Simple Mathematical Model for the Numerical Simulation of Formaldehyde and Acetaldehyde Formed in the Exhaust of a Combustion Engine Operating with Ethanol as Fuel

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Abstract

The following work presents the numerical simulation of the main aldehydes present in the exhaust of a 4-stroke internal combustion engine, which uses ethanol as fuel, varying the rotation speed from 2000 to 5000 rpm. The simulation consists of a first part made in a software specialized in engines where properties and initial concentrations are calculated that serve as input data to the mathematical model that calculates the concentration of formaldehyde and acetaldehyde, as well as their producers: ethane, methane and unburned ethanol in the exhaust duct. The simulation shows concordance in the trend of the substances analyzed with the data found in the literature. The formaldehyde and acetaldehyde concentrations calculated by the model are similar to those found in the literature, however, the concentration of unburned ethanol and, therefore, total acetaldehyde in the exhaust are lower than those reported by the different authors.

Keywords: Aldehydes emissions, Ethanol, Mathematical model, Internal Combustion Engine
1 Introduction

An alternative fuel must offer superior environmental benefits, financial competitiveness, enough production to supply a high energy demand, and provide a net energy gain over the total energy used in its production [1]. Ethanol is considered one of the most attractive biofuels for use in spark ignition engines, becoming a potentially sustainable resource that offers long-term environmental and economic advantages as opposed to fossil fuels. For this reason, the increase in the concentration of ethanol in fossil fuels is expected in the coming years, making necessary the study of the environmental impact of its use in combustion engines [2, 3].

The emissions of aldehydes are greater for the ethanol fuel due to the presence of the hydroxyl functional group (OH), absent in gasoline [4]. Among the various types of existing aldehydes, only those found in the gaseous state are considered contaminants in internal combustion engines: formaldehyde (CH₂O) and acetaldehyde (C₂H₄O) [5, 6].

Detailed kinetic models of ethanol combustion have been developed by several authors [7, 8, 9, 10, 11 and 12]. These models describe the simulation mechanisms of chemical reactions within reactors used for the study of combustion, including species concentration and flame behavior studies. However, they present a great chemical complexity, several hundred reactions being necessary to obtain the results.

On the other hand, Costa [13] presents a simplified modeling of the chemical kinetics of aldehyde formation in internal combustion engines powered by hydrated ethanol or gasoline-ethanol mixtures. The work describes a model of formaldehyde and acetaldehyde formation in the depletion from the oxidation of methane and ethane, formed as intermediates of ethanol combustion. The model of chemical kinetics developed by Costa [13] was taken as the basis in this work for the development of a model of numerical simulation of the emissions of formaldehyde and acetaldehyde by a motor with spark ignition supplied with ethanol.

2 Mathematical and Numerical Modeling

The simulation starts with a numerical modeling in software specialized in T engines, where the combustion of a 4-stroke spark ignition engine is simulated, operating with ethanol. The data of temperatures, pressures and concentrations, obtained from this simulation, serve as input data for the subsequent numerical modeling performed in the FORTRAN language. The differential equations of the reactions inside the cylinder and in the exhaust pipe are integrated as a function of time, obtaining algebraic expressions for the concentrations of formaldehyde, acetaldehyde and the corresponding formers of these substances at the sampling point.
The model was tested at rotation speeds of: 2000, 3000, 4000 and 5000 rpm; Number of simulation cycles: 50; Diameter x course (mm): 72 x 84; Compression ratio: 10.35: 1; Air / fuel ratio: 12; Fuel: ethanol. From this simulation, temperature, pressure, oxygen concentration and unburned ethanol concentrations were obtained inside the cylinder and in the extraction pipe.

