REVIEW

of official reviewer, Dr. of Chem. Sc., Kudaibergenov Sarkyt Yelekenovich for the PhD thesis of Yelemessova Zhanerke Komekovna on the topic: «New nano metal-organic framework energetic materials for pyrotechnics», submitted for the degree of Doctor of Philosophy (PhD) in specialty 6D073400 – «Chemical technology of explosives and pyrotechnics»

1. The relevance of the research topic and its connection with general scientific and national programs.

The thesis is devoted to development of highly efficient energy fuel based on ammonium nitrate (AN) containing carbon materials with metal oxides for improvement of combustion process. The problem is experimentally solved by investigating the effect of activated carbonized rice husk (CRH) with metal oxides on thermal decomposition and burning process of composite based on ammonium nitrate material.

The carbon nanomaterials including carbon nanotubes, graphene sheets and fullerenes are novel materials that can be used to improve thermal conductivity, heat release, and reactivity of various energetic materials (EMs). They help to achieve the desired performances, but certainly, they are usually not so cost-effective due to complicated technology for production. Among the possible substitutes for expensive carbon nanomaterials, the most promising one is the activated carbon (AC), which can meet all the requirements for applications in EMs and their compositions. For example, it has been reported that AC has been used as a technological additive for modifying the burning rate in nonmetallized and metalized energetic systems. The effects of an AC and its composites (ACs) on the thermal decomposition/combustion of EMs have also been studied in several works.

The AC with a high specific surface area (~3186 m^2/g) based on rice husk (RH) was investigated as a promising additive in this work. RH is a large-scale vegetable unique material, which is a highly cost-effective renewable green material. In comparison to the other carbon nanomaterials, ACs have some promising properties (handling, storage, and transportation) and their stocks are huge in rice-growing countries. Therefore, the replacement of expensive carbon nanomaterials with ACs will make these materials widely applied in the catalyst industry. A promising and economically effective method for the production of porous carbon materials with a high specific surface is to obtain it from renewable plant waste. In this connection, research was conducted on the development of new metal organic frameworks (MOFs) based on renewable raw materials such as rice husk with addition of nanosized transitional metal oxides and their influence on the main characteristics of the combustion process of pyrotechnic compositions was studied.

2. Scientific results and their relevance.

The following results were obtained in the frame of the thesis:

1. Based on waste plant materials with addition of transition metal oxides nanoparticles, a hybrid combustion catalyst was developed;

2. The experimental studies and thermodynamic calculations of the data revealed that the addition of activated carbon and metal-organic structures effectively reduces the initial temperature of the thermal decomposition of ammonium nitrate;

3. The conditions for the influence of a metal-organic framework (MOF) composite on the combustion conditions of pyrotechnic compositions with initial pressure values from 1 to 3.5 MPa were determined;

4. The conditions for initiating the combustion process of the pyrotechnic composition by laser radiation upon the addition of a metal-organic frame structure (MOF) were found;

5. It was determined that the addition of a metal-organic frame structure (MOF) significantly reduces the activation energy of the pyrotechnic AN/Mg/NC composition.

3. Degree of validity and reliability of each scientific result (scientific statement) and conclusions of the applicant formulated in the thesis.

The research results and conclusion are clearly described to achieve the main goal of the thesis. The reliability of obtained results is beyond any doubt due to competent choice of modern methods.

The results of research are presented in 12 publications: 2 articles in the journal included into Scopus database and 1 article in the journal included in the Thomson Reuters database, 4 publications were published in journals recommended by the Committee for Monitoring in Education and Science of the Republic of Kazakhstan, 4 publications in materials of International Conferences. 1 utility model patent № 2019/0488.2 «Carbon-containing metal-oxide fuel» was received.

4. The degree of novelty of each scientific result (scientific idea), conclusion of author that were obtained in this thesis.

It should be noted the most variable scientific results:

First novelty. The new metal-organic framework structure composites MOF (CRH-Me_xO_y) based on activated carbon obtained from carbonized rice husk with the addition of nanosized particles of transition metal oxides were developed.

Second novelty. An average activation energy was determined and compared to corresponding of obtained Kissinger plots. The additives of MOF (CRH-CuO) have been shown to reduce their energy to 8 kJ/mol and directly influence the decomposition process of the pyrotechnic AN/Mg/NC system.

Third novelty. MOF (CRH-CuO) has been investigated for the combustion of energetic mixture dependent on AN/Mg/NC. DSC technique and high-pressure chamber were used to determine the decomposition kinetics and combustion properties of the mixture with additives. The addition of activated CRH into the energetic mixture shifts the exothermic peaks to low temperatures region and decreases the onset decomposition temperature from 276 to 209°C. The thermal release rises from 1,2 to 7,2 mW by applying MOF (CRH-CuO).

Fourth novelty. It was established that MOF (CRH/CuO) have a promoting effect to increasing on the burning rate of composite based on ammonium nitrate, and also provide self-sustained combustion even at low pressures (1-3.5 MPa).

5. Practical and theoretical significance of scientific results. The theoretical significance of the work is to establish the main regularity of the influence of activated carbons in combination with metal oxides (such as MOFs) on thermal decomposition and combustion of AN, which can be used as energy-intensive fuels. The presence of activated carbons and metal oxides changes the initial decomposition temperature and modifies the burning rate.

The practical significance of the research is that the developed compositions based on ammonium nitrate, activated carbons and transition metal oxides (MOFs) with a high specific surface and developed topographic structure are promising materials for application as energy-intensive fuels and gas generators.

6. Comments, suggestions on the thesis.

1. Pages 30,31. In preparation protocol of activated carbon from the rice husk the yield of key products might be indicated for each stage. For example, it is unclear how much activated carbon can be obtained from 1 g of raw husk.

2. Page 45. Figure 24 (Obtaining of activated carbon with graphene layers). Low resolution of SEM image (1 micron) does not give fully representation of graphene structure. It would be better to make TEM measurements.

3. Who is interested in your outputs from practical point of view or your results represent only theoretical interest?

4. Many references contain the titles of papers but most of them not. It means that Normative Refs (GOST 7.1-2003. Bibliographic record. Bibliographic description. General requirements and compilation rules) were ignored.

5. The thesis contains some stylistic and grammatical typos, punctuation inaccuracies and typographical misprints.

All above-mentioned comments and question are associated only with my interest to this research work, and they have not fundamental nature and do not reduce the significance of this PhD dissertation work.

7. Compliance with the content of the thesis within the requirements of Rules for awarding academic degrees.

Based on the above relevance, scientific novelty, practical and theoretical significance, I consider that the dissertation work of **Yelemessova Zhanerke Komekovna** «New nano metal-organic framework energetic materials for pyrotechnics» corresponds to the requirements of «Rules for the award of academic degrees» and the author deserves the PhD degree in the specialty 6D073400 – «Chemical technology of explosives and pyrotechnics».

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