Gas fuel combustion and related problems

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Abstract. Combustion, as it is well known, is based on chemical reactions. If we look at a clear scientific definition of the term “combustion”, then combustion will be a process of rapid high-temperature oxidation, combining physical and chemical phenomena. Combustion consists of a large number of elementary redox processes leading to the redistribution of valence electrons between atoms of interacting substances. Modern theories of combustion relate flame spreading in gases to chemical chain reactions[1]. Nowadays, in a view of the wide spread of gas, understanding of a ship fuel and analysis of gas related problems of combustion are more and more critical. Gas itself is not able to ignite in a combustion chamber as a conventional fuel just because of compression and temperature rising. It requires a strong and efficient source of fire. The article is focused on analyzing igniting, flame spreading and detonation in a combustion chamber. The detonation condition was assessed in case of using gas as ships fuel.

1. Introduction
Gaseous fuel, in particular, natural gas, has a number of advantages over liquid fuel. These are good anti-detonation qualities of gas fuels, favorable mixing conditions, wide ignition limits in mixtures with air. In terms of specific power and fuel economy, the best modern gas and gas-liquid engines are close to liquid-fuel ones, and in terms of exhaust toxicity, wear and tear, they have significant advantages over liquid ones [2].

The patterns of chemical reactions, including those underlying combustion processes, are determined primarily by the mechanism and laws of chemical kinetics. Reaction kinetics also determines the rate of heat release, non-thermal modes of the process, and also plays an important role in heat and mass transfer and in gas dynamics of the explosion. For a long time, combustion of gases was considered only as dependent on the chemical reaction. But recent research[3] shows that influence of chain reactions is much greater and, in some circumstances, it plays a key role. Thus, consideration of the tasks of ignition and combustion of the mixture of gas and air in the engine, as well as environmental problems, is impossible without considering both factors. The first is related to calculation of the chemical reaction rate either in macrokinetic approximation (global kinetics) or in microkinetic approximation (detailed kinetics) [4]. And the second is concerned with a thermodynamic calculation of the state of chemical equilibrium based on the law of the acting masses, when the external conditions (temperature or pressure) change. The equilibrium shifts in accordance with the Le Chatelier-Brown principle, where excessive masses are reflected in exceeding quantities of active centers of chain reactions. Consideration of a process based on chemical equilibrium is possible only in a quasi-stationary approximation (when there is enough time to establish equilibrium, that is, at sufficiently high temperatures). At the present stage of combustion science, more and more
researchers are using a microkinetic approach to describe chemical transformations (despite difficulties associated with a large number of kinetics equations and the absence of simplified kinetic schemes, as well as the lack of numerical values of some kinetic constants in the scientific literature). An important feature of the considered processes of ignition and combustion in limited volumes and combustion chambers of ICE is the principle multizones associated with the presence of concentration, pressure, and temperature gradients. The previous results of the study of the self-ignition in the front of the flame of a mixture in an enclosed vessel and the model of the process of self-ignition of the mixture during adiabatic compression are the basis for the development of modern mathematical models for calculating the delay in ignition of fuel in diesel engines and gas diesel engines.

2. Mechanics of combustion
Combustion is the basis of the working process of the engine. Figure 1 shows the indicator diagram and combustion characteristics of the engine.

At some point, close to the top dead center, the ignited small volume of the mixture initiates a combustion process that gradually spans over the entire charge of fuel. In the process of combustion, fuel supplied to the engine cylinder $Q_c$ is burned out during the cycle [5]. The curve of combustion $m_{comb} = \frac{Q_c}{Q_c} = f(\varphi)$ (where $\varphi$ - the engine crankshaft angle of rotation from the top dead center in degrees) reflects burning out of fuel in time. The part of the heat released during combustion is lost for heat transfer to the environment $q = \frac{Q_{loss}}{Q_c} = f(\varphi)$. The remaining part of the heat is spent on performing work by a working medium and on increasing its internal energy:

$$\zeta = \frac{\int_0^\varphi pdV + \Delta u_\varphi}{Q_i} = f(\varphi).$$

The curve $\zeta = f(\varphi)$ is a characteristic of active heat releasing. It shows a character of heat transfer to working medium in time. The part of the heat released until the end of the cycle ($\varphi_{m_{burnmax}}$ on the indicator diagram) its heat in the lip sum could be shown as:

$$Q_c = Q_{act} + Q_{cons\varphi} + Q_{unb}$$

or in relative units:

$$\zeta_{m_{burnmax}} + q_{loss} + \Delta m_{unb} = m_{burnmax} + \Delta m_{unb} = 1.$$
The characteristic of active heat release \( \zeta(\varphi) \) with a sufficient accuracy could be constructed directly on the indicator diagram. The quantity of unburnt fuel \( \Delta m_{\text{unb}} \) is determined experimentally by the composition of exhaust gases.

