# Kinetics of ion formation in gasoline flames of internal combustion engines - numerical investigation

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### **1. Introduction**

Electrical probes are used for diagnostics of combustion processes in internal combustion engines (ICE). A wider application of these diagnostic techniques depends on an understanding of ionization processes in the gasoline flames [1]. The plasma kinetics during combustion of gasoline in ICE will be studied here.

# 2. Model

A modified kinetic mechanism of combustion in n-heptane/isooctane/air mixture is proposed, based on the model [2], reactions with nitrogen participation [3] and chemi-ionization mechanism [4]. The modified estimation procedure was proposed for the rate constants, for which only high temperature values are known and their low temperature estimations have shown unusual behavior. The correction technique was described in [5].

The mechanism consisting of 1078 chemical components and 4393 elementary reactions was verified using experimental data [6,7] on induction time – see Fig. 1. The agreement between simulation results and experimental data seems rather good.



Figure 1. Dependence of induction time in a stoichiometric isooctane/oxygen mixture diluted by 70% of argon at 2.1 bar on the initial temperature. Points – experimental data, curve – numerical results.

In the new plasma-kinetic model several chemi-ionization mechanisms were considered. The best known chemi-ionization reaction was proposed by Calcote in 1957 [8]:

$$CH + O = HCO^+ + e^-$$

The role of this reaction has been confirmed by a good correlation between substrates (CH and O) and charged particle concentrations in a flame front. Several other evidences proving its role have been listed by Fialkov [9].

The second important chemi-ionization process was discussed by Newstab [10]:

$$CH^* + C_2H_2 = C_3H_3^+ + e^-$$
.

In contrast to  $CHO^+$ ,  $C_3H_3^+$  is a more permanent ion; it can be traced among the most prevalent ions in a flame front.



Figure 2. Time evolution of ion concentration in gasoline flame under conditions of internal combustion engines.

Still another reaction takes into account the acceleration of ionization process due to CH radical excitation [9,11]

 $CH* + O = HCO^+ + e^-$ .

There is also at least one ionization channel that appears during soot formation. However, the conditions leading to soot formation are far from those typical for ICE operation. Therefore we do not take this channel into account.

Besides primary ionization we also took into account the following types of reactions: associative and dissociative recombination, electron attachment and detachment, charge transfer reactions, two- and three particle ion-molecular and ion-ion reactions – for detailed description see [4].

The thermodynamic database, which accompanies developed kinetic mechanism, contains temperature dependent data related to specific heat capacity, standard enthalpy of formation and entropy for all species involved; at least for some ions these could not be found in literature. In order to estimate the data and their dependence on temperature a special technique related to the expert approach was developed. It is based on an adoption in such case of the data, like ionization energy in the case of negative ions and electron affinity for positive ions, related to similar known particles [5].

### **3. Results and discussion**

The simulation of plasma kinetics during combustion of gasoline in an internal combustion engine (ICE) were performed for a isooctane/n-heptane/air mixture, which correspond to the A-92 gasoline widely used for automobile engines in Belarus.

### 3.1. Ionization in constant volume reactor

The initial conditions for combustion in ICE are assumed to be as follows: temperature T = 600 K, pressure p = 25 atm. The approximation of 0D adiabatic reactor of constant volume was used.

The spatial distribution of gas temperature and main ion mole fractions are shown in Fig. 2 for different equivalence ratios of gasoline/air mixture. The time t = 0 is assumed to be the point of ignition, when concentration of CH radical reaches its maximum. This is an accurate enough estimation of ignition point since CH concentration peaks at the time when rapid increase of temperature is observed under all considered conditions. Fig. 3 shows concentration of ions and electrons at mixture ignition point as a function of its equivalence ratio  $\varphi$ .



