Study of the Surface Morphology of the Granules Of Ammonium Nitrate And Decomposition with Dextran

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ABSTRACT

Although the system NH_4NO_3-Dextran is frequently used in the energetic materials, the fundamental kinetic study is still required for this system. In this work, we deploy thermogravimetric analysis to reveal activation energy change in this system depending on the Dextran concentration Fundamental study of the kinetics of combustion process allows us to precisely control parameters such as thermal front velocity, temperature, and the activation energy of the reaction. In this study we present the DSC/TGA analyses performed using Q600 analyzer (TA Instruments). Also shown is the study of the morphological structure of the surface of the granules of ammonium nitrate for the presence of nano pores and cracks.

INTRODUCTION

Ammonium nitrate is an important explosive of which vast amounts are produced yearly. [1-3]. Kazakhstan is one of the biggest platforms for the production of ammonium nitrate. For example, the company «KazAzot» LLP based at the chemical complex of Caspian Mining Metallurgical Plant is a leading producer of nitrogenous fertilizers and ammonium nitrate. Production capacities of ammonium nitrate - 1000 tonnes / day. With ammonium nitrate, three major hazardous phenomena need to be considered: fire, decomposition and explosion. [4] For using in energy intensive system ammonium nitrate must meet the following basic requirements. It should possess sufficient thermal effect, providing the best special effect composition, as well as have the ability to be easily oxidized by the oxygen of the oxidizer or by the air oxygen. Other requirements include the best special effect composition for the given combustion products, and being chemically and physically resistant in the temperature range from -60 °C to +60 °C, and whenever possible, be resistant to the action of mild acids and alkalis, as well as non-hygroscopic and accessible, and be environmentally friendly and abundant materials.

In this work, we deploy thermo-gravimetric analysis to reveal activation energy change in this system depending on the weight percentage of dextran. Fundamental study of the kinetics of combustion process allows us to precisely control parameters such as speed, temperature, and the activation energy of the reaction. We selected ammonium nitrate to play as the role of oxidizer, while dextran, $(C_6H_{10}O_5)n$ was used as a fuel. This oxidizer as a component of energetic materials inspired numerous investigations on decomposition at high temperatures and requires further study [5]. Lower activation energy ensures complete combustion at lower temperatures. It should be noted that the decomposition Activation Energy for the NH_4NO_3 was around 90 kJ/mol, which is in good agreement with literature data [6].

High interest is the morphological structure of the surface of the ammonium nitrate. It is known that ammonium nitrate has a low degree of adhesion. Therefore, the migration of the fuel from the column of charge in the preparation of igdanite and other compounds based on ANFO (or AN/FO, for ammonium nitrate/fuel oil) brings a lot of trouble. These mixtures are widely used in coal, mining industries, as well as in construction.

EXPERIMENTAL

a. Materials

Ammonium nitrate (NH_4NO_3), dextran $(C_6H_{10}O_5)_n$

b. Instrumentations

Optical microscope and scanning electron microscope (SEM), The Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyzer (TGA). The DSC/TGA analyses were performed using Q600 analyzer from TA Instruments. The experiments were carried out for heating rates 5, 10 and 20 ºC per minute under ambient (air) atmosphere. The experimental setup is given in Figure 1.

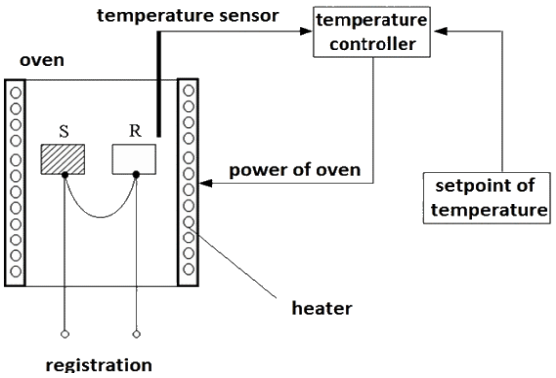

Figure 1 – Experimental setup of the Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyzer (TGA)

c. Method for determination of activation energy

To determine the activation energy we use the data obtained by the DSC graphs. The experiments were conducted at heating rates 5, 10 and 20 ºC/min under ambient (air) atmosphere. The systems with the Dextran concentration up to 20 wt. % were studied. We studied the systems with the dextran concentration up to 20 wt. %. We have estimated the activation energy from the DSC data by using the isoconversional method suggested by Starink [7, 8], which was shown to provide a more accurate value than the Kissinger and Ozawa methods. The Starink method determines the activation energy from the equation:

$$ln\left\{\frac{T^{1.8}}{\beta}\right\} = (1.007 - 1.2 \times 10^{-3} E_a)\frac{E_a}{RT} + const \quad (1)$$

d.