The determination of \( q_{\text{loss}} \) losses in the course of heat transfer to the environment during combustion is the most difficult task. Various empirical formulas have coefficients that can only be applied to engines which are very close in design and combustion process parameters to those for which these coefficients have been obtained. Let us note that for \( m_{\text{bur\_max}} \) the value of \( q_{\text{loss}} \) can be determined from the last expression, that is, from the data of the indicator diagram and the analysis of exhaust gases.

In the combustion process, individual phases or steps can be established:
- ignition of the primary source, which initiates the development of the combustion process;
- initial or inductive period, which corresponds to a section of the indicator diagram located between the moments \( u \) - the beginning of the injection of liquid fuel and \( c \) - separation of the combustion line from the compression line;
- combustion period. From the moment \( c \) to the end of burnout \( m_{\text{bur\_max}} \).

The period of combustion itself also has two stages: main or visible combustion – up to the moment corresponding to \( P_{\text{max}} \) or \( T_{\text{max}} \) and pre-combustion – from \( P_{\text{max}} \) or \( T_{\text{max}} \) to burnout \( m_{\text{bur\_max}} \).

Combustion in engines at all its stages is a complex of interacting physical and chemical processes. However, this complex is based on the chemical reaction between combustible and oxidizing agents. The main results of combustion as an exothermic chemical reaction are determined by simple thermochemical equations given above. According to these equations, the composition, volume and temperature of the final chemical conversion products, as well as the thermal effect of the reaction, can be determined.

However, these equations do not give an idea of the nature of the combustion process over time. These issues are addressed in chemical kinetics.

The onset of the chemical combustion reaction occurs in a very narrow layer of the medium that is directly adjacent to the heat source or front of the flame. In a sufficiently thin layer, which separates the burned and unburned parts of the substance, there is an active increase in temperature (from the temperature of the substance itself to the temperature of the flame). As the temperature of the substance layer increases, it burns, thus, increasing the temperature of the subsequent layer, and so on.

It is easy to understand that the more reliable and powerful the ignition source and the higher the rate of the combustion chain reaction, the more intense the heat generation and heating of subsequent layers of substance. Therefore, the flame spreading rate is higher.

In case of gas used as a fuel, the reaction is accompanied by rapid oxidation of simple combustible gases and pyrogenetic decomposition of complex gases. Pyrogenetic decomposition proceeds with the release of black carbon, as well as the formation of rapidly oxidizing low-molecular compounds. Black carbon in flame gives color to it and makes it luminous. Once the premixing of air with simple gases (CO, H\(_2\)) takes place, pyrogenetic decomposition is absent, and the mixture burns with a transparent flame. The presence of inert gases like N\(_2\) and CO\(_2\) in the mixture increases the ignition temperature, whereas oxygen decreases. Increasing the pressure, in its turn, decreases the temperature of combustion.

The temperature of combustion of gas mixtures can be approximately determined by the equation below:

\[
 t_{\text{ign}} \approx 0.01 \left( a t_a + b t_b + c t_c + \ldots \right)
\]

where \( a, b, c \) – combustible gas content, %;
\( t_a, t_b, t_c \) – ignition temperature of gases in mixture, °C.

3. Velocity of combustion

The linear velocity at which the flame front moves along the homogeneous combustible mixture is called the uniform velocity of flame spreading, depending on both the type of gas and its content in the
gas-air mixture [6]. The minimum speed for all types of flammable gases corresponds to the lower and upper ignition limits, whereas the maximum speed corresponds to the specific ratio of gases to air.

Figure 2 shows the curves of the uniform velocity of flame spreading $u_n$ defined in a pipe with a diameter of 25.4 mm for different gases[7].

As the comparative characteristic of the combustion properties of gases (regardless of the size of the tubes), the concept of "normal velocity of flame spreading" was introduced. This concept means the velocity related to the cold (not yet ignited) mixture at which the flame moves along the normal line to its surface. The flame front is assumed to be flat and equal to the tube diameter:

$$u_n = \frac{w_p \cdot \pi r^2}{S}$$

where:
- $u_n$ – normal velocity of flame spreading, m/s;
- $w_p$ – measured normal velocity of flame spreading, m/s;
- $r$ – tube radius, m;
- $S$ – surface area of the flame front, $m^2$.

As can be seen from Table 1, the maximum velocity of flame spreading corresponds to mixtures of gas and air with a lack of the oxidizer (not stoichiometric). In a condition of excessive fuel, the collision frequency and efficiency of the particles increased, causing increase of the chemical reaction rate.

