Modelling of kinetic combustion process of oxygen enriched mixture in SI engine

Abstract: The paper presents a proof of explanation of the formation process of toxic exhaust gas components during combustion process of oxygen enriched mixtures in SI engine. In order to explain this phenomenon the simulation process was carried out, in which the experimental data from dynamometer tests of the 4-stroke SI engine were used. The test were done at different mole concentration of oxygen and at increased ratio of exhaust gas recirculation until the mixture of oxygen and exhaust gases has not contained any air. In simulation process one makes use of the computer program Kintecus ver.3.95, where the functions of kinetic combustion process of complex chemical reactions taken place during combustion of fuel mixture (gasoline) in SI engine. The paper presents the graphs showing variations of mole concentration of chosen chemical species in the charge in a function of time and variation of temperature in the cylinder.

Key words: write oxygen enriched mixture, simulated investigation, exhaust gas toxic components emission.

1. SI engine with oxygen enriched mixture and EGR system

Nowadays the researcher are looking for innovation methods in order to increase an engine power with decreasing of specific fuel consumption and exhaust gas emission at the same cylinder capacity. The new technology called “downsizing” forces to find new filling systems in order to increase amount of charge in the cylinder and then to deliver higher dose of fuel. Applying of different types of charging enables to obtain higher engine work parameters and usually higher total efficiency. Another way, which was described, by Sliwinski and Papuga [8] is filling the SI four-stroke engine only by oxygen and fuel forming the mixture close to stoichiometric value. Adding higher amount of oxygen than in the air gives the same effect as a charging system. However, the burning such mixture causes significantly higher combustion temperature and also higher NOx emission. This phenomenon is not suitable for the turbocharger because of big thermal load of turbine blades and thermal stresses of the engine parts. Therefore, in order to decrease emission of NOx one put EGR system with different recirculation ratios. The paper introduces results of calculation of combustion process of the mixture contained only oxygen, fuel in stoichiometric value, and exhaust gases as rest of the charge. The authors determined such mixture as charge with 100% EGR, because of existence of maximum exhaust gases in whole charge. The 4-stroke engine was tested on dynamometer stand at different oxygen mass ratio in the charge, at different EGR ratios and by adding certain amount of air at different loads and speeds. The experimental results obtained from experiment showed big concentration of CO in the exhaust gases after burning of the mixture with 100% EGR and high concentration of NOx after burning the mixture contained an additional air. These factors forced to do a computer analysis by simulation of combustion process of oxygen-enriched mixtures.

2. Goal and scope of work

The target of the authors was to find dependencies between increased amount of oxygen in the charge delivered to the engine and emission of toxic components in exhaust gases. In order to reduce
amount of nitrogen oxides during combustion process, the EGR system was applied by delivering exhaust gases to the inlet pipe in specified ratio. This work concerns only the case when the engine was feeding by fresh oxygen, fuel in stoichiometric value (air excess coefficient $\lambda = 1.0$) in relation to oxygen and exhaust gases with decreased amount of water vapour by condensation in a special separator. The experimental work was done on 2-cylinder 4-stroke spark ignition engine Honda GX360 with cylinder capacity 180 cm³ and result were presented in the paper [8]. High amount of oxygen influences on an increase of NOx, thus EGR system was needed. This work concerns only to theoretical considerations of combustion process of such combustion system. Applying of chemical models of combustion process of the oxygen-enriched mixture explains problem of formation of chemical species. The main goal of the work was to verify experimental results with results from simulation. Formation of CO₂, CO and consumption of oxygen was the one of the most important factors in the work. The scope of the work concerns to the computer simulation of gasoline combustion in oxygen enriched mixture with high EGR ratio by using simple combustion model in CFD program and extended kinetic combustion 0-dimensional model.

