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USE OF THE NANOSTRUCTURED SOOT IN GAS GENERATORS FOR PROCESSING OF A BOTTOMHOLE ZONE OF OIL WELLS

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ABSTRACT

The work is devoted to the investigation the gas-generating composition of gas generator for processing of oil wells on the basis of ammonium nitrate, a magnesium, aluminum, an epoxy resin and a nanostructured soot. The regularities of combustion of carbonaceous nanomaterials in two gas generating compositions with regard to the conditions of the oil wells were determined. The influence of different amount of nanostructured soot on the regularities of combustion of pyrotechnic gas generator composition was investigated. By adding of 1.0 % nanostructured soot the lowest rate of combustion - 0.05 mm/s was reached. The content of the combustion products by the "Terra" program for composition No.2 was calculated. An optimal composition for the processing bottomhole zones of oil wells is proposed. To determine the morphology and sizes of the resulting soot particles electronic microscopic studies of the soot samples were carried out.

Keywords: *nanostructured soot, oil well, combustion rate, bottomhole zone of oil wells.*

INTRODUCTION

Nowadays, the combustion processes are widely used for the processing of oil wells. There are three types of the bottomhole zone treatment (BHZ): pressure, chemical reaction and heat. They are a basis of methods of increase in oil recovery [1 - 4]. Each of these types of influence (or their combination) is implemented during the work of thermogas generators. The use of heat, chemical energy and mechanical impact on the BHZ of the combustion products is the basis of the method of a thermogas-chemical method of influence (TCMI) [5 - 8]. Effectiveness of this method of influence is defined not only with the quantity of an added heat, but also the fact that as a working body are used the chemically aggressive, heated to high temperature products of combustion, getting into the pores and cracks of productive layer, destroying and deleting from them solid hydrocarbonic deposits and emulsions. One of the most efficient, cheap and available methods of impact on BHZ is the method of TCMI by means of power saturated systems (PSS) of various nature. PSS (as without a propelling, as comprising metal combustible, and gunpowder) are currently in widespread use in the methods TCMI for intensification of oil production. A large number of thermogas-chemical sources on the basis of gunpowder, mixed fuels and pyrotechnic systems are known [9 - 14]. One of the most efficient ways to increase the oil recovery of the well is the acid treatment of a bottomhole formation zone [15]. The hydrochloric acid for processing of the layers composed of carbonaceous rocks and the so-called mud acid (acid clay) for processing of layers from terrigenous rocks are used as chemical reagents.

The aim of the work is the investigation of the gas-generating composition of gas generator for processing of oil wells on the basis of ammonium nitrate, magnesium, aluminum, an epoxy resin and the nanostructured soot.

EXPERIMENTAL

In this work two pyrotechnic gas generating compositions were investigated. They were prepared by technique [16] with different ratios of the components: ammonium nitrate in powder of grade B (AN), nanostructured soot (NS), magnesium powder, aluminum powder, epoxy resin. Epoxy resin is used as a binder and combustible additive. For the synthesis of compounds a granulated AN was milled. The ingredients were weighed on an electronic balance and mixed in a porcelain mortar. The composition was molded and dried at temperature 323-333K for 1 h.

Composition No 1, mass %: AN: 35 - 40; NS: 0 - 5; magnesium powder: 15.0 - 20.0; epoxy resin: 35.0 - 40.0. **Composition No 2**, mass %: AN: 37.0 - 42.0; NS: 0 - 5.0; magnesium powder: 2.5 - 7.5; epoxy resin: 37.0 - 42.0; aluminum: 2.5 - 7.5.

The compositions were laid in a cardboard cartridge with a diameter of 1.0 cm and 10.0 cm high (Fig. 1). Then the combustion was initiated from the top part of the cartridge with the help of the initiation composition (50.0 % Mg + 50.0 % smokeless powder). The combustion duration of compositions was fixed by stopwatch. Linear speed of the compositions combustion was determined by dividing the height of the cardboard for the duration of combustion of compositions. The flashpoint of compositions was determined by combustion in the reactor (Fig. 2). The temperature of compositions combustion was fixed by an optical pyrometer Raytek 3 i 1M. Each study was performed five times, then the average value was calculated.

