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SOLID PROPELLANTS FOR ROCKETS: A METHODOLOGY TO OBTAIN HIGH PURITY KNO_3 FROM AN INEXPENSIVE SOURCE

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Abstract

Solid propellants are mainly used in rocket propulsion applications. The performance of a rocket is directly affected by the design of the solid propellant used. The presence of impurities in the propellant formulation can reduce the average thrust, specific impulse and characteristic velocity of a rocket. Oxidizers are the main compounds in propellants formulation, which produce the high energy on combustion. One the most commonly used oxidizers in amateur rocketry is potassium nitrate. KNO_3 is normally used because of its good characteristics that include compatibility with others ingredients and availability at low cost in fertilizer formulation. The main objective of this work is to propose a methodology to obtain higher purity potassium nitrate from a fertilizer, an available and inexpensive source that can be used as oxidizer in a solid rocket propellant formulation. The KNO_3 crystals were obtained by recrystallization process using a commercial fertilizer. The properties of purified fertilizer were compared with the properties of KNO_3analytical. The fertilizer, purified and analytical grade KNO_3 samples were evaluated by means of morphology, pH of saturated solution, Fourier transform infrared (FTIR) spectroscopy, and differential scanning calorimetry (DSC). The results demonstrated that recrystallization process effectively remove impurities from the fertilizer. The purified KNO_3 crystals were optically transparent with a planar shape, similar to higher purity KNO_3. The FTIR and DSC results showed that some impurities, such as, sulfur and alkaline compounds were removed after recrystallization and the purified KNO_3 presented a similar behavior than higher purity KNO_3. The recrystallization process used in this work can successfully used to obtain KNO_3crystals with high purity that can be used as oxidizer in solid propellants for rockets.

Keywords: - *Solid propellant, Rocket, Recrystallization, Oxidizer, Potassium nitrate*

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1. INTRODUCTION

Solid propellants are mainly used in gun and rocket propulsion applications [1,2]. The choice of a propellant is the main decision of any solid rocket motor design. The desirable characteristics for a solid propellant are high specific impulse, predictable and reproducible burning rate and ignition characteristics, high density, ease of manufacturing, low cost and good aging characteristics [1,3]. In safety point of view, propellants not should be prone to combustion instability [3].

A solid propellant consists of several chemical compounds such as oxidizer, fuel, binder, plasticizer, curing agent, stabilizer, and cross-linking agent [1,3]. The specific chemical composition of a solid propellant depends on the desired combustion characteristics for a particular application. However, the compounds used in the propellant formulation must present higher purity for improve its performance. For experimental rocketry the propellant used is normally based on a fuel and an oxidizer [4,5]. The fuel generally used includes carbon based compounds. The oxidizer is an essential compound, which produce the high energy during the combustion process. One of the most commonly oxidizer used is ammonium perchlorate, mainly because of its compatibility with other propellant ingredients and good performance [1,6]. However, others inorganic salts as ammonium nitrate, ammonium dintramide and potassium nitrate are also used. Although the inorganic nitrate salts are relatively low-performance oxidizer when compared to perchlorates, however they are used because of low cost, smokeless and non-toxic exhaust [1,7].

A mixture of potassium nitrate and sucrose (KNSu) is used as a propellant in the field of experimental rocketry, where sucrose acts as a fuel and potassium nitrate acts as oxidizer [5,7,8]. The basic ratio of fuel (sucrose) and oxidizer (potassium nitrate) in the propellant mixture is 65/35. However, the high purity potassium nitrate necessary for higher rocket performance can become an expensive compound to be used in experimental rocketry. So, several researchers used fertilizers as a source of potassium nitrate without further purification [9,10,11]. As a result, the performance of the rocket decreases, because the fertilizer contains impurities that will reduce the impulse promoted by the propellant. Therefore, the main objective of this work is present a methodology for purification and obtainment of potassium nitrate from a fertilizer with similar properties to that the high purity potassium nitrate, but from an available and inexpensive source.

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2. MATERIALS AND METHODS

2.1 Materials

The fertilizer used, Krista K, was supplied by Yara Fertilizers, São Paulo/ Brazil. Krista K is a potassium nitrate fertilizer that also contains 43 wt% K_2O, 12wt% N, 1wt% Mg and 1wt% S. A potassium nitrate with 99% of purity supplied by QuímicaModernawas used for comparison.

2.2 Potassium Nitrate Purification

The recrystallization process was used to purify the potassium nitrate from the fertilizer. In this process, 1kg of fertilizer as dissolved in 1L of boiling water and the solution was heated up to boiling point. After that, the solution was filtered to remove suspended impurities and then cooled at 0°C to initiate the formation of potassium nitrate crystals. Generally, the crystallization process occurs in 4h. The potassium nitrate crystals were formed by spontaneous nucleation. Then, the liquor was removed and the potassium nitrate crystals were obtained. The moisture was removed from the crystals by heating the suspension in a heating plate at 100°C.

