

# Prospects for use of O<sub>4</sub> as rocket fuel oxidizer

## Abstract

The article gives an overview of rocket fuel existing oxidants, their technical properties and their specific impulse with kerosene. Compounds of super peroxides (superoxides) as oxidizing agents with higher specific characteristics are proposed. It is calculated that the specific impulse of O<sub>4</sub> compound with kerosene can be about 4500 m/s, i.e. 30% more than with liquid oxygen, and the launch mass of the rocket can be halved. It is concluded that O<sub>4</sub> is promising as an oxidizer of rocket fuel. It is described: the principal possibilities of O<sub>4</sub> electrochemical production, methods for stabilizing of O<sub>4</sub> chemical compounds at normal temperature, the stages of O<sub>4</sub> possible industrial production. It is given the possible cost of O<sub>4</sub> in the production of 300 tons per year.

**Keywords:** rocket fuel, oxidants, ozone, combustion, super peroxides

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## Introduction

Researchers continue attempts to increase the specific impulse of rocket fuels used in space flight practice.<sup>1</sup> The most commonly used types of oxidizing agents for rocket fuel have the following characteristics (Table1).<sup>2</sup> The best characteristics among the most

common and inexpensive fuels has liquid oxygen-kerosene.<sup>3</sup> Due to its low boiling temperature it should be cryogenically stored, which poses an engineering challenge. However, in addition to very low boiling point, liquid oxygen also has rather low density. Low density causes to increase in the capacity and mass of oxidizer tanks that decrease in payload proportion in the rocket starting mass.

**Table 1** Characteristics of various oxidizing agents used for rocket fuel

Oxidizing agent/properties	O <sub>2</sub> Liquid oxygen	N <sub>2</sub> O <sub>4</sub> Nitrogen Tetra-oxide	H <sub>2</sub> O <sub>2</sub> Hydrogen peroxide	O <sub>3</sub> Ozone	O <sub>4</sub> Disuper oxide
Sustainability	steady	steady	decomposes	decomposes	steady
Boiling T, °C	-183	+21,4	+150,2	-112	?
Storage conditions	Cryogenic liquid	Usual liquid	Usual liquid	Cryogenic liquid	Usual liquid
Toxicity	non-toxic	toxic	toxic	toxic	non-toxic
explosion hazard	No	no	yes	yes	no
Density, kg/m <sup>3</sup>	1,140	1,443	1,450	1,597	2,150
Gibbs standard energy ΔH, kJ/mol	0	+51,5	-120,4	163	217
Specific impulse with kerosene, m/sec	3,500	2,707	3,006	3,750	3,990

Attempts have been made to use liquid ozone O<sub>3</sub> in missiles as oxidizing agent.<sup>4</sup> However, although liquid ozone has higher boiling point and higher density and heating capacity relative to liquid oxygen, it could not be introduced into practice of rocket production. As a matter of fact, liquid ozone itself can suddenly explode, that produces detonation wave at 2000 m/s speed. In addition, ozone slowly decomposes during storage.

Spontaneous decomposition time of ozone is too short to be stored and accumulated in significant quantities. Being poisonous, O<sub>3</sub> can cause serious poisoning to personnel when discharging gas drains through tank. Mixing of ozone with liquid oxygen in amount of 20-30% (it does not explode spontaneously in such mixtures) does not solve the problem of the rocket fuel specific impulse increasing. The difference in specific impulse of kerosene during oxidation with oxygen and ozone is 250 m/s. Therefore, addition of 30% ozone to oxygen will give 3500 + 250/3 = 3580 m/s with kerosene. This gives a specific impulse gain of 2.3%.

The problem could be solved by using of O<sub>4</sub> (disuperoxide) as oxidizing agent. Use of O<sub>4</sub> as an oxidizer of rocket fuel is unknown to the authors so far. The density of liquid O<sub>4</sub> compound must be two times higher than that of liquid oxygen due to twice the molecular weight. This means that capacity of the oxidizing agent tanks can be halved. Therefore their mass also can be reduced. In addition, their mechanical stability increases with the tanks height decrease. This allows reduce thickness of the walls and longitudinal stiffeners. All of the above will reduce the mass of rocket tanks significantly. The O<sub>4</sub> formation energy (Gibbs standard energy ΔH) calculated with chemical thermodynamics method is +217 KJ/mol or 3,391 KJ/kg. This energy is "stored" in O<sub>4</sub> molecules during their formation and is released at the moment of O<sub>4</sub> molecule dissociation, i.e. at the time of rocket fuel burning. When kerosene is oxidized with liquid oxygen, released specific energy is 43 MJ/kg of kerosene or 9.58 MJ/kg of kerosene-oxygen mixture. Replacing O<sub>2</sub> oxygen with O<sub>4</sub> disuperoxide it will be obtained additional 2.63 MJ per 1 kg of fuel mixture. To this it will be added surplus energy 160 kJ per 0.778 kg O<sub>2</sub>, or 1 kg of kerosene-oxygen mixture, which is spent for liquid oxygen heating from -183°C. As a result it will be obtained specific energy of kerosene-disuperoxide mixture combustion: 12,368 MJ/kg. This is 29.1% more than liquid oxygen + kerosene energy.