3. Modelling of combustion process

Understanding of chemical processes taking place in internal combustion engines is still actual and gives possibility to control of exhaust gas emission in respect to recent environmental requirements. Modelling of gasoline combustion requires obtaining many chemical reactions from literature and databases from known combustion institution such Sandia Laboratories, Livermore National Laboratory, Argonne National Laboratory or simple models developed in different universities. On the market, there are several computer software for calculation very complicated combustion process of many fuels in air with different air-fuel ratios. However, most of them take into account combustion of fuel in constant volume and are designated for cases in which such process starts in the whole space. For that reason, such chemical computer programs are not suitable for combustion of air-fuel mixture in internal combustion engines, where the change of volume, pressure and charge motion takes place. Besides that in spark ignition engines initiation of burning of fuel begins from point ignition in the spark plug. For such type of engines, the flame propagation is close to the spherical shape with changeable velocity. In order to recognize the combustion process for the spark ignition engine with enriched oxygen in the charge two types of computer programs were applied: the first Kiva3v[1] - the special CFD program for analysis of physical and chemical processes in internal combustion engines and the second Kintecus ver.3.95 [12]developed by James C. Ianni, which is close to Chemkin [5] from Sandia Laboratories. CFD program enables to simulate both gas motion in the cylinder and combustion process of various fuels with different local air-fuel ratios. However, Kiva3v takes into account very simple gasoline combustion model consisting only 10 chemical reactions with 12 species. Kintecus program enables calculation of combustion process with taking into account very large chemical model, which can consist of thousands of reactions and species. The both programs apply Arrhenius formula for kinetic combustion process and dissociation reaction for post-burning of fuel. It was assumed, that gasoline has chemical formula C₈H₁₇ and its properties are close to octane C₈H₁₈. Like in experimental work also in calculations a several values of oxygen mass ratio in the charge were taken into account in the range 21 – 31%. However, in this work it was shown the results for three values of oxygen mass ratio: 21, 26 and 31%. The assumed values of volumetric ratios of CO, CO₂ and HC in exhaust gases in EGR system are presented in table 1.

Table 1. Initial calculation data

<table>
<thead>
<tr>
<th>$O_2$ [%]</th>
<th>$\theta$ [deg]</th>
<th>Mo [Nm]</th>
<th>$T_{exh}$ [°C]</th>
<th>CO [%]</th>
<th>$CO_2$ [%]</th>
<th>HC [ppm]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>55</td>
<td>11.5</td>
<td>613</td>
<td>20.84</td>
<td>54.78</td>
<td>305</td>
</tr>
<tr>
<td>26</td>
<td>40</td>
<td>14.6</td>
<td>706</td>
<td>17.62</td>
<td>64.51</td>
<td>160</td>
</tr>
<tr>
<td>31</td>
<td>25</td>
<td>17.7</td>
<td>777</td>
<td>22.78</td>
<td>61.15</td>
<td>117</td>
</tr>
</tbody>
</table>

where $\theta$ signifies advance of ignition BTDC, Mo is engine torque and $T_{exh}$ temperature of exhaust gases. While experimental tests and calculations one assumes the constant value of mass filling ratio $\eta$ on the level 57%. The delivered exhaust gases to the inlet pipe were drained in the special device and water was partly removed from the gases, so almost dry gases were supplied to the cylinder by EGR system.

4. Simple model of combustion

Generally, in 0-dimensional and 2-zones models of combustion process in the piston engines the kinetic reactions are not taken into account. In the spatial modelling by using CFD (Kiva3v) the kinetic reactions are taken into consideration in the combustion process of hydrocarbon fuel and formation of NO. Four kinetic reactions were assumed in simulation calculations of gasoline burning according to the chemical formula C₈H₁₇:

1. equation of gasoline combustion:
   \[ 4 \text{C}_8\text{H}_{17} + 49 \text{O}_2 \rightleftharpoons 32 \text{CO}_2 + 34 \text{H}_2\text{O} \] (1)

2. equation of NO formation according to Zeldovich mechanism [4]:
   \[ \text{O}_2 + 2 \text{N}_2 \rightleftharpoons 2 \text{N} + 2 \text{NO} \] (2)
   \[ 2 \text{O}_3 + \text{N}_2 \rightleftharpoons 2 \text{O}_2 + 2 \text{NO} \] (3)
   \[ \text{N}_2 + 2 \text{OH} \rightleftharpoons 2 \text{H} + 2 \text{NO} \] (4)
The elementary reversible and irreversible reactions, which involve K chemical species can be represented by formula:

$$\sum_{i=1}^{K} v_{k_i} X_k \Leftrightarrow \sum_{i=1}^{K} v'_{k_i} X_k \quad (i=1,\ldots,I)$$  (5)

The stoichiometric coefficients $v_{k_i}$ are integer numbers and $X_k$ is the chemical symbol for the $k$-th species. On the other hand the superscript ‘ indicates forward stoichiometric coefficients and superscript ‘ ‘ indicates reverse stoichiometric coefficients.

The rate of formation of $k$-th chemical species can be written in the form of sum from all chemical reactions, in which that compound took place:

$$\dot{C}_k = \sum_{i=1}^{I} v_{k_i} \dot{n}_i \quad (k=1,\ldots,K)$$  (6)

where: $\dot{v}_{k_i} = \dot{v}_{k_i} - \dot{v}'_{k_i}$.