2.3 Potassium Nitrate Characterization

The samples of fertilizer, purified potassium nitrate, and high purity potassium nitrate were previously dried at 105ºC for 24 h in a vacuum oven before the tests. An optical digital microscope operating at a magnification of 150x was used to verify the presence of impurities and also to evaluated the type of crystal formed after recrystallization process. The presence of impurities in the fertilizer and purified potassium nitrate were also evaluated by measuring the pH of a saturated solution of potassium nitrate and water. A saturated solution was prepared by dissolving 15g of sample in 50mL of distilled water. A Digimed pH meter was used to determine the pH of the saturated solution. Three saturated solution were prepared for each samples and the pH values were averaged.

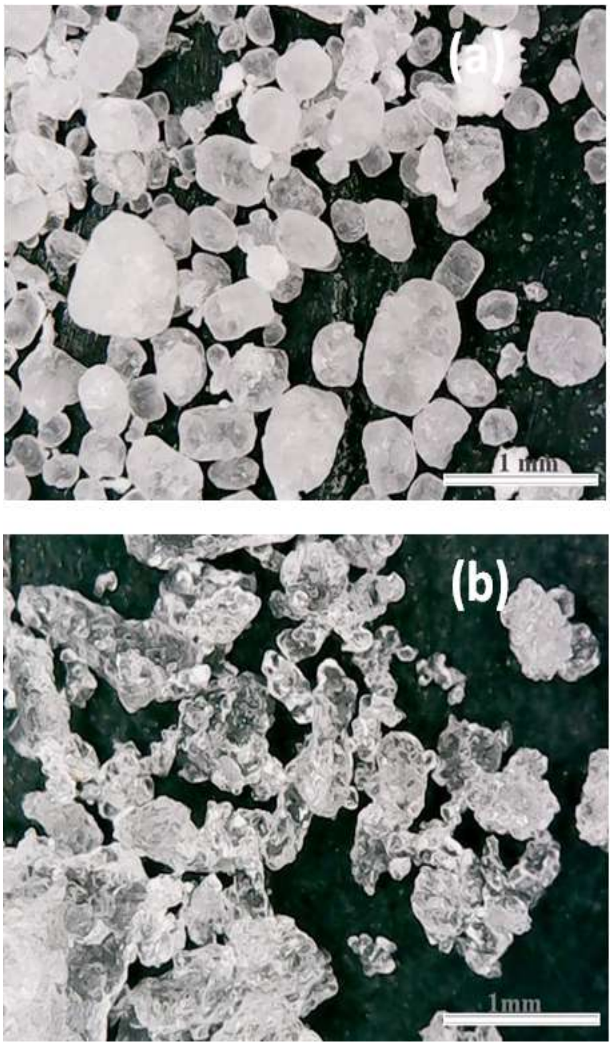
Fourier transform infrared (FTIR) spectra for all three samples were obtained by means of a Nicolet IS10- Thermo Scientific spectrometer. The samples (5 mg) were dispersed in a KBr matrix (100 mg), followed by compression to form pellets. The sample collection was obtained using 32 scans, in the range of 4000 cm^{-1} to 400 cm^{-1}, at a resolution of 4 cm^{-1}. The analysis was done in triplicate. The data from FTIR analysis and pH measurements were statistically analyzed for differences between means. The statistical analysis has been carried out using commercial software (EXCEL). A one-way analysis of variance and t-tests were used to evaluate the statistical difference among groups. Values of $p<0.05$ were considered significant.

Differential scanning calorimetry (DSC) analysis were carried out in a DSC-50 (Shimadzu) using aluminum crucibles containing approximately 10 mg of sample, under dynamic nitrogen atmosphere (50 mL min^{-1}) at a heating rate of 10 °C min^{-1}in the temperature range of 20 to 380°C.

3. RESULTS AND DISCUSSIONS

3.1 Morphological Results

The morphological aspect of the samples studied is shown in Figure 1. The crystals in fertilizer presented an oval shape and were opaque, as shown in Figure 1(a). Optically transparent and defect free crystals with planar shape were obtained for purified KNO_3 due to spontaneous nucleation during the crystallization process, as can be seen in Figure 1(b). KNO_3 with higher purity presented a similar morphological aspect. Some agglomerates of KNO_3 crystals with an irregular shape can also be seen in Figure 1(b). It is possible that such agglomerates with irregular shape may be formed if the surfaces of two crystals collided during the crystallization process. Therefore, the intergrowth of KNO_3 crystals occurs due the formation of nucleus-bridges between crystals. The same crystal growth behavior and morphological aspect were also observed by Linnikov*et al*[11].



