The composition determination of combustion products of modified ethanol

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Abstract. The content of pyrolysis products during combustion of modified ethanol in the Rapid Compression Machine (RCM) was studied. It was found that significant reduction in the ignition delay time for lean reactive mixture ($\phi=0.6$) with a decrease in maximum pressure and unchanged mean rate of pressure. It indicates an increase in the burning rate of the mixture. It has been observed that the modification of ethanol with carbon nanoparticles leads to decrease in the content of methane and hydrogen in combustion products, but ignition delay time does not change (A1) or reduce by 35% (A2) at $\phi=1$.

1. Introduction
In heat engines, different combustion products are formed by combustion of a fuel with using air as an oxidant. More than 200 different chemical substances in their composition were determined [1]. The formation mechanisms of these substances are various and depend on a lot of factors [2]. Therefore, the determination of the interaction mechanisms of the initial fuel with the oxidizer in closed volumes and the formation of combustion products is a complex task.

In this paper, it presents a comparison of the products that are formed at the combustion of the original ethanol and ethanol, modified by ultradispersed carbon structures.

2. Methodology and experimental setup
Three fuel samples that were made of ethyl alcohol were used in this studying. The first is the original ethanol "Ethyl alcohol rectified "Lux" STB 1334 - 2003". The second and third fuel samples were obtained by the process presented in paper [3].

The plasma treatment of ethanol vapor in a helium flow and deposition of graphitization products on the surface of a nickel substrate were performed. The substrate with the deposited coating was input in ethanol and carried out electrolysis at controlled amperage. The graphitized particles were removed from the electrode surface and dispersed in ethanol. Electrolysis was carried out in both cases: fuel A1 – with positive electrode polarity and A2 – with negative.

Fuel samples A1 and A2 are colloidal solutions of nanosized carbon particles in ethanol [3]. The analysis of the resulting particles was made by a transmission electron microscope JEM100CX. It was observed that particles of both nanometer and micron sizes are formed during the synthesis. Holding the samples for seven weeks causes the aggregation and precipitation of the largest particles.
The current work has been performed in a rapid compression machine (Figure 1) used to study the ignition of reactive mixtures for a long period of time [4]. The main purpose of such a machine is to heat a test gas as quickly as possible to the ignition temperature. This is accomplished using a piston for rapid compression of an investigated mixture. The main elements of the machine are a piston and a compression cylinder with a test combustion chamber mounted at its end. A chamber depth in the final position can be adjusted with high precision – from 15 to 25 mm. The piston is driven via driving gas (compressed air). The chamber pressure is recorded using a high-temperature piezoelectric pressure transducer (Kistler 6031U18) connected to a charge amplifier (Kistler 5015A). To transmit radiation emission from the chamber volume, a double fiber-optic cable is used, which transmits an irradiation signal to two photomultiplier tubes (PMT). The emission of excited CH radicals (λ=431.5 nm) and the emission of a flame at combustion of ethanol are recorded using a PMT with a sensitivity of 300–600 nm. All signals are recorded using a multichannel memory oscilloscope. Fuel supply was carried out with the help of an injector, which is mounted in the end-wall of the combustion chamber. The test bench allows obtaining data necessary for verification of the kinetics of chemical reactions to occur at temperatures below 1100 K.

![Figure 1. Schematic view of the test bench based on the rapid compression machine.](image)

Tests of original fuel and modified samples were carried out under initial conditions (before compression): pressure – 12 kPa, temperature – 290 K. Compression ratio was 45:1. The liquid fuel and air were separately supplied into compression cylinder by system built in end-wall of combustion chamber. The error of the fuel system was not more than 7%. The system for preparing and supplying the fuel-air mixture provides the composition of the mixture with a stoichiometry coefficient of φ = 1 ± 0.1. The combustion completeness of reactive mixtures depends on the conditions of the combustion process [5]. Fuel combustion was carried out both with the stoichiometric ratio of ethanol and synthetic air (C₂H₅OH – 6.5%, O₂ – 19.5%, N₂ - 74%), and with an excess of oxidizer (φ = 0.6). The temperature at the end of the compression stroke reached 1130-1150 K, pressure 1.78-1.94 MPa. During each experiment, the pressure in the combustion chamber was recorded as a result of compression and ignition of the mixture.

