combustion heat value of propellant using the local source of nitrate compounds.

Based on the combustion energy of the tested nitrate compounds. The most potent compound used as a propellant is ammonium nitrate and in fact, also proves that ammonium nitrate is the most widely used compound as a propellant compared to other tested nitrate compounds. The higher combustion energy of ammonium nitrate can be caused because the ammonium nitrate molecule has a greater number of atoms and its decomposition will produce larger atoms or gas molecules which directly produce greater energy. Another thing that affects the combustion energy is a better oxygen balance [22]. The oxygen balance is the amount of oxygen in weight percentage, which is liberated as a result of the complete conversion of the energetic material into CO_2, H_2O, SO_2, Al_2O_3, etc. The oxygen balance calculation of the tested nitrate compounds (**Table 8**) shows that the oxygen balance value of ammonium nitrate is closest to zero so the combustion of ammonium nitrate is more effective than the other two nitrate compounds.

Table 8. Oxygen balance of nitrate compounds.

Oxidizing Agent/ Nitrate Compounds	Oxygen Balance (%)
NH_4NO_3	20
$NaNO_3$	37
KNO_3	47.5

From the discussion above, it can be seen that the factors that affect the combustion energy are the type of compound, both from the oxidizing group, and the fuel and the oxygen balance in the compound. Thus, the combustion of a chemical compound will depend on the type and composition of the chemical compound in it, not on the impurities contained in the material. The temperature of the combustion products that have high energy will also burn the impurities. With a high compound content of local nitrate compounds (≥ 98%), the combustion energy of nitrate compounds will be the same regardless of the source. This causes the energy of burning nitrate compounds from the local market to have a value equivalent to imported nitrate compounds.

Effect of polyester resin

The polyester resin used was an unsaturated polymer. The unsaturation of the polymer chains causes this compound to carry out cross-linking reactions that change the physical properties of the compound from a fluid to a solid [6,16]. In the mixture with the variation of the polyester resin binder in the four experiments with variations in the composition of the percent by weight of the polyester mixture from 26% to 33%, it is given according to **Table 5**.

Based on **Table 1** and **Table 4** shows the difference in combustion energy between the two compositions with a ratio of 65/35 to 80/20 in a mixture without and with a binder having a fairly large value, namely 754 cal/g without a binder and 153 cal/g with a binder (**Figure 4**). These conditions prove that there is an uneven distribution of the mixture without binder.

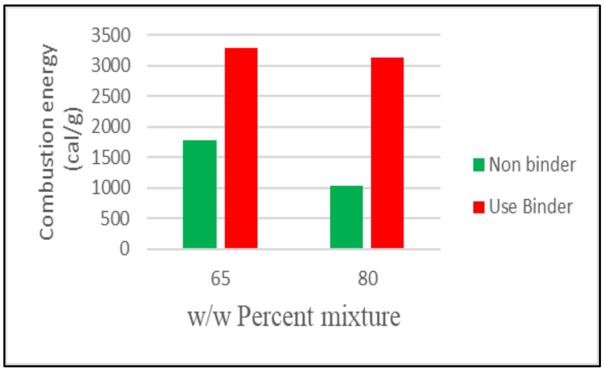

Figure 4. Comparison of the combustion heat of propellant with and without binder.

The resin composition in the test was 26% to 33% (**Figure 5**). For a 26% resin composition, mixing becomes difficult due to a lack of binder. The resin mixture yield of 26% has properties that do not bind the oxidizing-fuel mixture completely, or the resin only binds the mixture only to the outside of the mixture. This can be seen from the more brittle mixture and the presence of a loose mixture. For the largest mixture, which is 33%, the stirring can run more smoothly without any problems. However, observations show that the resin content is excessive. Experimental data showed that the composition of polyester of as much as 33% obtained the maximum combustion energy. Thus the 33% polyester resin content has the right composition, namely the resin can bind the propellant mixture not too much or too little and not too much affect the combustion process.

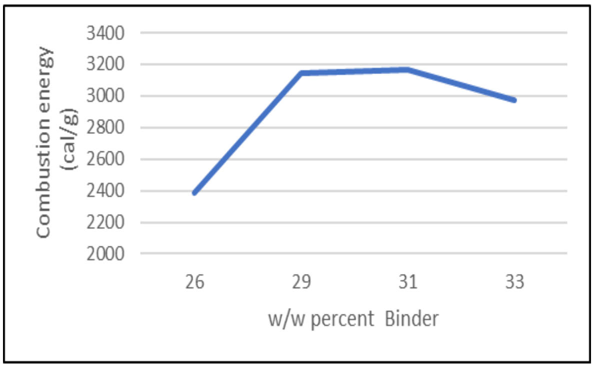

Figure 5. Combustion energy of propellant with a variety of binder percent.

CONCLUSION

Experiments that have been carried out have shown that propellants using a mixture of oxidizing nitrate compounds derived from fertilizers obtained in the local market have combustion energy that meets the requirements of high-energy compounds. This also shows that the existing impurities have little effect on the combustion energy. Propellant mixtures using a binder have higher combustion energy than a mixture without a binder. This condition occurs because the oxidizing agent and fuel in the mixture without a binder cannot be distributed according to their respective specific gravity which results in the composition of the mixture not changing significantly. Ammonium nitrate compound has the best oxidizing properties compared to other tested nitrate compounds. This better result can be seen in the number of atoms that are more in one molecule than other compounds and the oxygen balance value, ammonium nitrate has a value closest to 0. This makes the combustion process perfect in terms of quality. exhaust gases in addition to being more environmentally friendly. Polyester resin affects the physical stability of the mixture where this compound binds the mixture so that the composition of the propellant mixture does not change. The resin used, namely polyester, is quite good at absorbing solid materials from oxidizing agents and fuels and does not have a negative impact on combustion energy.

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