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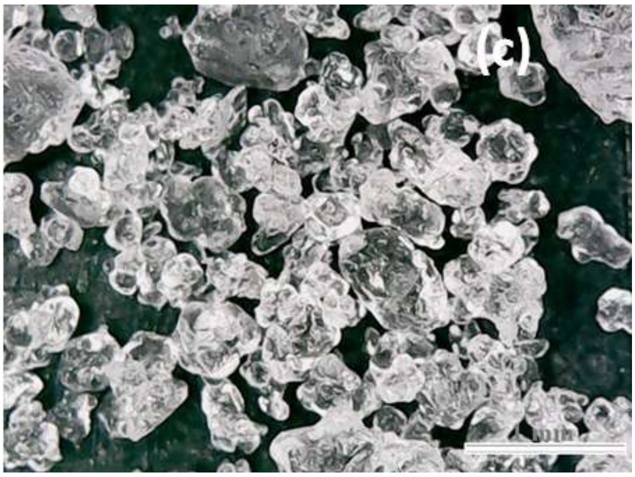

Fig 1: Optical microscopy images of fertilizer crystals (a) and purified (b) and higher purity (c) KNO_3 crystals.

3.2 pH Values

The impurities in the fertilizer may cause deviation from the expected chamber pressure and thrust of a rocket motor reducing the rocket performance. The presence of impurities can be detected by measuring the pH of a saturated solution of KNO_3 and water [12]. If the pH value is higher than 7, the presence of impurities can compromise the rocket motor performance [12]. On the other hand, better results can be obtained if the saturated KNO_3 solution presents a neutral or slightly acidic pH [12]. The pH values of the samples evaluated were presented in Table 1.

The fertilizer presented the highest pH value, as expected, probably due the presence of alkaline compounds. The pH value for purified KNO_3 was drastically reduced after removal the impurities. The pH value for the saturated solution of purified KNO_3 was closer to neutral, which indicate that the recrystallization process effectively remove the impurities presented in the fertilizer.

Table 1: pH values for saturated solution of the samples studied

Sample	pH*
Fertilizer	9.19 ± 0.09^{a}
KNO_3 Purified	7.76 ± 0.11^{b}
KNO_3 99% Purity	5.59 ± 0.12^{c}

*Results with the same superscript letter in their respective column are significantly the same.

3.2 FTIR

Figure 2 shown the FTIR spectra of the samples studied. For the fertilizer and the purified $KNO_3$the peaks at 1380 cm^{-1} and 830 cm^{-1} confirm the presence of a nitrate ion (NO_3^-) [13,14,15]. The KNO_3presents a characteristic band assigned to antisymmetric stretching mode typical of the free nitrate ions at 1380 cm^{-1} and the band associated to the angular antisymmetric deformation O-N-O at 830 cm^{-1}[14,15]. The very weak band at 1767$cm^{-1}$is also assigned to the nitrate ion [16]. On the other hand, the band at 3430 cm^{-1} is assigned to hydroxyl ion (OH^-), that may be associated with the presence of moisture or impurities. This band is more intense in the fertilizer than in purified KNO_3, as can be seen in Figure 2. This result may indicate the presence of alkaline compounds, such as potassium hydroxide (KOH), which corroborates the highest pH observed for the fertilizer, as presented in Table 1. Higher quantities of alkaline compounds in the propellant formulation can accelerate the corrosion process and as consequence reduce the lifetime of the rocket motor.

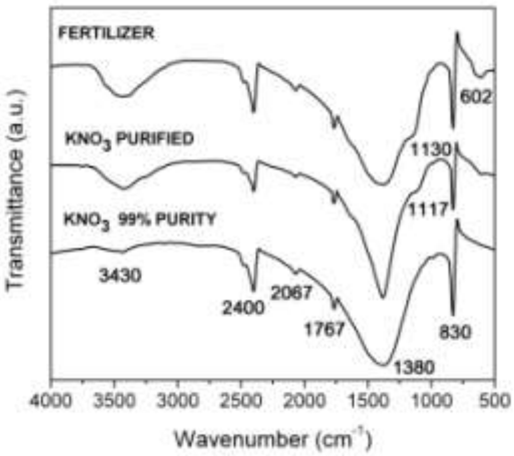

Fig 2: FTIR spectra of the samples studied.

The recrystallization process removes part of the hydroxyl ion from the purified KNO_3, so the band area for purified KNO_3 is smaller and the pH is slightly alkaline, see Table 1. In addition, the shoulders at 1130 cm^{-1} and 1117 cm^{-1} for fertilizer and purified KNO_3 could be associated with the sulfate ion [16]. The inorganic sulfate ions absorbs at 1130-1080 cm^{-1} due to asymmetric SO_4 stretching [16,17,18]. The weak band at 602 cm^{-1} observed for the fertilizer may also be associated with the sulfate ion. However, for purified KNO_3 only a shoulder can be seen, which indicate that the recrystallization process also contributed to remove part of the sulfur compounds. The removal of sulfate ion either contributes to extend the lifetime of the rocket motor, since sulfate ion can react with water molecules from air to form sulfuric or sulfurous acid compounds.