E_a is the apparent activation energy (in kJ/mol), β the heating rate in thermal analysis (in K/min), T is the peak temperature of the exothermic curve (in K), and R the universal gas constant. E_a is estimated from the slope of the graph of $\ln(T^{1.8}/\beta)$ vs. 1/T.

RESULTS AND DISCUSSION

Reaction mechanism of the mixture of ammonium nitrate and the dextran

We need to determine the reaction of the oxidizer decomposition with fuel (ammonium nitrate and dextran). The reaction scheme can be given according to the following equation:

$$12NH_4NO_3 + C_6H_{10}O_5 = 6CO_2 + 12N_2 + 29H_2O \quad (2)$$

with decomposition factor of NH_4NO_3 (85.5 wt. %) and $C_6H_{10}O_5$ (14.5 wt. %)

$$NH_4NO_3 \rightarrow N_2 + 1/2O_2 + 2H_2O \quad (3)$$
$$C_6H_{10}O_5 + 6O_2 \rightarrow 6CO_2 + 5H_2O \quad (4)$$

Study of the surface of ammonium nitrate granules by optical microscope and scanning electron microscope (SEM)

Investigations has been conducted for examining their morphological properties of surface of ammonium nitrate to identify the potential depressions and irregularities. The process that increases aquatic resistance of ammonium nitrate (AN) with the addition of carbonaceous materials and the retention capacity of the surface of ammonium nitrate, by the generation of mesopores is described. The generation of the mesaporous structure explains retention the deposition of carbonaceous materials on the surface of the granules. Figure 2 and Figure 3 shown the pictures taken with by optical microscope and scanning electron microscope (SEM).

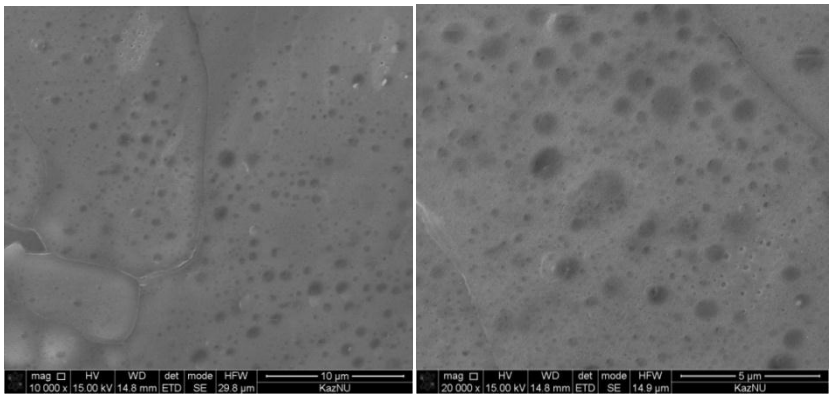

Figure 2 – Samples of the surface of the granules of ammonium nitrate on scanning electron microscope (SEM)

Figure 2 can be seen that the ammonium nitrate granules to have the potential wells, deepening and irregularities.

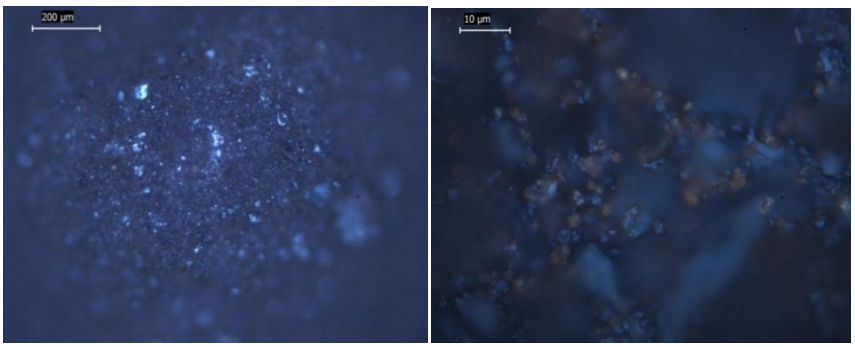

Figure 3 – Samples of surface of the mixture ammonium nitrate and the dextran by optical microscope.