It had been proved by series of experiments that the velocity of flame spreading depends on the diameter of the cylindrical tube through which it spreads: the larger the diameter, the higher the velocity of spreading. Accordingly, at some approximation, the combustion chamber of the engine can be considered as a variation of a large diameter tube. The increase in the tube diameter reduces the effect of the chamber walls on the combustion process, flame front movement and promotes increased convection (Figure 3) [7]. Graphic data analysis shows that at very small tube sizes, flame spreading becomes impossible (due to strong relative heat removal). The dimensions of tubes, channels and slots in which the flame does not spread are called critical. For different gases this dimension is different:
• cold mixture of methane and air – 3 mm;
• mixture of hydrogen and air – 0.9 mm;
• heated mixture of methane and air – 1.2 mm.

| Gas            | Stoichiometric mixture | Mixture with maximum velocity of flame spreading |
|----------------|------------------------|-----------------------------------------------|
|                | Content, vol. % | $v_{n\text{max}}$, m/s·10^{-3} | Content, vol. % | $v_{n\text{max}}$, m/s·10^{-3} |
|                | gas | air     |                                     | gas | air     |
| Hydrogen       | 29.5 | 70.5   | 1600–1800                           | 42–43 | 57–58   | 2650–2670 |
| Carbon oxide   | 29.5 | 70.5   | 280–300                             | 43–52.5 | 47.5–57 | 410–460 |
| Methane        | 9.5  | 90.5   | 280–370                             | 9.5–10.5 | 89.5–90.5 | 370–380 |
| Propane        | 4.03 | 95.97  | 406–408                             | 4.26  | 95.74   | 429–432 |
| Butane         | 3.14 | 96.86  | 340                                 | 3.3   | 96.7    | 370     |
| Acetylene      | 7.75 | 92.25  | 1000–1280                           | 10–10.7 | 89.3–90 | 1310–1570 |
| Ethylene/Ethane| 6.54 | 93.46  | 600–630                             | 7.0–74 | 92.6–93 | 630–810 |

Velocities of flame spreading for gas mixtures with oxygen are much higher than those for gas mixtures with air. The maximum normal flame propagation rate in the mixture of complex gas and air, m/s, is determined by the formula:

$$u_{n \text{max}} = \frac{r_1 u_1 + r_2 u_2 + \cdots + r_x u_x}{r_1 + r_2 + \cdots + r_x}$$

where:

$r_1, r_2, \ldots, r_x$ – content of individual components in the complex gas, vol\%;

$u_1, u_2, \ldots, u_x$ – maximum normal flame propagation rates of complex gas components in the mixture with air, m/s.

These ratios are suitable for gases having more or less equal normal velocities of flame spreading, such as natural and liquefied hydrocarbon gases. For gas mixtures having significantly different velocities (e.g. natural and artificial gas mixtures, high-hydrogen content mixtures), they give only approximate values.
If ballast impurities (nitrogen and carbon dioxide) are present in the mixture, they can be used in the formula below:

\[ u_{n} = u_{n\ max}(1 - 0.01N_{2} - 0.012CO_{2}) \]

The velocity of flame spreading significantly increases along with heating the gas-air mixture:

\[ u'_{n} = u_{n}\left(\frac{T'}{T}\right) \]

where

- \( u_{n} \) - velocity of flame spreading in the heated mixture with the absolute temperature \( T' \), K;
- \( u_{n} \) - velocity of flame spreading in the cold mixture with the temperature \( T \), K.

The preheating of the mixture changes its density inversely in proportion to the absolute temperature, so the velocity increases in proportion to this temperature. This fact must be taken into account in the calculations, especially when calculating engine forcing by increasing the compression ratio.

Uniformity of flame spreading is possible under the following conditions:

- the fire tube has a small length;
- combustion spreads at a constant pressure close to atmospheric pressure.

4. Detonation

If the length of the tube is significant or combustion occurs at high pressure, then uniform flame spreading for some mixtures can switch into vibrating combustion. Then, with a further increase in pressure, combustion can go into detonation, with a supersonic combustion rate (2000 m/s or more), when the ignition of the mixture occurs due to a shock wave, which heats the mixture to temperatures higher than the self-ignition temperature. Detonation occurs in mixtures having the high velocity of flame spreading. Detonation concentration limits are narrower than flammability limits of gas-air and gas-oxygen mixtures (propane - 3.2-37, i-butane - 2.8-31, hydrogen - 15-90, vol.%). The pressure generated by detonation combustion can exceed the initial pressure ten or more times. Such rapid increasing can lead to the destruction of pipes and other vessels designed for high pressures.

