Calculation of the process of nitrogen oxides formation during combustion of methanol in the engine

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Abstract. The developed method is based on a two-zone model and allows calculating the pressure and temperature (fresh mixture and combustion products), cycle indicators, as well as the current concentration of nitrogen oxides (NO) in the combustion chamber as a function of the crank angle. It can be used to evaluate the influence of parameters such as the beginning and duration of combustion, the composition of the mixture, heat loss from the gas to the walls, compression ratio, etc. on indicator indicators and output. In this model, the cylinder charge during combustion is divided into two zones: the zone of unburned mixture and the zone of combustion products. It is assumed that the fuel-air (unburned) mixture before and during the combustion process is homogeneous. The zone of combustion products at each moment of the cycle has a uniform composition and temperature. The combustion process is calculated according to the specified fuel burnout law, taking into account the dissociation of the combustion products. The equilibrium concentrations of individual combustion products necessary to account for dissociation (CO and H₂) and the formation of NO (O₂, H₂, O) are determined by approximating polynomials.

Methanol (CH₃OH) under normal conditions is a colorless, easily evaporating flammable liquid with a characteristic alcoholic smell. In nature, it is practically not found in the free state, but many of its derivatives are found in a number of vegetable oils, esters, natural dyes, and alkaloids. The physical characteristics of methanol are as follows: density 810 kg/m³; viscosity 0.793 MPa; boiling point 337.65, solidification 175.3, ignition 286, flash 201, self-ignition 737 K; concentration limits of explosion of vapors with air — lower 6.0, upper 34.7 (% by volume) [1-7].

The triple point of methanol is characterized by a temperature of 175.3 K, vapor pressure of 0.1887 Pa, critical state parameters T_c=512.65 K, p_c=8.103 MPa, ρ_c=274.73 kg/m³. Methanol mixes with water and other organic compounds in any ratio, but has poor solubility in hydrocarbons, absorbs water vapor, carbon dioxide, and a number of other substances well, so storage of anhydrous methanol is difficult.

The high solubility of gases in methanol is widely used in industry, using it as an absorber. This property also contributes to the saturation of methanol with combustible gases CH₄, C₂H₆, H₂ in binary fuel systems to increase the energy density of gas fuels [8-16]. Methanol combines the properties of a very weak base and an even weaker acid, due to the presence of alkyl and hydroxyl groups, acts aggressively on many products made of rubber and other elastomers, and corrodes non-ferrous metals (copper, zinc, aluminum). Methanol is a highly toxic substance, the maximum permissible concentration of it in the working area is 5 mg/m³, and the maximum permissible concentration of gasoline vapors varies depending on its composition and is on average 100 mg/m³. Methanol in contact with soil or water is
easily dissolved, well-purified biologically [17-21].

Interest in industrial raw methanol, which contains mainly methanol and water, is due to the possibility of using it for fuel purposes without prior rectification, which is economically feasible. According to their properties, water-methanol solutions differ significantly from anhydrous methanol. As the water content of methanol increases, the solidification temperature decreases. The density of solutions increases with a decrease in temperature and decreases with an increase in the concentration of $CH_3OH$ [22-27].

The law of fuel combustion is defined by the equation:

$$x = 0.5 \cdot (1 - \cos \frac{\phi_0 - \phi_z}{\phi_z}),$$

(1)

where $\phi_0$, $\phi_z$, $\phi$ – the angle of combustion start, the angle of visible combustion duration, and the current value of the crank angle, respectively.

To calculate the pressure and temperature we use a system of four equations:

$$Q = \Delta U + L_s,$$

(2)

$$pV = 8.314MT,$$

(3)

$$Mmc_{pm}T = M_mmc_{pm}T_m + M_mmc_{pm}T_r,$$

(4)

$$T_m = T_s \left( \frac{D_m}{D_s} \right)^{k-1}.$$

(5)

Amount of heat

$$Q = (Q_s \cdot B_c \cdot x - Q_d)\psi,$$

(6)

where $B_d$ – amount of methanol;

$\psi$- coefficient of heat loss as a result of heat exchange.

Change in internal energy

$$\Delta U = U - U_s, U = Mmc_{vm}T, V_s = M_mmc_{vm}T_s,$$

where $U$, $U_s$ – internal energy of the gas;

$M, M_m$ – the charge of the cylinder;

$mcc_{vm}$ - average molar heat capacity of the charge during combustion and fresh mixture;

$T, T_s$ – the temperature in the cylinder.

The heat capacity of fresh mixture:

$$mc_{vm} = r_a mc_{vm}^a + r_t mc_{vm}^t + r_f mc_{vm}^f,$$

where $r_a$, $r_t$, $r_f$ – the relative volume content of air, residual gases and fuel vapors, respectively:

$$r_a = \frac{\alpha M_o}{(\alpha M_o + \frac{1}{m_i})(1 + \gamma)}, \quad r_t = \frac{\gamma}{1 + \gamma}, \quad r_f = \frac{1}{m_i(\alpha M_o + \frac{1}{m_i})(1 + \gamma)},$$

where $mc_{vm}^a$, $mc_{vm}^t$, $mc_{vm}^f$ – average molar heat capacities of air, residual gases and fuel vapors.