Fig.3. Concentrations of ions and electrons at the ignition point (t = 0)

It can be seen that for lean and stoichiometric mixtures the dominating positive ions in a flame front are  $CH_3CO^+$  and  $H_3O^+$ , while  $C_3H_3^+$  and  $CH_3CO^+$  ions prevail in rich mixtures (for equivalence

ratio larger than  $\alpha > 1.1$ ). The  $C_3H_3^+$  ion dominates plasma for very rich mixtures, where  $C_2H_2$  concentration is higher than [O] concentration ( $\alpha > 1.3$ ). The  $H_3O^+$  ion become the major one, very close behind the flame front at least for all the mixtures under consideration. These results resemble the plasma in methane flames [12]. The role of NO<sup>+</sup> ion becomes important in the lean and stochiometric mixtures but further behind the flame front (0.3 ms after ignition and later).

Among the negative ions,  $HCO_3^-$  predominates in the flame front (its concentration exceeds  $1 \cdot 10^{-6}$  %) and behind flame front in the case of rich mixtures. In lean and stoichiometric mixtures the  $CO_3^-$  and  $NO_3^-$  ions dominate plasma very close behind the flame front.



Fig. 4. Distribution of main ions in a combustion front propagating in gasoline/air mixture with 1 and 1.2 equivalence ratio at 1 atm and 300K

#### 3.2. Ionization during combustion wave propagation

Also, a series of numerical simulations has been carried out to model the combustion wave propagation in gasoline/air mixtures with different equivalence ratios at atmospheric pressure and 300K. It is seen that in contrast to the model of 0D adiabatic reactor the same ions prevail behind the flame front independent from the considered value of equivalence ratio, i.e. the  $H_3O^+$  ion – see Fig 4. The most significant positive ions in the flame front are  $H_3O^+$  and  $NO^+$ , while  $HCO_3^-$ ,  $CO_3^-$ ,  $OCHO^-$  and  $OH^-$  dominate among negative ions. The same ions (except the  $OH^-$ ) dominate also in region behind the flame front. However, the  $OCHO^-$  ions appear behind the front, only for rich gasoline/air mixtures.



Fig. 5. Spatial profiles of electrons', total positive ions and negative ions concentration without (solid lines) and with (dashed lines) diffusion for equivalence ratio  $\varphi = 0.8$  (a) and 1.2 (b).

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Figure 5 presents spatial profiles of total charged-particle concentrations with (solid lines) and without (dashed lines) diffusion processes considered. As expected, a significant widening of spatial profiles can be observed. This should be related to the spatial profiles of ionization substrates CH,  $C_2H_2$ , O, etc. – see Fig. 6. It is accompanied by a decrease of concentration maxima, more significant in the case of equivalence ratio 1.2.

It should be emphasised that although a much higher positive ion concentration is predicted for the case of  $\phi = 1.2$  when diffusion is ignored, in reality a slightly higher concentration for  $\phi = 0.8$  is found in the full model. The electron concentration is much higher (and close to positive ion concentration) in rich flame.



Fig. 6. Spatial profiles of electrons', total positive ions and negative ions concentration without (solid lines) and with (dashed lines) diffusion, for equivalence ratio  $\varphi = 0.8$  (a) and 1.2 (b).



Fig. 7. Main ions in gasoline/air flame without (a) and with (b) diffusion considered, for equivalence ratio,  $\phi = 0.8$ .



Fig. 8. Main ions in gasoline/air flame without (a) and with (b) diffusion considered, for equivalence ratio,  $\varphi = 1.2$ .

Figures 7 and 8 present the main ions in gasoline/air propagating flame for equivalence ratio,  $\varphi = 0.8$  and 1.2. Here we study the influence of gas-diffusion processes for ion concentration in a flame front. Rather surprisingly one finds that diffusion not only influences width of ion spatial distributions but it can also influence which ions prevail. In the case without diffusion, the H<sub>3</sub>O<sup>+</sup> ion dominates in the flame front. Electrons and HCO<sub>3</sub><sup>-</sup> ions (the latter in significantly lower concentration) prevail among negative species.

The  $C_3H_3^+$  and  $HCO_3^-$  ions dominate when species diffusion is taken into account. This results not so much from an increase of their concentrations, as from a significant decline of  $H_3O^+$  and electron densities. In this case (with diffusion considered) the role of electrons increases in rich mixtures.

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