The rate of progress variable $\dot{n}_i$ for i-th reaction is given by the difference of the forward and reverse rate as shown in formula (7):

$$\dot{n}_i = k_f \prod_{i=1}^{K} (X_i)^{v_{k_i}} - k_r \prod_{i=1}^{K} (X_i)^{v'_{k_i}}$$  (6)

where:

- $X_i$ - molar concentration of the $k$-th species,
- $k_f$ - forward rate constant of i-th reaction,
- $k_r$ - reverse rate constant of i-th reaction.

The first reaction decides of combustion rate of the fuel (increment of pressure and temperature). The constant rate of the individual forward and reverse reactions are calculated from the Arrhenius equations:

$$k_f = A_f T^n \exp\left(-\frac{E_a}{RT}\right)$$  (7)

$$k_r = A_r T^{n'} \exp\left(-\frac{E_a}{RT}\right)$$  (8)

where $A_f$ and $A_r$ are constants of given reactions and $E_a$ is the molar activation energy of reactants and products, on the contrary $n$ is temperature exponent.

The constants $A_f$ in Arrhenius equations for calculations of gasoline burning were chosen in such way, that several times the results from simulation by using Kiva3v (cylinder pressure traces and mole concentration of chemical species) were compared with results from experimental tests at assumed rotational speed 3000 rpm. Activation energy and temperature exponent were assumed according to Amsden [1] as an unchanged values.

The rate of formation of the components of exhaust gases depends closely on charge temperature, by the way the constants in Arrhenius formula for NO are significantly higher than in the first reaction of fuel combustion.

Besides the kinetic reaction the program Kiva3v takes into account also dissociation (equilibrium) reactions, which occur during expansion stroke at high temperature above 2000 K:

$$\text{CO}_2 \leftrightarrow \text{CO} + \frac{1}{2} \text{O}_2 \quad (9)$$

$$\text{H}_2\text{O} \leftrightarrow \text{H}_2 + \frac{1}{2} \text{O}_2 \quad (10)$$

$$\text{OH} \leftrightarrow \frac{1}{2} \text{H}_2 + \frac{1}{2} \text{O}_2 \quad (11)$$

$$\text{O} \leftrightarrow \frac{1}{2} \text{O}_2 \quad (12)$$

$$\text{H} \leftrightarrow \frac{1}{2} \text{H}_2 \quad (13)$$

The model of kinetic reaction and equilibrium reactions enables to carry out the analysis of toxic components during combustion process in 4-stroke engines with high EGR ratio and enriched charge with oxygen.

5. CFD in combustion process

Analysis of combustion process in Kiva3v program was carried out for three mass ratios of oxygen at rotational speed 3000 rpm. Simulation process began after closing of the inlet valve at 50 deg ATDC with initial cylinder pressure 0.096 MPa and temperature 495 K. Calculations were finished at 120 deg CA ATDC before opening of the exhaust valve. It was needed the change of pre-exponential constant in Arrhenius reaction for every case of change of oxygen mass ratio in order to obtain the same pressure variation in cylinder as in the experiment. The mixture delivered to the cylinder did not contain any amount of nitrogen, so NOx were not expected in exhaust gases. The exhaust gases in EGR system contained small amount of water. Mass fractions of chemical compounds in the cylinder charge are presented in Table 2.

<table>
<thead>
<tr>
<th>Mass ratio of O₂ [%]</th>
<th>O₂ [-]</th>
<th>fuel [-]</th>
<th>CO₂ [-]</th>
<th>CO [-]</th>
<th>H₂O [-]</th>
</tr>
</thead>
<tbody>
<tr>
<td>21</td>
<td>0.21</td>
<td>0.0605</td>
<td>0.500</td>
<td>0.121</td>
<td>0.1085</td>
</tr>
<tr>
<td>26</td>
<td>0.26</td>
<td>0.075</td>
<td>0.508</td>
<td>0.09</td>
<td>0.067</td>
</tr>
<tr>
<td>31</td>
<td>0.31</td>
<td>0.09</td>
<td>0.46</td>
<td>0.109</td>
<td>0.031</td>
</tr>
</tbody>
</table>

These data were put as initial parameters to Kiva3v for three simulation cases. Figure 1 shows variation of cylinder pressure in a function of crank angle for three values of oxygen-enriched mixture. For higher mass ratio of oxygen in the charge, the higher maximum of pressure is reached in the cylinder and this maximum point takes place at 15 deg CA ATDC. For assumed constant value $A_f$, and $A_r$ an increment of pressure changes for each case. At the same initial charge mass a change of temperature depends on pressure variation. Also at higher oxygen enriched mixtures, the higher value of temperature is obtained as shown in Fig.2. Maximum of temperature takes place a little bit higher mass ratio of oxygen in the charge.
later than for maximum of pressure at 25 deg CA ATDC.

