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Safety issues of high-concentrated hydrogen peroxide production used as rocket propellant

O.V. Romantsova [a,*], V.B. Ulybin [b]

[a] Saint Petersburg State Polytechnical University, Russia
[b] Saint Petersburg State Technological Institute, Technical University, Russia

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ABSTRACT

The article dwells on the possibility of production of high-concentrated hydrogen peroxide with the Russian technology of isopropyl alcohol autoxidation. Analysis of fire/explosion hazards and reasons of insufficient quality is conducted for the technology. Modified technology is shown. Non-standard fire/explosion characteristics required for integrated fire/explosion hazards rating for modified hydrogen peroxide production based on the autoxidation of isopropyl alcohol are defined.

1. Introduction

Spaceflight safety has recently become a topic of heated discussion. Safety in spaceflight includes various aspects. One of them is proper choice of fuel. Many researches are devoted to different types of rocket propellants analysis and their characteristics comparison [1–5]. Over hundreds of different liquid propellants were lab tested. The primary factors which are needed to choose a propellant include ease of operation, cost, hazards/environment and performance. One of the promising agents for the propellants is hydrogen peroxide. It is considered to be used as both an oxidizer and a monopropellant. Propellant based on hydrogen peroxide has a number of advantages such as high density, non-toxic, high specific impulse and others. In order to use the hydrogen peroxide as a propellant it must be of high quality and above 90% concentration to reduce the decomposition on the surfaces of contact [6–8]. High-concentrated hydrogen peroxide is very insensitive to detonation by shock or impact.

Obtaining hydrogen peroxide of required quality is a particular problem.

Nowadays three major industrial methods of hydrogen peroxide production exists (electrochemical, anthraquinone autoxidation, and isopropyl alcohol autoxidation). The first technology provides the highest quality product but with a very high power consumption. It is used only to obtain a highly concentrated product. It can be used in a special technique because of its high quality despite of its cost.

Comparison of other two methods shows that product quality is practically the same, as well as its cost. However, in Russia method of isopropyl alcohol autoxidation has spread. This technology is more environment friendly but more explosive compared to anthraquinone autoxidation, which is spread in the rest of the world [9]. Ensuring safety in the hydrogen peroxide production based on the isopropyl alcohol autoxidation is a complex scientific and technical task.

2. Features of the hydrogen peroxide production technology based on the isopropyl alcohol autoxidation

Hydrogen peroxide production consists of three main steps: isopropyl alcohol autoxidation, hydrogen peroxide extraction, and acetone extraction. Hydrogen peroxide is obtained as a result of reaction of isopropyl alcohol with

* Corresponding author. Tel.: +7 812 552 97 14.
E-mail addresses: olga.v.romantsova@gmail.com, ovromantsova@rambler.ru (O.V. Romantsova).

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air (1). This process is carried out at 105–134 °C and 1.1–1.2 MPa (10–12 atm) in a liquid-phase. There are also concurrent reactions (2)–(5). Exothermic reaction heat of some of them is bigger than heat of the main one (1), so uncontrolled concurrent reaction can cause the thermal explosion.

$$CH_3CHOHCH_3 + O_2 \rightarrow H_2O_2 + CH_3COCH_3 + 117.21\ \text{kJ/mol} \quad (1)$$

$$CH_3CHOHCH_3 + H_2O_2 \rightarrow CH_3COCH_3 + 2H_2O + 313.27\ \text{kJ/mol} \quad (2)$$

$$CH_3COCH_3 + 2H_2O_2 \rightarrow CH_3COOH + CO_2 + 3H_2O + 1114.28\ \text{kJ/mol} \quad (3)$$

$$3CH_3COCH_3 + 3H_2O_2 \rightarrow C_9H_{18}O_6 + 3H_2O - 359.44\ \text{kJ/mol} \quad (4)$$

$$H_2O_2 \rightarrow H_2O + 0.5O_2 + 98.03\ \text{kJ/mol} \quad (5)$$

Besides in the process a dangerous by-product acetone peroxide $C_9H_{18}O_6$ occurs (4), which is primarily a high explosive. It is susceptible to heat, friction and shock.

