ABSTRACT

It is shown by modeling that the discharge activation of C₃H₈-air mixture brings to disappearance of negative temperature coefficient (NTC) of overall oxidation rate at low initial temperatures. The reason of this effect is discussed with a point of key reactions which provide the NTC behaviour. The relation between the determinant component and specific input energy was obtained.

1. INTRODUCTION

Negative temperature coefficient behaviour of the overall rate of chemical process is one of the important peculiarity of hydrocarbon-oxygen (air) mixture under definite conditions (low initial temperatures T₀=500-700 and higher pressures), for example, in conditions of internal combustion engine. NTC is relevant to the problem of engine knock. Recently [1] by modeling it was shown that discharge action may reduce the appearance of NTC and, moreover, NTC disappears. In given work the influence of discharge operation on chemical kinetics responsible for NTC is investigated.

Only a few papers are devoted to the experimental study of discharge influence on the ignition in closed volume, simulated the conditions of internal combustion engines, for example [2-5]. In those papers several kinds of discharges are investigated to find the best igniter for combustible mixture. The common property for considered discharges [2-5] is a non-uniformity filling by discharge filaments (channels) of volume in contrast to spark plug (small hot area). It was also demonstrated a reduction of induction time of ignition. However there are no papers where the discharge impact on NTC region would be presented.

Usually, the induction time of ignition of combustible mixture decreases when an initial temperature increases. In NTC region the induction time increases with growth of initial temperature. The reactions which control the NTC behaviour are following reactions:

\[ R + O_2 \leftrightarrow RO_2 \]  
\[ RO_2 + C_3H_8 \rightarrow ROOH + C_3H_7 \]  
\[ ROOH \rightarrow RO + OH + \Delta E \]

where \( R = n-C_3H_7, i-C_3H_7, CH_3, C_2H_5, CH_3CO_3 \), \( \Delta E \) is a released energy. In considered propane-air mixture main radicals affecting NTC are i-C₃H₇, n-C₃H₇, CH₃ radicals with corresponding of alkyl peroxy radicals n-C₃H₇O₂, n-C₃H₇O₂ and CH₃O₂. These peroxy radicals are stable in the NTC region. The primary radicals in the concerned mixture are i-C₃H₇, n-C₃H₇ radicals. Radical CH₃ and other appear later (See Fig.1).

![Fig.1. Dependence of temperature and concentration of components on time in self-ignition case.](image-url)

According to reactions (1)-(3) one radical \( R \) produces three radicals RO, OH, C₃H₇. And this reactions sequence is chain branching. With increase of temperature the equilibrium in the
reaction (1) is shifted to the left, RO₂ concentration decreases and overall rate of chain branching (or the oxidation rate of mixture) decreases also. The NTC region is reached.

If to forced shift the equilibrium in reaction R+O₂ ↔ RO₂ to the right then the NTC region will decrease and, moreover, disappear. By means of discharge it is possible to increase the production rate of peroxy radicals.

2. STATEMENTS AND ASSUMPTIONS OF MODEL FOR SIMULATION OF COMBUSTION PROCESS

We use own developed database which is based on chemical reactions taken from literature and NIST database for CH₃, C₂H₄, C₃H₆, C₄H₈, CH₃CHO fuel (see references in [1]). To solve the problem of inflammation at low temperatures we used the reaction system which consists of 103 components and 700 reactions.

Description of low temperature ignition does not include the second O₂ addition to isomerization form of propylperoxy radical C₃H₇O₂, because for propane (and CH₄, C₂H₆, too) this process is rather difficult due to structural stress [6]. Moreover, according to experiments [7] alkylperoxy isomerization route is not very important in the propane oxidation mechanism.

Multistage inflammation is described rather good and includes the cool flame stage (T~550-750 K), blue flame (T~800-1000 K) and hot flame (T>1000 K) stages, and also NTC. Every stage is characterized by the peak increase of OH and stepped release of fuel mixture chemical enthalpy via the organic peroxy decomposition.

The modeling was performed at a constant volume and adiabatic conditions. The cooling of walls is included in the model in principal and may be taken into account for specific device. Peroxide decompositions on the walls are accepted in some reactions just approximately and included if it is needed.