Typical signals observed in experiments are shown in Figure 2.

The gas temperature was calculated by the measured pressure in the approximation of adiabatic compression, taking into account the polynomial dependence of the heat capacity on temperature.

The combustion chamber was equipped with an evacuated sampler built into the gas main to select combustion products for chromatographic analysis.
Figure 2. Typical pressure history (solid line), light emission (dotted line) and CH-radicals emission (dashed line) recorded at the ignition of the ethanol/air mixture

Agilent Technologies 7890A gas chromatography system was used for the analysis of gaseous products of pyrolysis of ethanol. It include a thermal conductivity detector, a heated tap with a metering loop, a pressure monitor at the entrance to the dosing loop. Molsieve 5A PLOT 25 × 0.53 (Part No. CP7538) chromatography column was used in order to separate the sample components. Prevention of contamination of the sample when entering the chromatograph was provided by means of an atmosphere isolation system.

3. Results and discussions
Content of only six components – hydrogen, argon, oxygen, nitrogen, methane and carbon monoxide (I) – has been determinated (in vol.%) from all the combustion products, that are formed during combustion processes of various fuels. Investigation of original and modified (A1) ethanol was carried out with stoichiometric fuel/air mixture – \( \phi =1 \) and lean – \( \phi =0.6 \). Tests were only performed with stoichiometric air/fuel mixture \( \phi =1 \) in the case of modified ethanol A2. All experiments with different compositions were carried out under similar conditions (temperature and pressure) in order to determine the reproducibility of the obtained data.

The chromatographic analysis results of synthetic air and combustion products for original and modified ethanol are given in the Table 1. The presented data illustrates that composition of used air mixture fully satisfies as an oxidizer.

| Nucleus            | \( \phi \) | \( \text{H}_2 \) | \( \text{Ar} \) | \( \text{O}_2 \) | \( \text{N}_2 \) | \( \text{CH}_4 \) | \( \text{CO} \) |
|--------------------|------------|----------------|----------------|----------------|----------------|---------------|-------------|
| Air                | –          | absent         | 0.972          | 20.849         | 79.854         | absent        | absent      |
| Original ethanol   | 1          | 2.554          | 1.081          | 1.171          | 77.732         | 0.101         | undefined   |
| A1                 | 1          | 1.838          | 1.137          | 1.185          | 79.254         | 0.067         | undefined   |
| A2(1)              | 1          | 1.961          | 1.110          | 1.239          | 77.655         | 0.076         | 6.225       |
| A2(2)              | 1          | 1.742          | 1.074          | 1.074          | 77.238         | 0.083         | 5.711       |
| Original ethanol   | 0.6        | absent         | 1.312          | 9.047          | 82.046         | undefined    | 0.059       |
| A1                 | 0.6        | absent         | 2.932          | 9.986          | 81.776         | undefined    | 0.041       |
Combustion of unmodified ethyl alcohol at $\varphi=0.6$ (lean mixture) leads to the absence of hydrogen and methane in combustion products as opposed to the case with using stoichiometric composition of fuel and oxidizer. It was found decrease of the hydrogen and methane concentrations in combustion products of modified sample A1 ($\varphi=1$) in comparison with the results of original ethanol under similar conditions. An increase in the amount of oxidizer to the value $\varphi=0.6$ results in the absence of hydrogen and methane in the products of combustion.

It is observed decrease of hydrogen and methane concentrations in the experiment with modified ethyl alcohol A2 by comparison with unmodified alcohol. A repetition of test under similar conditions (experiment A2(2)) demonstrates results reproducibility.

The results of measuring the autoignition and combustion parameters of fuel samples are represented in the Table 2. The ignition delay time was estimated by three criteria: $\tau_P$ – pressure change, $\tau_{CH}$ and $\tau_L$ – the increase in the $CH$-radicals emission and visible light; in the combustion chamber of the RCM.

The data given are mean values for several measurements ($n\leq5$). The values of the relative standard deviation of the measurement results are given in the Table 3.

The obtained data shows that ignition delay time for the stoichiometric mixture (unmodified ethanol and synthetic air) is from 1.12 ms to 1.80 ms depending on the using criterion, the maximum pressure is 2.99 MPa, and the mean rate of increase in pressure is 1283 MPa/s. Negative values of the autoignition delay are related to the ignition of the test mixture during compression stroke before reaching the specified parameters at top dead centre.