Considering the combustion of the fuel mixture in engines, the scheme of flame spreading over the volume of the cylinder should be analyzed. From the point of view of the organization of the working process in the internal combustion engine, the value of the normal combustion speed and its static characteristics play a significant role. The average combustion rate depends on the duration of the combustion process, the temperature and pressure of the cycle, and, accordingly, the effective performance of the engine. Random deviations from the average value determine inter-cycle non-identity, which limits the degree of depletion of the mixture. Moreover, depletion of the mixture is the way to increase the economy of the engine.

When the gaseous fuel is ignited, an explosion is possible under some conditions, especially when the combustible mixture of a certain composition is rapidly ignited in a small volume, which corresponds to the combustion chamber of the engine. The heat generated thereby is spent almost entirely for heating of combustion products. Rapid expansion of lasts causes compression of the surrounding layer. At a high ignition rate, compression does not have enough time to spread on entire volume and is localized. This again causes compression and expansion, so an explosive wave is formed and then propagating takes place at a speed of 2000-3000 m/s.

Thus, it is easy to understand that the combustion of the gas has explosive nature, so detonation can occur during combustion. The detonation process should be considered for better understanding how gas combustion can proceed within the combustion chamber of the engine.

Detonation, as a phenomenon, is possible with a combination of certain chemical and physical factors that occur in a combustible mixture. The expansion of the gases during combustion of the mixture leads to the formation of a shock wave spreading in the front of the flame. Compression of the gas and its heating in the shock wave are as stronger, as the speed of movement of the expanding gases greater, which in its turn depends on the rate of the combustion reaction. With rapid combustion, the heating of the mixture in the shock wave can become so strong that it ignites in the front of the flame.
In this case, a combustion mode is created in which the layer-by-layer ignition process is carried out not by thermal conductivity, but by a pressure pulse, in other words, by detonation. During detonation combustion, a complex of a shock wave and the next zone of a compressed and heated mixture is formed – the so-called detonation wave.

The results of the experiments of Professor of the USSR Academy of Sciences A. Sokolik, described in his book "Self-ignition, flame and detonation in gases" [8] show that on the forward edge of the flame front, under the influence of high temperature and compression, the molecules of the fuel mixture are oxidized with the formation of unstable peroxides.

After ignition of the fuel mixture, pressurized zones are formed on the forward edge of the flame front, which causes the still unburned mixture to compress even more. Accordingly, the rate of peroxide formation increases, and the presence of these compounds further increases the rate of the combustion reaction. Individual zones create the conditions necessary for detonation. As soon as zones with conditions satisfying the occurrence of detonation occupy a sufficiently large space to involve in process the entire volume of the working mixture, and the concentration of peroxides reaches some critical limit, unstable peroxides decay with instantaneous combustion of fuel and a rapid increase in pressure and temperature.

A rapid increase in the temperature during detonation causes dissociation of combustion products in separate zones of the combustion chamber with the release of black carbon and increased heat transfer to the chamber walls. Significant increasing in the pressure creates many times reflected high pressure waves, which under certain conditions can have a destructive effect on the design of the engine. The occurrence of detonation in the cylinder is always accompanied by a ringing sound.

Detonation could be prevented by dilution of the combustible mixture with an inert substance, which slows down the reaction rate. However, not all combustible mixtures are prone to detonation, and in some cases, there is no detonation at all. For example, a methane combustible mixture is difficult to detonate. Detonation is possible only if there is a strong local shock wave.

Thus, when it comes to the use of gases as fuel for ship ICE, the anti-detonation properties of engines increase significantly.

5. Results and Discussion
The current status of marine transportation and shipbuilding industry indicates a significant increase in a number of gas-fueled and dual-fuel engines onboard modern vessels and not only gas carriers, but also conventional tankers, ro-ro and ro-pax ferries, container ships and others. In certain cases some extra demands dictate the need to retrofit and upgrade conventional diesel engines (where applicable) for usage of gaseous fuels and sometimes changeover from one type of gas to another. Thus the importance of the analysis related to theoretical aspects, including fuel combustion features for such engines, is proven. As a result of the analysis performed, the following can be concluded:

- Analyzed experiments have proved that in gas systems the maximum velocity of flame spreading is achieved in a state approximately at the central point between the flammability limits. Lack of an oxidizing agent also accelerates the process.
- The engine combustion chamber was considered as a conventional large-diameter tube. The reviewed experiment shows that as the diameter of the chamber increases, the velocity of flame spreading increases.
- The detonation process related aspects were reviewed: possible conditions required for detonation initiation and further spreading within the combustion chamber. In this respect when using gas as a fuel gas-fueled engines may have relatively increased anti-detonation properties in maximum modes. This is due to the fact that vaporized or gas fuels are generally less susceptible to detonation.

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