**Aldehydes Formation Model**

The model used in the calculation of concentrations of aldehydes assumes the following considerations:

a) Aldehydes are compounds formed during the post-flame oxidation of the unburned fuel (formed mainly through the openings between the piston-cylinder-segment rings and the process of absorption/desorption of fuel in the lubricating oil film), which starts in the combustion chamber and propagates in the extraction pipe.

b) The post-flame oxidation process of unburned ethanol (C$_2$H$_5$OH) is the main acetaldehyde former. The acetaldehyde emitted in the exhaust is also formed in the intermediate phase of the post-flame oxidation of the unburned fuel ethanol in the combustion chamber and, mainly, in the exhaust pipe.

c) Formaldehyde and acetaldehyde are also formed when the oxidation of methane (CH$_4$) and ethane (C$_2$H$_6$), which originate during the decomposition process of alcohol fuels or unburned hydrocarbons, is interrupted in the intermediate phase of the chemical reaction. The interruption occurs mainly due to the reduction of temperature and the concentration of oxygen.

d) The first product of the methane oxidation reaction is methanol, which is oxidized to formaldehyde immediately in the presence of remaining oxygen.

e) Ethane is a hydrocarbon generated mainly during the post-flame oxidation process of unburned hydrocarbon fuel. The oxidation of ethane will produce acetaldehyde.

f) The aldehydes formed in the intermediate stages of the combustion process are consumed immediately by the flame front due to the high temperature in that region inside the combustion chamber.

g) For the modeling of the concentration of aldehydes released into the atmosphere through the exhaust pipe of the engine, the oxidation reactions of their main producers are considered separately. The final concentration is the sum of the plots produced in each reaction.

h) The calculation of aldehydes is made from the moment of the opening of the extraction valve to the sampling point in the exhaust pipe. The calculation of unburned ethanol, ethane and methane inside the cylinder is made from the moment of opening of the extraction valve until the end of the extraction process.

i) The concentrations of aldehydes and their formers were calculated from the simulated mean concentrations from the start of the exhaust pipe to the sampling point.

j) The modeling was carried out by varying the engine rotation speed from 2000 rpm to 5000 rpm with the input data obtained from a previous simulation in the software specialized in engines.
The calculation of the ethane concentration is made from the concentration of unburned ethanol at the end of combustion. The set of equations representing the chemical process of conversion of ethanol to ethane is presented by Marinov [7]. To determine the rate of methane formation from the decomposition of ethanol in its radicals CH•3 and • CH2OH, it is necessary to establish the equilibrium constant of the oxidation reaction.

Marinov’s experimental study [7] determined that the reactions represented by equations (1) and (2) are first-order reactions. The reaction rate of CH3 and C2H6 by the oxidation of ethanol is expressed in equations (3) and (4):

\[ C_2H_5OH \rightarrow^* CH_3 +^*CH_2OH \]  \hspace{1cm} (1)

\[ 2^*CH_3 \rightarrow C_2H_6 \] \hspace{1cm} (2)

\[ \frac{d[CH_3]}{dt} = k_1 [C_2H_5OH] \] \hspace{1cm} (3)

\[ \frac{d[C_2H_6]}{dt} = k_2 [CH_3]^2 \] \hspace{1cm} (4)

The constants were obtained from Marinov’s work [7] following the Arrhenius expression, as shown in equations (5) and (6):

\[ k_1 = 5.94 \times 10^{-23} \cdot T^{-1.68} \cdot \exp\left(-\frac{45880}{T}\right) \] \hspace{1cm} (5)

\[ k_2 = 9.22 \times 10^{16} \cdot T^{-1.177} \cdot \exp\left(-\frac{636}{T}\right) \] \hspace{1cm} (6)

Substituting and considering the initial value of C2H6 equal to zero, equation (7) is obtained:

\[ [C_2H_6] = \frac{k_2 \cdot (k_1 \cdot [C_2H_5OH])^2 \cdot t^3}{3} \] \hspace{1cm} (7)

The values used in the calculation are the average concentration of unburned ethanol, as well as the average temperature during the exhaust process. The units of the reaction rate constant are given in \( (s^{-1}) \), and the time evaluated is that corresponding to the escape process. Integrating and replacing the concentration of C2H6 can be written as follows:
Simple mathematical model for the numerical simulation

\[
[C_2H_4] = \frac{5.94 \cdot 10^{23} \cdot T^{-1.68} \cdot \exp\left(-\frac{45880}{T}\right) \cdot \left(9.22 \cdot 10^{16} \cdot T^{-1.77} \cdot \exp\left(-\frac{636}{T}\right) \cdot [C_2H_5OH]\right)^2}{3} \cdot 1^3
\]  
(8)

Equation (8) represents mathematical modeling to determine the concentration (molar fraction) of ethane produced in the cylinder and in the exposure conduit as a function of exposure time, temperature and ethanol concentrations present. The results of ethanol methane formation modeling, methane formaldehyde, ethane acetaldehyde, ethanol acetaldehyde and consumption of unburned ethanol were performed following the same procedure.