Average molar heat capacity of air and $CH_3OH$:

$$mc_{vm}^a = 19.8 + 209.3 \cdot 10^{-5}T, \quad mc_{vm}^t = 21.15 + 7.09 \cdot 10^{-2}T.$$

The average molar heat capacity of residual gases is found by approximating polynomials [28-35].
Express \( mc_{ym}^\gamma \cdot T_s \) in terms of enthalpy:

\[
mc_{ym}^\gamma \cdot T_s = mc_{pm}^\gamma \cdot T_s - 8.314T_s',
\]

where \( mc_{pm}^\gamma \cdot T_s = H_i^\gamma \) – enthalpy of gases.

The internal energy of the gas

\[
U_s = M_m \left( r_m mc_{vm}^\alpha + r_t mc_{vm}^\gamma \right) T_s + r_t H_i^\gamma - 8.314T_s' \right].
\] (7)

The amount of gas in the cylinder during combustion is determined from the expression \[36-43\]

\[
M = M_m \left[ 1 + x (\frac{\beta - 1}{\beta}) \right].
\]

The internal energy \( U \) is found similarly to \( U_s \), using expressions for the enthalpy of residual gases \( H_i^\gamma \) and combustion products \( H_i^{r} \). The final expression for \( U \) has the form

\[
U = M \left( 1 - x \right) \left( r_m mc_{vm}^\alpha + r_t mc_{vm}^\gamma \right) T + r_t H_i^\gamma - 8.314 \right] + M \left( H_i^{r} - 8.314T \right).
\] (8)

The value \( H_i^{r} \) is set by the approximating equation depending on \( T, \alpha, p \).

The work performed by the gas at this point in the cycle is determined by the equation

\[
L = L_4 + 0.5( p_t + \Delta p ) \Delta V,
\]

where \( p_t, p \) – gas pressure at the beginning and end of the calculation interval;

\( \Delta V \) – change in volume during the interval under consideration \( \Delta V = V - V_t \).

The gas parameters \( p_t, V_t, T_i \) are known at the beginning of each calculation step. The pressure at the end of the calculated interval \( p \) can be determined by the equation of state. Then

\[
L = L_4 + 0.5 p_t \Delta V + 4.15M T \frac{\Delta V}{V}.
\] (9)

Substituting the values of \( Q, U_s, U \) and \( L \) found in equations (6) – (9) into equation (2) allows us to bring it, after appropriate transformations, to a square equation with respect to the average temperature of the gas in the cylinder, which is then determined in the usual way \[44-52\].

After calculating \( T \), you can determine the current value in the cylinder according to equation (3) and the temperature of the mixture according to equation (5). The temperature in the zone of combustion products of \( T_r \) is obtained using the original equation (4):

\[
mc_{pm}^r T_r = \frac{1}{M_r} \left( Mmc_{pm}^r T - M_m mc_{pm}^m T_m \right).
\]

Replacing the value \( mc_{pm}^r T_r \) with the enthalpy of combustion products determined by the approximating polynomial in the function of \( T, \alpha, p \) (for the temperature range of 1700-3300 K), we obtain:

\[
M_r \cdot H_i^r - Mmc_{pm}^r T + M_m mc_{pm}^m = 0.
\]

Substituting a second-order approximating polynomial instead, after the corresponding transformations, we get a square equation with respect to the \( T_r \), which is solved in the usual way \[53-60\].

Cycle indicators are calculated using the value of the cycle indicator equal to

\[
L_i = L_r + L_p - L_c,
\]
where $L_n$, $L_p$, $L_{c}$—the work of combustion, expansion and compression, respectively.

To calculate the process of NO formation during combustion, we use the values of temperatures in the zone of combustion products and assume that the formation of NO occurs by two chain reactions and one reaction of a bimolecular mechanism, with the chain mechanism being the determining one. The calculation of NO formation was performed using the equation [61-64]

$$
\frac{dr_{NO}}{dp} = \frac{p r_{N_2}}{249.4 n T_r} \left(1 - \frac{r_{NO}^2}{k_{in}^{c} \cdot r_{O} \cdot r_{N_2}} \right) \left(1 + \frac{k_{ip}^{c} \cdot r_{NO}}{k_{2n}^{c} \cdot r_{O}} \right),
$$

where $r_{N_2}$, $r_{O}$, $r_{NO}$ — concentrations of combustion product components determined by equilibrium conditions;

$k_{in}^{c}$, $k_{ip}^{c}$, $k_{2n}^{c}$ - reaction rate constants.

The calculation is performed using the Euler - Cauchy numerical integration method. Concentration $NO$ the zone of combustion products at the end of the calculated section with iterations at each step

$$
r_{NO} = \left( r_{NO} \right) + \Delta r_{NO}.
$$

Verification of the adequacy of the model of NO formation based on experimental data was performed by comparing diagrams of gas pressure in the cylinder, the formation of nitrogen oxides and their integral emissions. As an experimental pressure diagram, we used the average diagram obtained from numerous consecutive cycles. The formation of nitrogen oxides in the combustion chamber as a function of the crank angle was studied experimentally using stroboscopic gas sampling by gas sampling valves [65-69].

Comparison of experimental and calculated results showed good adequacy of the model. Additionally, the model adequacy was checked for the case of using methanol for integral NO emissions depending on the excess air coefficient during combustion, which confirmed the good adequacy of the model.

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