In Figure 3 shows the surface coverage quality ammonium nitrate granules with coatings dextran by optical microscope. According to figures obtained it can be assumed that dextran particle settle in certain areas on the surface of the ammonium nitrate.

The Differential Scanning Calorimetry (DSC) and Thermogravimetric Analyzer (TGA) for thermogravimetric investigations

The kinetic parameters of decomposition of oxidizing agent (ammonium nitrate NH_4NO_3) with the addition of dextran $(C6H_{10}O_5)n$ was investigated using Differential Scanning Calorimeter (DSC).

Each formulation was studied experimentally by different heating rate (5 °C/min, 10 °C/min, 20 °C/min.). DSC data analysis showed a tendency to lowering the activation energy of the oxidizer by adding dextran component. Apparently this is due to catalytic action of dextran.

The DSC/TGA analyses were performed using Q600 analyzer from TA Instruments. The experiments were caried out for heating rates 5, 10 and 20 ºC per minute under ambient (air) atmosphere. We studied the systems with the dextran concentration up to 20 wt. %. Increasing the concentration of dextran in it does not react.

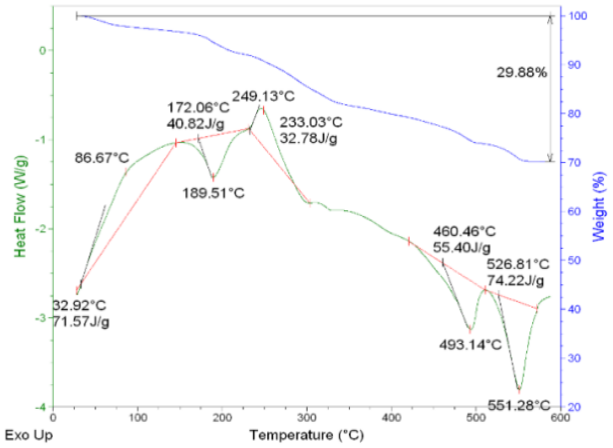

Figure 4 – DSC curves and thermal decomposition of dextran under argon environment.

Figure 4 is representing the decomposition pathway for dextran under argon flow (100 ml/min). We have gradual mass decline with removal of about 5 wt. % absorbed water until 100 °C. Near 200 °C partial decomposition of dextran polymeric molecule chains occurs, which continues with two major endotherm peaks near 490 °C and 550 °C. The overall weight loss until 600 °C is about 30 wt. %. The red curve is the weight loss curve and its 1st derivative is the blue curve. The red curve shows that weight loss occurred in a segment with 32.92 ºC to 526.81 ºC. The total weight loss of the dextran was 29.88%. That is, until the complete decomposition of dextran

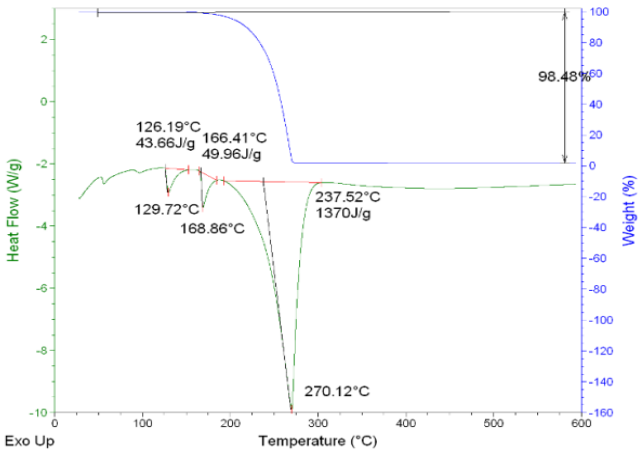

Figure 5 – DSC curves and thermal decomposition of NH_4NO_3 under argon environment.