### Table 2. The ignition experiment results of fuel samples.

| Sample   | Conditions at the end of compression | Ignition delay time, ms | Maximum pressure, MPa | Mean rate of pressure, MPa/s |
|----------|--------------------------------------|-------------------------|------------------------|-------------------------------|
|          | $P$, MPa | $T$, K | $\tau_P$ | $\tau_{CH}$ | $\tau_L$ |                             |                             |
| Original ethanol | 1       | 1.849 | 1142 | 1.80 | 1.75 | 1.12 | 2.99 | 1283 |
| Original ethanol | 1.7   | 1.91  | 1150 | 0.54 | -0.37 | -0.19 | 2.24 | 1217 |
| A1       | 1.0     | 1.93  | 1142 | 1.87 | 1.87 | 1.48 | 3.09 | 1548 |
| A1       | 1.7     | 1.83  | 1140 | 0.95 | 1.02 | 0.69 | 2.36 | 1453 |
| A2       | 1       | 1.87  | 1146 | 1.18 | 1.18 | 1.17 | 3.02 | 1621 |

### Table 3. The relative standard deviation of the measurement results (%) at $\varphi=1$.

| Sample   | Conditions at the end of compression | Ignition delay time, ms | Maximum pressure, MPa | Mean rate of pressure, MPa/s |
|----------|--------------------------------------|-------------------------|------------------------|-------------------------------|
|          | $P$, MPa | $T$, K | $\tau_P$ | $\tau_{CH}$ | $\tau_L$ |                             |                             |
| Original ethanol | 3.4 | 0.8 | 39.5 | 54.5 | 83.9 | 5.2 | 22.3 |
| A1       | 3.6     | 0.9  | 30.6 | 24.1 | 49.5 | 2.9 | 13.1 |
| A2       | 2.2     | 0.6  | 60.0 | 4.7  | 7.2  | 12.2 | 11.5 |

It could be marked from comparing parameters that define the autoignition process of modified and unmodified samples of ethyl alcohol:
- A significant reduction of the ignition delay time for experiments with unmodified ethanol at $\phi = 0.6$, with decreasing of maximum pressure by 25% and the mean rate of pressure by 5%;
- The close values of the results for sample A1 and original ethanol at $\phi = 1$, the increase in oxidizer quantity to $\phi = 0.6$ approximately halves the ignition delay time, the maximum pressure decreases by 24% and the mean rate of pressure – by about 6%;
- Ignition delay time for sample A2 at $\phi = 1$ is less by 35% than for sample A1 and unmodified ethanol, the maximum pressure increase is comparable, and the mean rate of pressure increase in comparison with the original ethanol and sample A1

4. Conclusions

It can be concluded on the basis of the data obtained, that modification of ethyl alcohol by carbon nanoparticles results in a decrease in methane and hydrogen content in combustion products, while ignition delay time at $\phi = 1$ does not change (A1) or decreases by 35% (A2) at constant maximum pressure and increase in mean rate of pressure. The increase in oxidizer in mixture to $\phi = 0.6$ leads to a significant reduction in ignition delay time with a decrease in the value of maximum pressure and unchanged mean rate of pressure. It indicates a rise of flame speed in mixture. This can be explained by assuming a change in the heat capacity and thermal conductivity of the fuels produced. It is known that one of the basic requirements for fuels is that the components that are presented in fuel must have a good cooling capacity. In this case, the fuel should also have a sufficiently high heat capacity, thermal conductivity and high latent heat of evaporation [6]. Assuming that oxidation processes and pyrolysis of fuel proceed simultaneously and also hydrogen and methane are formed as a result of pyrolysis it can be concluded modified ethanol has more resistance to temperature loads (less pyrolyzed). Perhaps, it is due to the higher heat capacity and thermal conductivity of the sample because of the presence of carbon nanoparticles in the fuel. The higher resistance of the fuel to pyrolysis reduces the processes of carbon formation and reduces the content of toxic substances (soot, polycyclic aromatic hydrocarbons etc.) in combustion products and it leads to a reduction in their emissions into the environment.

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