Calculation of specific impulse<sup>5</sup> for kerosene-disuperoxide fuel according formula:

$$Isp = \sqrt{16641 \cdot \frac{Tg}{uM} \cdot \left(1 - \frac{pa}{pc} M\right)} \quad (1)$$

where  $Tg$  is the gas temperature in the combustion chamber (decomposition);  $pc$  is the gas pressure in the combustion chamber;  $pa$  is the gas pressure at the exit of the nozzle;  $M$  is the molecular weight of the gas in the combustion chamber;  $u$  is the coefficient characterizing the thermophysical properties of the gas in the chamber (usually  $u \approx 15$ ). As can be seen from the formula, to a first approximation, the higher the temperature of the gas, the lower its molecular weight, the higher the pressure in the combustion chamber and the lower the pressure in the surrounding space, the higher the specific impulse.<sup>6</sup>

To calculate the theoretical combustion temperature  $Tg$ , we write the heat balance equation:

$$Q = Vc(Tg - Tn) \quad (2)$$

where  $Q$  is the calorific value of the fuel, J/kg;

$V$  is the volume of combustion products resulting from the

combustion of 1 kg of fuel, m<sup>3</sup>/kg;

$c$  is the volumetric specific heat of the combustion products, J/(m<sup>3</sup>·deg);

$Tg$  - theoretical combustion temperature, °C;

$Tn$  is the initial air temperature, °C.

When burning under normal conditions ( $Tn = 0^\circ\text{C}$ ), equation (2) takes the form:

$$Q = VcTg \quad (3)$$

From (3) follows the formula for calculating the theoretical combustion temperature:

$$Tg = \frac{Q}{Vc} \quad (4)$$

Thus, the temperature of the gases in the combustion chamber is directly proportional to the specific energy of combustion of the fuel-oxidation mixture. As shown above, the specific heat of combustion of kerosene in O<sub>4</sub> is 1.29 times higher than in O<sub>2</sub>. Substituting 1.29Tc in the formula (1) instead of Tc ceteris paribus we can write:

$$\frac{IspO_4}{IspO_2} = \frac{\sqrt{1.29Tc}}{\sqrt{Tc}} = \frac{\sqrt{1.29}}{\sqrt{1}} = 1.14 \quad (5)$$

from here:

$$IspO_4 = 1.14IspO_2 \quad (6)$$

Substituting data on the specific impulse of kerosene with liquid oxygen from table 1, we obtain 3990 m/s for kerosene with disuperoxide.

We calculated the characteristic velocity of the rocket according to Tsiolkovsky's formula:

$$V_r = V_f \cdot \ln\left(1 + \frac{M_f}{M_r}\right) \quad (7)$$

where:  $V_r$  – velocity of a rocket,  $V_f$  – velocity of fumes,  $M_r$  – rocket "dry" mass,  $M_f$  – fumes mass.

Substituting the values of outflow velocity (which is equal to the specific impulse in the SI) from the table, we obtain the characteristic velocity for an oxygen rocket of 10,305 m/s, and for a disuperoxide rocket – 11,748 m/s.

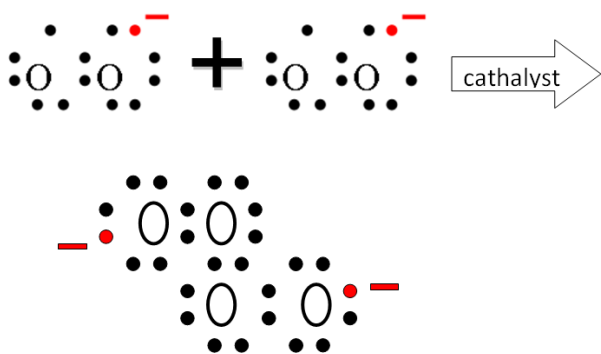
### Substantiation for the O<sub>4</sub> disuperoxide production

To increase the specific heat of rocket fuel combustion, it is necessary to use an oxidizing agent containing oxygen compound in sufficient quantity and in the lowest degree of oxidation. The lower the oxidation degree of the oxygen atom in the oxidizer molecule, the more electrons it will take away from the fuel. Therefore, fuel will require less oxidizing agent for oxidation.