3. DISCHARGE OPERATION MODELLING

It is assumed that a discharge is a non-uniform and has the filamentary structure. Filaments are close to each other. Ignition is initiated in the channels. It is suggested that after generation of combustion flame the volume is ignited very quickly, appreciably faster than the induction time in air-C₃H₆ mixture at T₀=500-800 K. The propagation of combustion flame is not considered.

The initial concentrations of radicals were determined in an approximation of specified electric field and estimated on bases of BOLSIG+ kinetic code [8]. The value of electric field was chosen to be equal 100 Td, what is usual for example in SDBD [9]. Active species are produced in following processes: 

\[ \text{O}_2 + e = \text{O}(^3\text{P}) + \text{O}(^1\text{D}) + e \]
\[ \text{N}_2(\text{A},\text{B},\text{C}) + \text{O}_2 = \text{O}(^3\text{P}) + \text{O}(^3\text{P}),^1\text{D} + \text{N}_2 \]
\[ \text{C}_3\text{H}_8 + e = \text{C}_3\text{H}_7 + \text{H} + e \]

G-values were obtained for C₃H₈-air mixtures for three equivalence ratios \( \varphi=0.7, 1, 1.66 \). \( ^3\text{D} \) is considered as atom O. Initial conditions are \( P_0=5.5 \) bar and \( T_0=500-800 \) K.

Table. Initial concentrations of active particles and gas heating coming from discharge operation. \( \varphi=1.66 \).

<table>
<thead>
<tr>
<th>W</th>
<th>O</th>
<th>n-C₃H₇</th>
<th>i-C₃H₇</th>
<th>H</th>
<th>ΔTₑ</th>
<th>ΔTᵦₑ</th>
<th>ΔTᵦᵢₑ</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.005</td>
<td>410</td>
<td>19</td>
<td>38</td>
<td>12</td>
<td>9</td>
<td>3</td>
<td>2</td>
</tr>
<tr>
<td>0.05</td>
<td>4100</td>
<td>190</td>
<td>380</td>
<td>120</td>
<td>92</td>
<td>28</td>
<td></td>
</tr>
</tbody>
</table>

The discharge energy is divided on two parts: a part of energy is spent on a gas heating \( \Delta Tᵦₑ \) (VT-relaxation and fast heating) and other one is on production of active particles \( \Delta Tᵦᵢₑ \). The estimations of full gas heating \( \Delta Tₑ \) (total input energy instantly releases in the heat - equilibrium thermal impact) and \( \Delta Tᵦᵢₑ \) in conditions of \( P=\text{const} \) for 5 input energy values W=0.005, 0.01, 0.02, 0.03, 0.05 eV/molecule have been made. In the Table the radical initial concentrations (in ppm) and heating (in degrees) are presented for rich mixture, \( \varphi=1.66 \). \( \Delta Tᵦₑ = \Delta Tₑ - \Delta Tᵦᵢₑ \). It is suggested that initial temperature in the case with activation by discharge is the same initial temperature as in self-ignition case. Additional heating from discharge is included into preheating of mixture with an appropriate lowering of primary gas temperature. Thus, we consider the effect only active particles on inflammation equating initial conditions. Concentrations of active particles were the initial
conditions for solving of set of chemical kinetics equations.

4. RESULTS AND DISCUSSION

In self-ignition case the initiation reactions are following:

\[ \text{O}_2 + \text{C}_3\text{H}_8 \rightarrow \text{HO}_2 + i-\text{C}_3\text{H}_7 \]
\[ \text{O}_2 + \text{C}_3\text{H}_8 \rightarrow \text{HO}_2 + n-\text{C}_3\text{H}_7 \]
\[ \text{HO}_2 + i-\text{C}_3\text{H}_7 \rightarrow \text{CH}_3\text{CHO} + \text{CH}_3 + \text{OH} \]
\[ \text{HO}_2 + n-\text{C}_3\text{H}_7 \rightarrow \text{OH} + n-\text{C}_3\text{H}_6\text{O} \]