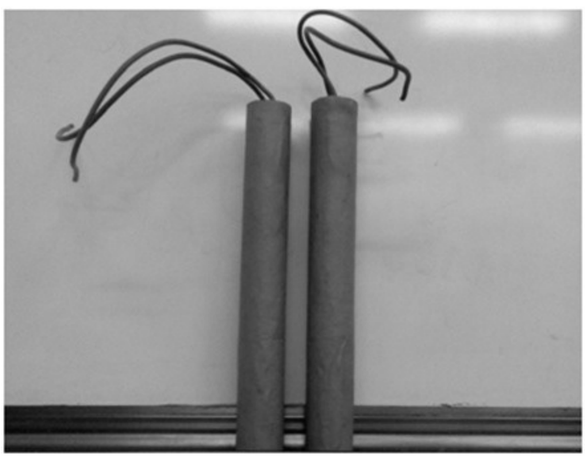

Fig. 1. Industrial gas generator cartridge.

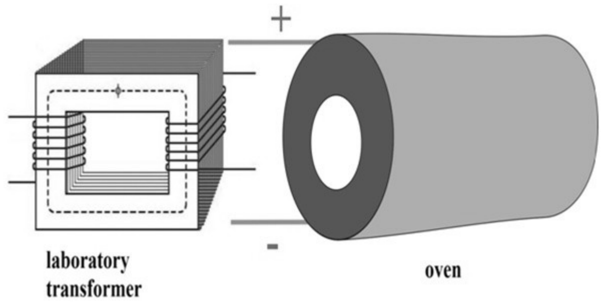

Fig. 2. Reactor for flash point testing of pyrotechnic compositions.

RESULTS AND DISCUSSION

The burning rate of the studied pyrotechnic composition No 1 (Fig. 3, Table 1) was from 2.5 to 7.28 mm/s, flash point - 348 K. Combustion temperature of this composition was equal to 2,273K. The data in the Table 1 and Fig. 3 show that the amount of NS does not have a significant effect on the combustion temperature of the samples. Apparently from the Table, the influence of NS on burning rate of pyrotechnic composition depends on the content of NS in composition. 0.1 % of NS in the composition No 1 reduces the burning rate of composition by 20 %, but with increase in amount of NS the rate of combustion increases and the increase of speed is about 30 - 40 %.

Since the composition of the gas generator in the conditions of oil wells should burn for a long time, therefore, in this work, to reduce the burning rate in the composition, aluminum powder was added.

The compositions with aluminum under the condition of identical shredding of metal are burning much slower than formulations with magnesium [17 - 21]. Moreover, AN was used in case if a large time of combustion of mixture is necessary because it has low combustion rate [18 - 20]. The data of the Table 1 show that in the case of the composition No 1 without aluminum addition, the combustion rate was higher in comparison with the rate of the composition No 2.

Tests of composition No 2 (Table 1, Fig. 4) show that burning rate of the studied pyrotechnic composition was varied from 0.11 to 0.25 mm/s, and flash point - 383 K. The combustion temperature of this composition was equal to 2,773K. In the case of increasing the content of NS (Fig. 4) was not observed a rectilinear dependence of increasing the combustion rate of the pyrotechnic

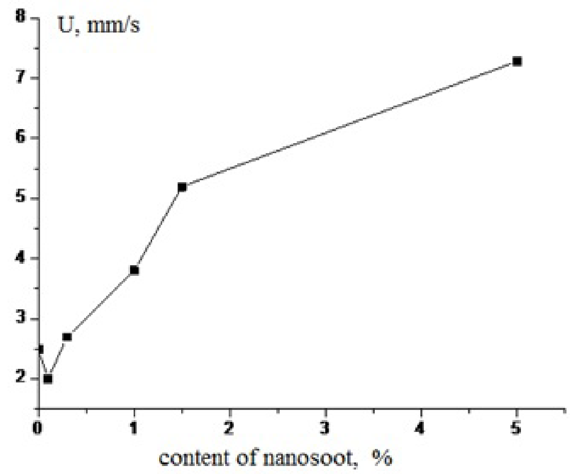

Fig. 3. The dependence of the combustion rate on NS content in the composition No 1.