The ratio between band areas at 1380 cm^{-1} and 830 cm^{-1} (A1380/A830) and the ratio between the band areas at 1380 cm^{-1} and 1767 cm^{-1} (A1380/A1767) were used as an empirical evaluation about the presence of nitrate ion in the samples studied. The high purity KNO_3 presents the highest values, while the fertilizer showed the lowest values, as can be seen in Table 2. The values obtained for purified KNO_3 were approximately two times higher than those obtained for the fertilizer, which may also indicate that the recrystallization process effectively remove impurities from the purified KNO_3.

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Table 2: Ratio between band areas in FTIR spectra of the samples evaluated.

Sample	A1380/A1767*	A1380/A830*
Fertilizer	44.3 ± 0.4[a]	4.8 ± 0.2[a]
KNO_3 Purified	81.9 ± 1.4[b]	11.1 ± 0.4[b]
KNO_3 99% Purity	90.9 ± 0.5[c]	13.5 ± 0.6[c]

*Results with the same superscript letter in their respective column are significantly the same.

3.3 DSC

The differential scanning calorimetry was used to evaluate the influence of the impurities on the melting point and solid state phase transitions of KNO_3. Figure 3 shows the DSC plot of the heating cycle applied to the KNO_3 samples studied. Two endothermic peaks can be seen in the figure. The first refers to solid state phase transition that occurs in KNO_3[19], while the secondly is associated with the melting of KNO_3 crystals. The solid-solid transition in KNO_3 involves a discontinuous change from one crystal structure (orthorhombic) to another (rhombohedral) at 133°C [20].

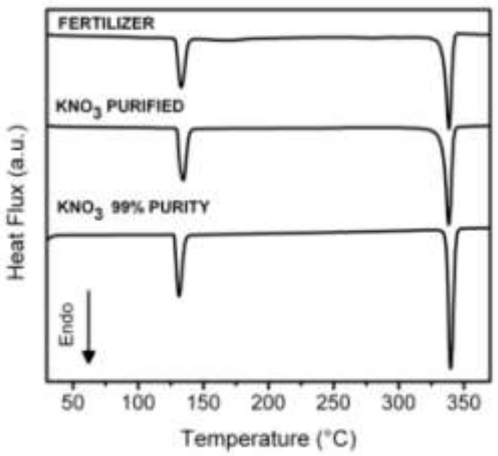

Fig 3: DSC analysis of the samples studied.

All samples studied presented similar results for the temperature (T_t) associated with the solid state phase transition, as can be seen in Table 3. However, the enthalpy values differ between the samples studied. The fertilizer presents the lowest value, which could be an indicative of the presence of impurities, while the value for purified KNO_3 was slightly higher than those obtained for high purity KNO_3.

	Peak 1		Peak 2	
Sample	T_t (°C)	ΔH_t (J/g)	T_m (°C)	ΔH_m (J/g)
Fertilizer	133.1	42.5	338.4	77.4
KNO3 Purified	134.7	46.2	338.3	85.7
KNO3 99% Purity	131.3	44.5	339.6	86.6

The peak temperature associated with the melting of KNO_3 crystal generally occurs between 333-339°C [21,22]. All the samples studied presented melting temperatures in agreement with the results found in the literature. However, the fertilizer presents the lowest enthalpy associated with the melting of KNO_3 crystals (ΔH_m), while the enthalpy value for purified KNO_3 was near to that obtained for high purity KNO_3. After recrystallization, the impurities presented in the fertilizer such as clay, sand, small pebbles and others compounds were removed from KNO_3, which corroborates the FTIR results, forming a high purity crystal, as showed in Figure 1(b), as a result purified KNO_3 presents a melting enthalpy value similar to the higher purity KNO_3.

3. CONCLUSION

The recrystallization process was used to obtain high purity KNO_3 crystals. The results showed that purified KNO_3 was a morphological aspect similar to commercial high purity KNO_3. In addition, the FTIR results demonstrated that part of the sulfur compounds presented in the fertilizer were removed from the purified KNO3 which improves the performance of the oxidizer and also reduce the emission of toxic during rocket fly. The peak temperature associated with the melting of KNO_3 crystal and the enthalpy values for purified KNO_3 and high purity KNO_3 were very close, which corroborates that the recrystallization process used is a effectively methodology to obtain higher purity KNO_3 crystals that can be used in solid rocket propellants.

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