Figure 5 is representing the decomposition pathway for pure ammonium nitrate under argon flow (100 ml/min). We have gradual mass decline with removal of about 5 wt. % absorbed water until 100 °C.

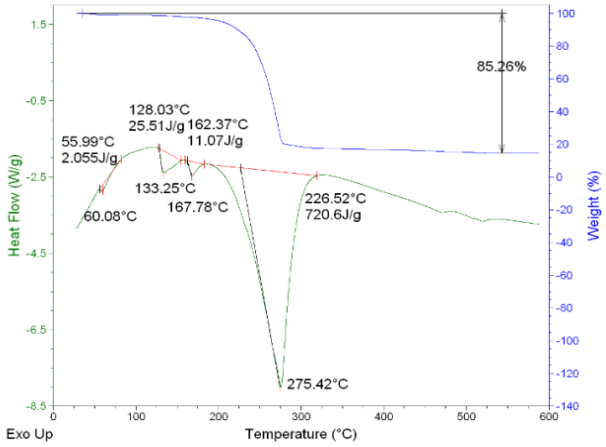

Figure 6 – DSC curves and thermal decomposition of NH_4NO_3/Dextran 20 wt. %.

Figure 6 is representing the interaction behavior in the mixture of NH_4NO_3 - 20 wt. % dextran. The decomposition takes place at around 250 ºC. Figure 5 is demonstrating the decomposition characteristics of NH_4NO_3. Crystallographic water molecules are removed at around 130 °C and 170 °C with endotherm heat values of 44 J/g and 49 J/g, respectively. Major decomposition takes place at around 250 J/g with decomposition energy of 1370 J/g. The red curve shows that weight loss occurred in a segment with 55.9 ºC to 226.52 ºC. The total weight loss of the Ammonium nitrate was 85.26%.The small endotherms before decomposition are due to small amounts of moisture in the mixture, as well as polymeric chain scission of dextran molecules.

energy Figure 7 is showing the plots of activation energy calculations for 5, 10 and 20 wt. % dextran containing compositions, as well as pure NH_4NO_3 decomposition. For all mixtures the peak temperatures were taken and the activation calculations were made by plotting the $\ln(T^{1.8}/\beta)$ vs. 1/T. The calculated activation energies were in the range 65-82 kJ/mol, and the energy values increase for the systems with higher dextran concentration (Table 1).

The lowest activation energy has the system with 5 wt. % dextran concentrations. As expected increasing the heating rate results on increasing of decompositon temperature in the system. It should be noted that lower activation energy ensures complete combustion at lower temperatures.

Table 1

The calculated activation energy for diferent ratios of NH4NO3/Dextran

Conc. Wt. % Dextran	Heating rate	Ea, KJ/mole	Tpeak	T, ° C
0	5 10 20	86..59	282,27 298,59 310,52	600
5	5 10 20	64.606	242,78 263,6 288,72	600
10	5 10 20	69,15	236,07 253,14 277,73	600
20	5 10 20	82.93	239,89 259,17 275,42	600