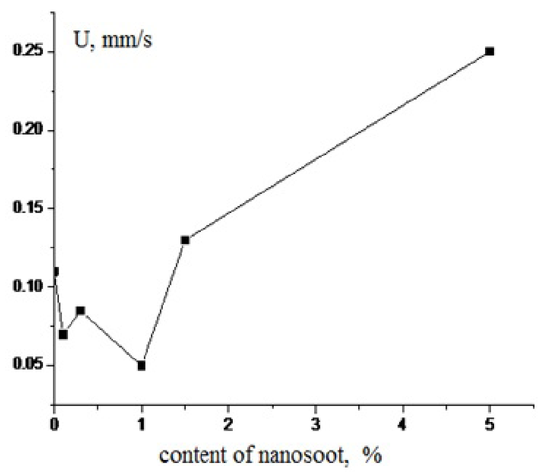

Fig. 4. The dependence of the combustion rate on NS content in the composition No 2.

composition, as shown in Fig. 3. NS content in the composition can increase (Fig. 4) the rate of combustion (52.0 - 60.0 % with 0.3 % and 5.0 % of NS) and reduce it (about 37.0 - 60.0 % at 0.1 and 1 % of soot). At 1 % of NS there is the lowest burning rate: 0.05 mm/s (Fig. 4).

The optimum composition for the processing of oil wells is the composition No 2, mass %: AN - 42.0; NS - 1.0; magnesium powder - 7.5; epoxy resin - 42.0, aluminum - 7.5 (Figs. 3, 4).

For the composition No 2 by the «Terra» program calculation the composition of the combustion products in the temperature range of 300 - 2,000 K and an atmospheric pressure of 0.100 Pa was determined. Fig. 5 shows the composition of the gas phase of the process gasification.

It is visible that the gas phase consists mainly of synthesis gas ($CO + H_2$), a thermodynamically stable to by-products of the gasification process. At T = 1,400K, the concentration of the synthesis gas in the gas phase reaches the maximum - 52.5 %.

The concentrations of CH_4 and CO_2 impurities are reduced to zero at increasing the temperature up to 1,200K.

Nitrogen-containing substances are mainly presented by the molecular nitrogen which concentration, at temperature increase is decreased due to emergence in a gas phase of synthesis gas and increase of its concentration.

Concentration of CO reaches the maximal value (35.0 %) at a temperature 1,950K. Concentration of molecular hydrogen (H_2) in the range of temperatures 400 - 1,300K is sharply increased and reached the maximum (55.0 %) at T = 1,600K.

Samples of soot were studied to determine the morphology and sizes of the resulting soot particles using electronic microscopy (Fig. 6, 7). The size of soot

Table 1. Characteristics of the studied samples with NS.

Composition No 1			Composition No 2		
NS content, mass %	The temperature of combustion, K	The combustion rate, U, mm/s	NS content, mass %	The temperature of combustion, K	The combustion rate, U, mm/s
0.0	1,184	2.5	0.0	1,229	0.11
0.1	1,196	2.0	0.1	1,248	0.07
0.3	1,198	2.7	0.3	1,246	0.085
1.0	1,210	3.8	1.0	1,258	0.05
1.5	1,184	5.2	1.5	1,239	0.13
5.0	1,226	7.28	5.0	1,245	0.25

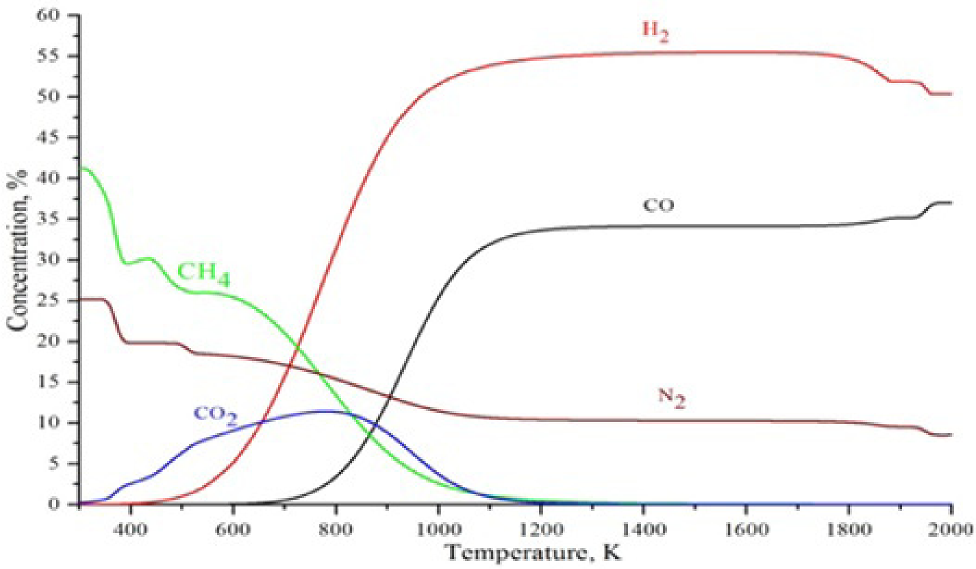

Fig. 5. Temperature dependence on the concentration of components in the gas phase in the composition No 2.