3 Results

Figure 1 presents the graphs corresponding to the simulated engine responses in the software specialized in engines for temperature, pressure, ethanol and oxygen concentration, respectively. These responses are a function of the angle of the crank simulating an engine cycle. The figure shows a pronounced increase in temperature and pressure during combustion. Figure 1 indicates that the concentration of ethanol after combustion is zero. The software assumes that combustion is complete, which is incongruent with actual combustion, where unburned fuel remains in the gases within the Heywood combustion chamber [15].

Figure 2 shows the concentrations of formaldehyde and acetaldehyde, as well as those of their producers, methane, ethane and unburned ethanol (in exhaust). The model was made considering percentages of 3%, 5% and 7% of unburned fuel (UBE) inside the chamber at the end of the combustion, as the initial concentration value of ethanol. The concentration of acetaldehyde observed in the figure corresponds to the sum of the plots formed by the oxidation of ethanol and ethane. The trends presented for the three concentrations of unburned fuel (3, 5 and 7%) are of concentration increase for all substances with the increase of the engine’s speed of rotation, up to 4000 rpm. In the case of acetaldehyde, the concentration tends to decrease above this speed, while the concentrations of methane, ethane and formaldehyde increase. It is observed that, by increasing the concentration of unburned ethanol inside the cylinder, the concentrations of the simulated substances increase, maintaining a similar trend for all conditions.
In Figure 3 the trend presented is similar to that of the total acetaldehyde observed in Figure 2, which is the increase with the speed of rotation of the engine. However, the calculated concentration is much lower than expected. The concentration of acetaldehyde formed from the oxidation of ethane, as well as in total acetaldehyde, increased with the increase in the concentration of unburned ethanol.

The results of the trends for formaldehyde and acetaldehyde are in agreement with the work of Pang et. Alabama. [15] and Song et. Alabama. [16] that associate the increase in speed and rotation with the increase in the concentration of these pollutants. The work of He et.al. [17] shows that with the increase in the concentration of ethanol in the mixture with gasoline the increase in the concentration of acetaldehyde is higher.

Figure 3 shows that the simulated acetaldehyde concentrations are higher than those of formaldehyde when ethanol is used as fuel, a result similar to that found by Amaral and Sodré [18]. Analogous results were found by He et. to the. [19], Pang et. to the. [15], Song et. to the. [16], Magnusson et. to the. [20], Hasan et. al. to the [21] for mixtures of gasoline, diesel and biodiesel with ethanol.
Figure 2. Concentration of acetaldehyde, formaldehyde, methane, ethane and unburned ethanol in the exhaust Vs. Engine rotation speed (For 3%, 5% and 7% of unburned ethanol in the cylinder).

Figure 3. Concentration of total acetaldehyde and unburned ethanol in the exhaust pipe vs engine rotation speed (For 3%, 5% and 7% of unburned ethanol in the cylinder).
4 Conclusions

There is specialized software in the market in engines that allow us to calculate various variables during the combustion processes for different fuels. However, the emissions that are evaluated by these do not include aldehydes that exist in important concentrations, mainly in alcohol fuels. In this way it was possible to complement the simulation of the specialized software with a mathematical model developed in the FORTRAN software through which it was possible to calculate formaldehyde, acetaldehyde and its formers in the exhaust duct. The simulation showed that the trend for all the analyzed substances was increasing with the increase of engine revolutions, as found in the related studies. Likewise, the concentration of formaldehyde, acetaldehyde, ethane and methane increases with the concentration of unburned ethanol remaining in the combustion chamber, confirming the direct relationship between these substances. The concentrations of formaldehyde and acetaldehyde calculated by the model show concordance with the values found in the literature. The calculated concentrations of unburned ethanol are lower than those observed in the different studies. In the same way, the calculated total acetaldehyde was lower than that found in the literature. It is necessary to make adjustments in this last calculation so that the model can offer a more precise calculation of these two substances.

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