COMBUSTION OF MAGNESIUM–SODIUM NITRATE MIXTURES. III. CONCENTRATION LIMITS OF THE COMBUSTION OF MAGNESIUM–SODIUM NITRATE–ORGANIC FUEL MIXTURES


A theory of concentration limits for the combustion of magnesium–sodium nitrate–organic fuel mixtures is suggested. Experimental and calculated compositions of the mixtures corresponding to the combustion limits are compared. The results of special experiments that support the validity of the theoretical assumptions are reported.

In our previous works [1, 2] we have reported experimental data and developed a combustion mechanism for magnesium–sodium nitrate mixtures. The theory is based on the assumption of the decisive role of the heat released during the combustion of magnesium particles in the gaseous decomposition products of sodium nitrate. Sodium nitrate decomposes via two stages. The first stage involves the decomposition of the nitrate to the liquid nitrite and gaseous oxygen.

Let us use the same assumptions to consider the concentration limits of the combustion of magnesium–sodium nitrate mixtures. In terms of the theory of the concentration limits of flame propagation in gas fuel–oxidizer mixtures [3], the limits are related with the heat release from the combustion zone via conduction or radiation to the walls of the reaction cell or to the environment. In the case under consideration, the combustion limits of a magnesium–sodium nitrate mixture whose components are solid at the initial temperature are of a different nature. While for gas fuel mixtures the temperature dependence of the reaction rate is continuous (Arrhenius function), the same dependence for magnesium–sodium nitrate mixtures has a break at a certain temperature. The reaction rate is practically zero up to the ignition temperature of the mixture (820-970 K is the temperature at which sodium nitrate converts to the nitrite and oxygen, and magnesium melts). After the ignition of magnesium particles the reaction is diffusion-controlled and its rate increases dramatically. Now the burning rate of the magnesium particles is determined by the diffusion and thermal conductivity of the oxidizing medium rather than by the kinetics of magnesium oxidation and is weakly dependent on the temperature of the medium.

Hence, a magnesium–sodium nitrate mixture can burn only when its components are heated up to the ignition temperature, i.e., when sodium nitrate decomposes and magnesium particles ignite. Thus, the temperature of the reaction products in the zone of influence (which determines the burning rate) is higher than the ignition temperature of the mixture. This is the condition for a nonzero burning rate of magnesium–sodium nitrate mixtures.

Calculations of the combustion product temperature for different binary mixtures are shown in Fig. 1 of [1]. The same figure also shows plots for the dimensionless diameter of magnesium particles \( \tilde{d} \) vs the nitrate content of the mixture \( \eta \) (\( \tilde{d}_c \) corresponds to the combustion temperature \( T_c \) and \( \tilde{d}_b \) corresponds to the burnout of the oxygen evolved in the nitrate-to-nitrite conversion). As explained in [1], in magnesium-rich mixtures the temperature of the combustion products decreases to the value \( T_c \approx 900 \text{ K} \), which corresponds to the ignition temperature of a magnesium–sodium nitrate mixture with a mass content of nitrate as low as \( \eta = 0.195 \); in the "lean" mixtures the value \( T_c \approx 900 \text{ K} \) is reached at \( \eta = 0.91 \).
Fig. 1. Schematic of the operating part of the setup:
1) sleeve; 2) graphite electrode; 3) stop; 4) oxygen collector; 5) igniting mixture; 6) mixture under investigation; 7) spring.

Thus, the combustible composition for magnesium–sodium nitrate mixtures ranges from $\eta = 0.195$ (the upper limit for magnesium content) to $\eta = 0.91$ (the lower limit). A comparison between experimental and calculated data for a two-component mixture at room temperature and 100 KPa shows the following: The upper-limit content of magnesium in experiment and in calculation is 0.855, while the lower-limit content of sodium nitrate is 0.83 in experiment and 0.91 in calculation. Thus, the theory fits the experimental results well.

If the decomposition of sodium nitrate in the influence zone proceeds somewhat beyond the nitrite, as is assumed in the calculation, and, hence, an additional amount of oxygen is produced, the combustion limits are shifted to lower values of sodium nitrate content in the mixture. It has been estimated that at the lower limit the decomposition of just 5% of the sodium nitrate to the final products (not to the nitrite) accounts for the difference between the calculated and experimental lower-limit compositions of the mixture.

Another reason for the aforementioned difference, which in the main refers to the upper limit, is that the calculation is performed for an average composition of the mixture, while local compositions, particularly those for mixtures containing large magnesium particles, can differ substantially from the average one. The combustion can be sustained in local areas of the burning surface where the content of the oxidizer is higher than average, with the mixture as a whole (in the calculation with respect to the average composition) being incombusible.

In this connection, it could be predicted that for mixtures that include large magnesium particles (up to a certain limiting size), the content of sodium nitrate at the upper limit of combustion is lower than that for mixtures containing smaller particles. This prediction is confirmed by the experimental results given in Fig. 2 of [4].

The notion of the nature of the concentration limits of the combustion of magnesium–sodium nitrate mixtures as well as the consequent assumption of the decisive role of the combustion of magnesium particles in the oxygen arising in nitrate decomposition need special experimental verification.

Since the existence of an upper concentration limit depends on a decrease in the temperature of the combustion products to the ignition temperature of the mixture due to a deficiency in oxygen, an external supply of oxygen to the interface (the end of the charge) must provide the combustion of mixtures more "rich" than the upper-limit mixture, i.e., those with a sodium nitrate content lower than the limiting one.

The assumptions were checked experimentally on the setup shown schematically in Fig. 1. A charge consisting of the composition under study (6 g) and an igniting mixture (50% magnesium and 50% sodium nitrate; total mass 1.75 g), at 15 mm in diameter, was inserted in a socket and forced with a spring against the stop to fix the charge end. The igniting mixture was initiated by an electric arc between a graphite electrode and the charge end. Cool gaseous oxygen was supplied tangentially to the charge end through 12 holes, 2 mm in diameter, circularly and uniformly distributed over the sleeve. The oxygen flow rate was measured by a calibrated diaphragm.