Those reactions have very low rate constants at \( T \approx 650 \text{ K} \). There are some ways for subsequent interactions of products indicated reactions. One of the main routes is the sequence of reactions:

\[ i-\text{C}_3\text{H}_7 + \text{O}_2 \leftrightarrow i-\text{C}_3\text{H}_7\text{O}_2 \] (1a)
\[ n-\text{C}_3\text{H}_7 + \text{O}_2 \leftrightarrow n-\text{C}_3\text{H}_7\text{O}_2 \] (1b)
\[ i-\text{C}_3\text{H}_7\text{O}_2 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7\text{OOH} + n-\text{C}_3\text{H}_7 \] (2a)
\[ n-\text{C}_3\text{H}_7\text{O}_2 + \text{C}_3\text{H}_8 \rightarrow \text{C}_3\text{H}_7\text{OOH} + i-\text{C}_3\text{H}_7 \] (2b)
\[ \text{C}_3\text{H}_7\text{OOH} \rightarrow i-\text{C}_3\text{H}_7\text{O} + \text{OH} + \Delta \text{E} \] (3a)
\[ \text{C}_3\text{H}_7\text{OOH} \rightarrow n-\text{C}_3\text{H}_7\text{O} + \text{OH} + \Delta \text{E} \] (3b)

The temporal dynamics of main components are shown in Fig. 1. The components of \( \text{C}_3\text{H}_7\text{OOH} \), \( \text{C}_3\text{H}_7 \), and \( \text{C}_3\text{H}_7\text{OOH} \) change simultaneously and similarly. At the beginning of oxidation \( [\text{C}_3\text{H}_7] \) is very low.

In the case of discharge impact the initial concentrations of \( \text{C}_3\text{H}_7 \) radicals reach appreciably amounts during 100 ns in reactions

\[ \text{O} + \text{C}_3\text{H}_8 \rightarrow \text{OH} + \text{C}_3\text{H}_7 \] (4)
\[ \text{OH} + \text{C}_3\text{H}_8 \rightarrow \text{H}_2\text{O} + \text{C}_3\text{H}_7 \] (5)

The considerable growth of active centers number (\( \text{C}_3\text{H}_7 \)) leads to the fast formation of propylperoxy radicals (\( \text{C}_3\text{H}_7\text{OOH} \)) during 1 µs. In Fig. 2 one can see the behaviour of main components determining the appearance of NTC. The energy releases in fast chemical transformations after addition of active particles in the mixture. For example, in Fig. 2 the temperature increased at 20° during 1 µs.

The discharge effect on the negative temperature coefficient is illustrated in Fig. 3. As it is seen even a small value of input energy \( W = 0.005 \text{ eV/molecule} \) noticeably reduces the amplitude of NTC. At \( W = 0.02 \text{ eV/molecule} \) NTC disappeared.

In Fig. 4 the difference of discharge operation for three equivalence ratios are shown for \( W = 0.005 \text{ eV/molecule} \). Note, that for \( \varphi = 0.7 \) (lean mixture) the NTC behavior is not observed. The worse a mixture ignites the more a discharge influences. This fact was noticed in several works relevant to plasma assisted ignition, for example in [2].
NTC region disappears or almost disappears at $W=0.005$ eV/molecule as it is shown in Fig. 6. Before that W value a mixed behaviour of induction time curves is clearly seen in dependence on $T_0$. With increase of W value the curves array in right order: the induction time reduces with increase of initial temperature. In a certain sense the threshold effect of discharge impact for disappearance of NTC is observed.

![Fig. 5 Concentration and induction time for self-ignition case (solid line) and under discharge impact (dash line), $W=0.005$ eV/molecule. $s=1.66$.](image)

![Fig. 6 Dependence of induction time on input specific energy and initial temperature](image)

Initial concentrations of O atoms and C$_3$H$_7$ radicals coming from discharge are closely related with maximum value of propylperoxo radical C$_3$H$_7$O$_2$. Dependence of induction time on their ratio $([O]_0+3[C_3H_7]_0)/[C_3H_7O_2]_{max}$ gives the point of intersection of curves and minimum ratio for disappearance of NTC. This ratio is equal to 1 and independent of $\phi$. The same results as in Fig.6 have been obtained for lean and rich C$_3$H$_8$-air mixtures.

**5. CONCLUSIONS**

It is shown that under the discharge impact the negative temperature coefficient (NTC) of overall oxidation rate of propane-air mixture is disappeared. Effect of discharge has a threshold character. The relation between specific input energy, concentrations of primary radicals from discharge and key component (C$_3$H$_7$O$_2$) determinant NTC behaviour has been obtained. To get rid of NTC the minimum ratio $([O]_0+3[C_3H_7]_0)/[C_3H_7O_2]_{max}$ should be equal to 1.

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**REFERENCES**