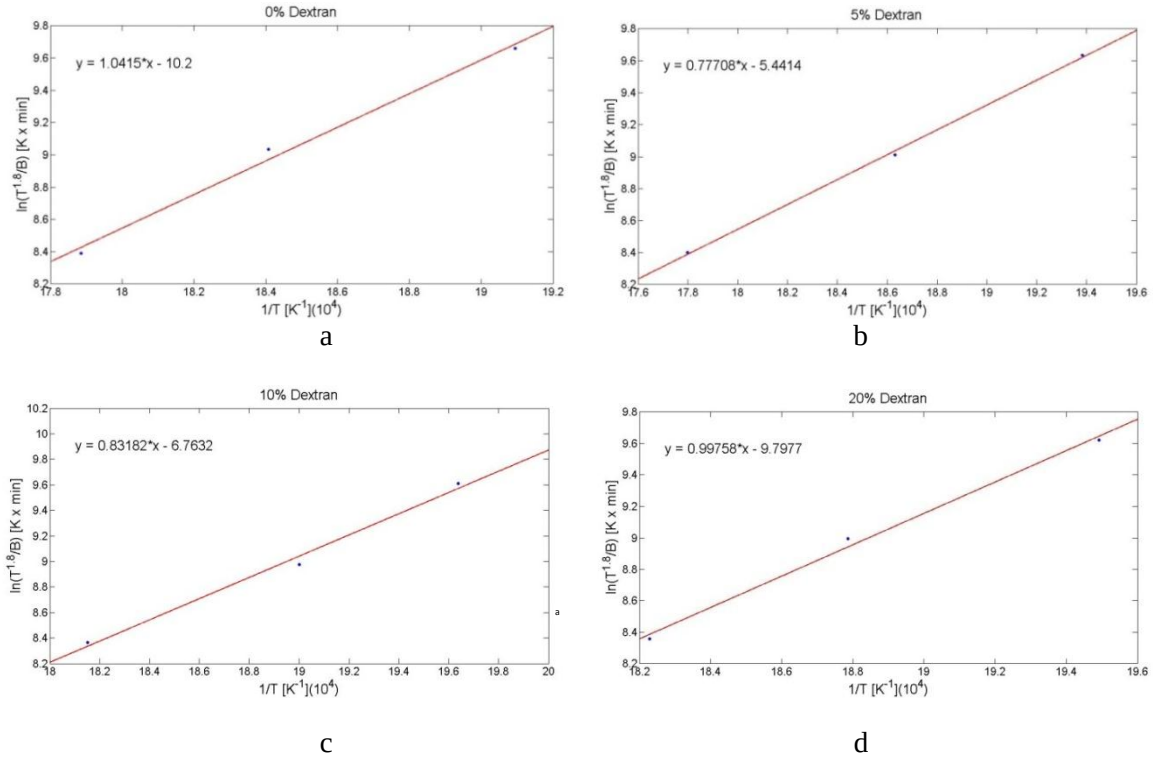

Figure 7– Arrhenius plots for the exothermic peaks in the system NH_4NO_3/Dextran: (a) NH_4NO_3 decomposition, (b) NH_4NO_3-5 wt.% Dextran, (c) NH_4NO_3-10 wt.% Dextran, (d) NH_4NO_3-20 wt.% Dextran

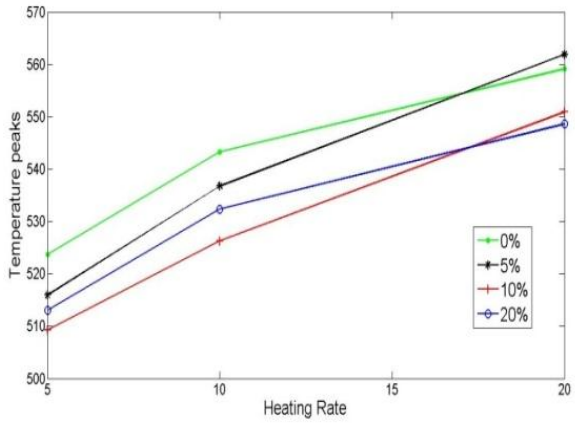

Figure 8 – Dependence of decomposition temperature of NH_4NO_3 and NH_4NO_3-dextran on a heating rate

The decompositon activation energy for the NH_4NO_3 was around 86 kJ/mol, which is in god agrement with literature data [5]. Thus, smal amount of dextran is acting as a catalyzer for decomposing the NH_4NO_3 with leser amount of activation energy [6]. Dependence of activation energy on dextran concentration in compositons was determined. The minimum value of activation energy was determined at the dextran concentration of 5 wt. % in the mixture

CONCLUSIONS

Determined the dependence of activation energy to ratio of ammonium nitrate and dextran concentration.

The minimum value of activation energy was determined at the dextran concentration of 5 wt. % in the mixture.

Thus, small amount of Dextran is acting as a catalyzer for decomposition reaction of NH_4NO_3 with lesser amount of activation energy.

Take pictures of the surface of the granules of ammonium nitrate in pure form and mixed with dextran with an optical microscope and SEM microscopy which showed the presence of nano-pores, cracks and deepening.

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