Another feature of the technology is simultaneous presence in the working mixtures of flammable liquids (isopropyl alcohol and acetone) and oxidizers (oxygen and hydrogen peroxide). In this connection there is a risk of forming an explosive mixtures inside the equipments. Also characteristics of working mixtures are different from the characteristics of the components which it consists of. For example, autoignition temperature of working mixture decreases with increasing concentration of hydrogen peroxide in it (Fig. 1) [10].

These factors increase the dangers of the process, risks of explosive on every step of the production.

3. Modification of the hydrogen peroxide production technology based on the isopropyl alcohol autoxidation

Nowadays hydrogen peroxide after isopropyl oxidation can be concentrated up to 55% [11]. Current technology does not provide enough quality of the product. Increasing the concentration is not possible because of the organic impurities containing in the product. So that sort of hydrogen peroxide cannot be used as rocket propellant.

However, the production can be modified to improve the quality of the product. The main idea is to change the order of the working mixtures separation [12]. Under the current technology after the step of isopropyl alcohol autoxidation working mixture of hydrogen peroxide, isopropyl alcohol, acetone and other by-product enter in a vacuum distillation column where aqueous solutions of hydrogen peroxide are separated from the mixture of acetone, isopropyl alcohol and other low-boiling impurities with the further refining and concentration. The next step is the separation of mixture of acetone, isopropyl alcohol in another vacuum distillation column (Fig. 2).

According to the modified technology acetone should be separated first in a distillation column at atmospheric pressure. And after that use a vacuum distillation column to extract aqueous solutions of hydrogen peroxide from its mixture with isopropyl alcohol (Fig. 3).

This method can significantly reduce energy costs, improve the quality of hydrogen peroxide and eliminate the possibility of the acetone peroxides formation, one of the most hazardous by-products [12]. However, this process is still explosive.

4. Non-standard fire/explosion characteristics

To control potential risks of the modified technology of hydrogen peroxide production standard and non-standard fire/explosion characteristics should be evaluated. The list of the standard fire/explosion characteristics are given in Federal law of Russian Federation no. 123-FZ [13]. Their values

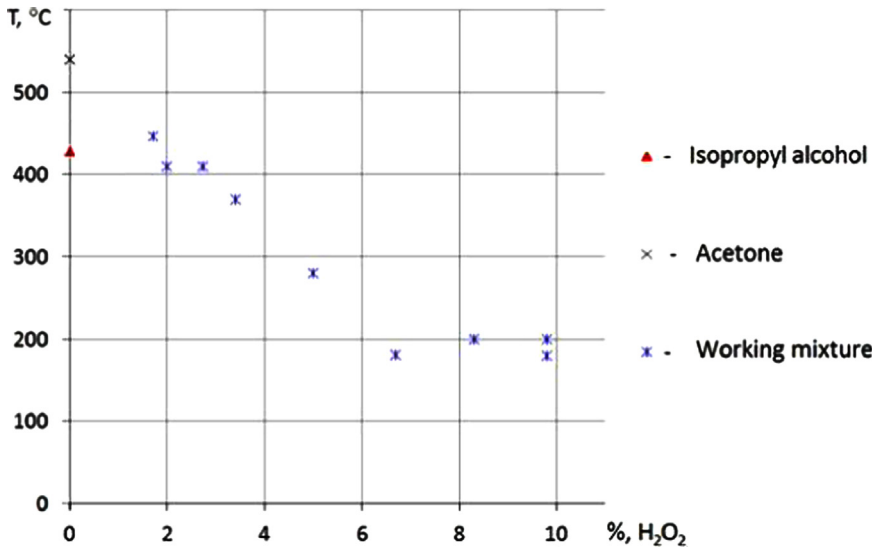

Fig. 1. Autoignition temperature of working mixture.

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