In addition, it is desirable that the oxidizing agent could be high boiling and has high density. Super-peroxides satisfy these conditions. Oxygen compounds that contain 4 oxygen atoms bonded to each other are known – for example, alkali metals super-peroxides (superoxides) such as Na<sub>2</sub>O<sub>4</sub>, K<sub>2</sub>O<sub>4</sub>, Rb<sub>2</sub>O<sub>4</sub>, Rb<sub>4</sub>(O<sub>2</sub>)<sub>3</sub>, hydrogen super-peroxide H<sub>2</sub>O<sub>4</sub>, etc.<sup>6</sup> Oxidation degree of oxygen in such compounds is from -1 to -1/2. These superoxides are compounds of so-called superoxide-anion-radical with peroxide radical. All these compounds are good oxidizers in chemistry and they are used in chemical technology, in particular, for air regeneration in hermetically sealed devices with people (submarines, spaceships). However, use of alkali metal peroxides for liquid rocket engines is impossible due to the fact that

they are refractory solids. Hydrogen super-peroxide has also not yet been used for rockets because of its extreme instability - it decomposes at temperatures above minus 70°C.

Therefore, creation of a stable liquid compound with zero ash content containing a super-peroxide group solves the problem of superoxide employing as a liquid rocket fuel oxidizer. In our opinion, the problem can be solved by cryo-synthesis of two-basic disuperoxide-anion in liquid ammonia medium from superoxide anions on a catalyst.

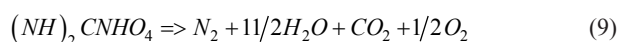


The stoichiometric reaction equation has the form:



Superoxide anions appear in solution upon dissociation of super peroxides (for example, rubidium super-peroxide) in polar solvents (however, in the absence of water and at a temperature below -72°C).<sup>7</sup> After neutralization of disuperoxide anions with a strong base, it will be obtained a neutral stable salt of disuperoxide. It can be used, for example, guanidine (mono-acid alkali), hydroxylamine or basic tertiary amine<sup>8</sup> as the base, as they do not leave ash during combustion. Such salts are low melting and high boiling compounds.<sup>9</sup>

Guanidine disuperoxide is stable at ordinary temperatures and the solvent can be distilled off.<sup>10</sup> As a rule, salts of organic bases and weak acids, such as peroxides and superperoxides, are fusible substances.<sup>11</sup> The oxygen balance of guanidine disuperoxide is positive, therefore, it can serve as an oxidizer of rocket fuel. However, the main part of oxygen will be spent on oxidation of guanidine itself:

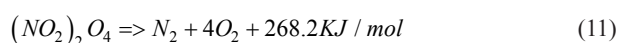


Thus, guanidine disuperoxide itself is a mono-fuel with high calorific value. Adding kerosene to it increases the specific impulse to the above value (see the table). We have to note, however, that use of mono-fuel greatly complicates rocket engines design. The drawback of a mono propellant is its sensitivity to temperature and shock. This sensitivity results in instability and restricts its handling. Generally, monopropellants also require more heat for ignition and react more slowly than bipropellants. These factors mean that monopropellants require larger combustion chambers.<sup>12</sup>

It is much more promising and safer to use disuperoxide salts with cations not of reducing but of oxidizing nature. Such a salt may be, for example, the salt of nitronium cation and disuperoxide anion:



When heated above 200°C, this salt decomposes, forming only nitrogen and oxygen:



We have to note, however, that the technology of such salts production presents significant difficulties due to low basicity of nitronium cation. However, way is known for production of nitronium derivatives in anhydrous environments, such as acetyl nitrite, solution of benzoylnitrite in acetic anhydride,<sup>13</sup> as well as a solution of tetranitromethane in pyridine.<sup>14</sup>

Thus, the technology for producing of the rocket fuel oxidizer based on disuperoxide includes steps:

- Oxidation of rubidium with oxygen in the form of solution in liquid ammonia in the presence of a catalyst;
- Cryo-synthesis of rubidium disuperoxide in liquid ammonia in the presence of another catalyst;
- Substitution of rubidium cations with guanidine in disuperoxide;
- Distillation of ammonia, removal of rubidium chloride;
- Substitution of guanidine cations with nitronium cations in an anhydrous medium;
- Separation of guanidine nitrite and selection of the finished salt of nitronium disuperoxide.
- Regeneration of metallic rubidium from chloride (melt electrolysis).

All operations are carried out in devices carefully isolated from the environment in the absence of moisture.<sup>15</sup> Stainless steel equipment is platinum plated inside.<sup>16</sup> Production refers to explosive and chemically hazardous. Having 1 ton of rubidium, it is possible to produce about 300 tons of disuperoxide per year. The preliminary estimated prime cost of nitronium disuperoxide is about \$10,000 per ton.

## Summary

- Using oxidizing agents with a high Gibbs formation energy makes possible to increase rocket fuel specific impulse.
- High-energy oxidizing agents can be compounds of superoxides (super-peroxides).
- The specific impulse of disuperoxide with kerosene can be 3990 m/s.
- Ashless disuperoxides production in industrial quantities is technically possible.

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## Conflicts of interest

Authors declare that there is no conflict of interest.

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