![Graph 1: Pressure traces in cylinder at different mass oxygen ratios and 100% EGR](image1)

**Fig. 1.** Pressure traces in cylinder at different mass oxygen ratios and 100% EGR

![Graph 2: Variation of temperature in cylinder at different mass oxygen ratios and 100% EGR](image2)

**Fig. 2.** Variation of temperature in cylinder at different mass oxygen ratios and 100% EGR

Very interesting is variation of CO volume fraction in the cylinder as shown in Fig. 3. Big mass fraction of CO, delivered to the cylinder by EGR system, is very fast consumed during first stage of the combustion process after ignition. Oxidation of CO is faster than oxidation of fuel. For that case amount of oxygen should be higher in order to oxides both fuel and CO. The water is formed during combustion process and thus CO volume fraction in the charge is decreased after this process in comparison to the initial stage. Participation of water in the charge after burning of fuel influences also on volume fraction of another gas components. At highest temperature a maximum of mass ratio of CO is reached. Later oxidation of CO takes place. Formation of CO is connected with equilibrium reactions where CO\(_2\) decomposes on CO and O at temperature about 2000 K. Like in experiment at 26% of oxygen mass ratio the simulation indicated lower emission of CO, where mass ratio of CO\(_2\) in EGR system amounted 64.51%. For this case, lower amount of O\(_2\) was needed for oxidation of CO. Decomposing of CO\(_2\) run significantly slower during expansion stroke. For middle range of oxygen mass ratio in the fresh charge the lower values volumetric fraction of CO are obtained. On the other hand, volumetric ratio of CO\(_2\) is higher for middle range of oxygen mass ratio in the fresh charge as shown in Fig. 4. Because the fuel is consumed fully while combustion process, therefore, the change of CO and partly CO\(_2\) volumetric ratio is caused by dissociation process. Volumetric fraction of CO\(_2\) reaches maximum values close before opening of exhaust valve.

![Graph 3: Volumetric fraction of CO in cylinder at different mass oxygen ratios and 100% EGR](image3)

**Fig. 3.** Volumetric fraction of CO in cylinder at different mass oxygen ratios and 100% EGR

![Graph 4: Volumetric fraction of CO\(_2\) in cylinder at different mass oxygen ratios and 100% EGR](image4)

**Fig. 4.** Volumetric fraction of CO\(_2\) in cylinder at different mass oxygen ratios and 100% EGR

Almost 30% of charge volume in the cylinder amounts water in vapour state and the higher increase of water mass is formed for higher oxygen mass ratio of the fresh charge. In spite of condensation of water in exhaust gases flowing through the EGR system and its separation in a special separator some amount of water is delivered do the inlet pipe. It was assumed, that exhaust gases in EGR system consist of CO, CO\(_2\) and small amount of water. The rest of chemical species was not considered, because of their small volume fraction.
While experiment and simulation the constant value of mass ratio of air and oxygen was assumed and amounted 3.47, which is adequate to the air excess coefficient $\lambda = 1$ for gasoline. With increasing of oxygen amount in the charge the mass of fuel was also increased. Simulation proved total burning of fuel, however, at lower oxygen mass fraction the time of fuel burning lasted longer. Fig. 6 shows variation of volumetric fraction of gasoline vapours (hydrocarbons) in the cylinder as a function of crankshaft rotation. Fuel burns fully for considered cases and combustion process ended at 40 deg ATDC.

**6. Detailed combustion chemistry**

Gasoline consists of hundreds hydrocarbons and simulation of combustion process requires thousands of chemical reactions both kinetic and equilibrium reactions with coefficients coming in Arrhenius formula (7),(8). On the market is there common used the commercial program Chemkin for calculation of combustion process in steady conditions, where whole object is treated as 0-dimensional. The authors used academic version of the program Kintecus ver. 3.95, which works like as the Chemkin program. The chemical model consists of the chemical reactions tables and thermochemical tables of properties of species taking place in the reactions. The accessible sources of these data are adapted for the program Chemkin. Kintecus accepts other form of chemical reactions than Chemkin and therefore a special conversion program is required, which is included in program packet. Thermochemical properties and the extended chemical mechanism was given by Curran et al [3] and was adapted for this work by reduction of number of reactions. However this model was extended by adding additional model of nitrogen oxides formation which was taken from GRIMECH [11]. Finally it was used the chemical mechanism with 197 species and 1092 chemical reactions. The model takes into consideration both kinetic and equilibrium reactions. Kintecus enables the change of volume and heat exchange in a function of time. Initial temperature of combustion should be given as a start of ignition in whole space. Kintecus and Chemkin calculate every time a volumetric molar concentration of individual species in mole/cm$^3$. The fuel was treated as iso-octane and its initial molar concentration was given for every case like as for the other species: O$_2$, CO, CO$_2$ and water. In addition, this simulation took into account only fuel, oxygen and exhaust gases from EGR system. Nitrogen was removed from the fresh charge.