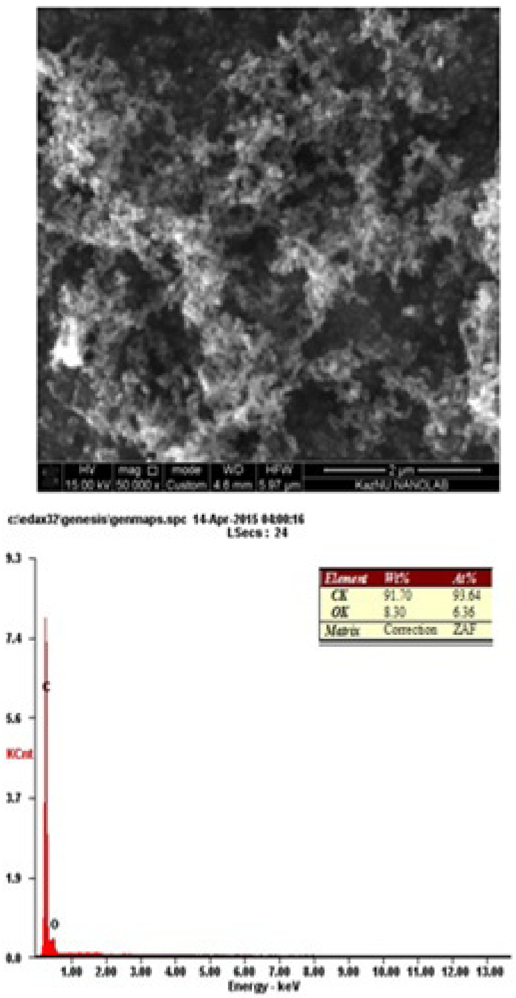

Fig. 6. SEM of the sample of soot (a) and the elemental analysis of the sample of soot (b).

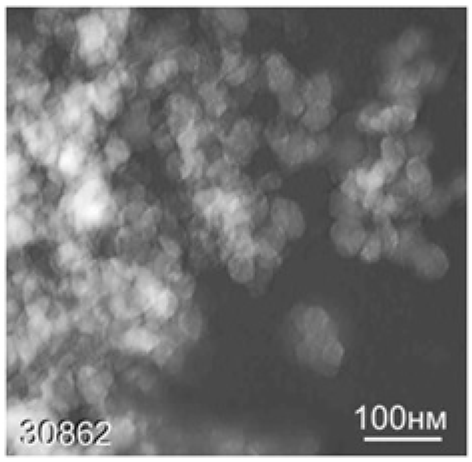

Fig. 7. Transmission electron - microscopic photograph of soot sample.

particles is in the range of 20.0 - 45.0 nm (Fig. 6a). The sample consists of rounded dominant (in the researched grid ~ 70 %) and the film formations (about 30.0 %). The size of the flattened, rounded particles, often collected in volumetric units was approximately 15.0 - 50.0 nm (Figs. 6a, 7).

The elemental composition of soot shows that the sample is composed of 92.0 % carbon and 8.0 % oxygen (Fig. 6b). The results of compositions test and SEM and TEM-studies showed that the composition with 1.0 % NS with sizes less than 50 nm exactly decreased the combustion speed, which in turn increased slow burning of gas generator composition.

CONCLUSIONS

The gas-generating composition of gas generator for processing of oil wells on the basis of ammonium nitrate, magnesium, aluminum, an epoxy resin and the nanostructured soot were researched. It was found that soot depending on the amount in the composition may both increase the rate of combustion (about 52.0 - 60.0 % with 0.3 % and 5.0 % of soot) and reduce it (about 37.0 - 60.0 % at 0.1 and 1.0 % of soot). At introduction of 1.0 % NS the lowest rate of combustion -0.05 mm/s was revealed. With the use of the program "Terra" it was found the content of the combustion products for the composition No 2. The most suitable composition for the processing of oil wells is No 2 containing NS 1.0 %.

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