**7. Calculation in Kintecus program**

Calculation in Kintecus program were carried out at initial temperature 1500 K and pressure 1.0 MPa with assumption that ignition begins 10 deg CA BTDC and lasted 36 deg CA at rotational speed 3000 rpm. Function of volume change was given in order to simulate a real condition of combustion process. Table 3 shows the initial molar concentration of individual species for 3 calculation cases.

<table>
<thead>
<tr>
<th>O$_2$ mass fraction</th>
<th>O$_2$</th>
<th>fuel</th>
<th>CO$_2$</th>
<th>CO</th>
<th>H$_2$O</th>
</tr>
</thead>
<tbody>
<tr>
<td>21%</td>
<td>3.97e-5</td>
<td>3.24e-6</td>
<td>6.9e-5</td>
<td>2.6e-5</td>
<td>3.64e-5</td>
</tr>
<tr>
<td>26%</td>
<td>4.92e-5</td>
<td>4.02e-6</td>
<td>7.0e-5</td>
<td>1.95e-5</td>
<td>2.25e-5</td>
</tr>
<tr>
<td>31%</td>
<td>5.86e-5</td>
<td>4.82e-6</td>
<td>6.3e-5</td>
<td>2.36e-5</td>
<td>1.04e-5</td>
</tr>
</tbody>
</table>

Based on presented assumption one carried out the calculations for three cases identical as for simulation in Kiva3v program. Taking into account that combustion process is initiated in the whole volume this leads to sudden change of temperature...
after 0.4 ms. Variation of temperature is shown in Fig. 7 and maximum of temperature is reached after 1 ms, which corresponds to 8 deg CA ATDC. Temperature is higher for higher oxygen mass ratio like it was obtained in CFD simulation. Rapid combustion process causes also a big increase of molar concentration of CO$_2$ in 1 cm$^3$, which is shown in Fig. 8. After the kinetic combustion process the equilibrium reactions take place (decomposing of CO$_2$), which cause change of molar concentration of CO$_2$.

![Fig. 7. Temperature of combustion with different initial oxygen mass ratios and 100% EGR](image)

![Fig. 8. Mole concentration of CO$_2$ in changeable volume with different initial oxygen mass ratios and 100% EGR](image)

Amount of CO$_2$ depends on initial value of this species in the cylinder charge. Figure 9 shows variation of molar concentration of CO. At first stage amount of CO rapidly increases, which is caused by decomposition of hydrocarbons bonds on radicals and then on CO. Increase of temperature influences on rapid oxidation of CO from decomposition and this part, which was delivered to the volume at the beginning of whole process. Next, an increase of CO follows as a result of dissociation process. Like in previous simulation for 26% oxygen mass ratio a lower molar concentration of CO also takes place. Figure 10 presents variation of molar concentration of water. Big increment of water concentration takes place at higher initial oxygen mass ratio in the charge. Higher initial water concentration influences also on its final molar concentration, which is also high.

![Fig. 9. Mole concentration of carbon monoxide in changeable volume with different initial oxygen mass ratios and 100% EGR](image)

![Fig. 10. Mole concentration of water in changeable volume with different initial oxygen mass ratios and 100% EGR](image)

Decomposition of CO$_2$ during dissociation process influences on an increase of molar concentration of oxygen (Fig.11). However, finally amount of oxygen is very small independently on initial oxygen mass ratio. During kinetic reaction different radicals are formed and they have most important significance on whole combustion process. The radicals such as CH, OH, O, H, HO$_2$ and others should be taken into account during simulation of combustion process. Figure 12 shows change of molar concentration of radical OH, which is present almost at whole time during gasoline combustion and higher amount of this radical takes place for big amount of oxygen in the mixture. On the other hand, duration time of radical CH is very short (several microseconds). Higher molar concentration of CH is for lower initial oxygen mass ratio.
Besides of radicals and main species in exhaust gases during decomposition of fuel, one exists also non-oxidized specie such $H_2$. Simulation of combustion process in Kintecus program indicates on existing of significant value of $H_2$ (Fig.14). Amount of this specie increases during combustion process. Maybe it was not enough of oxygen in the mixture. This tendency is the same for three analyzed cases.

8. Conclusions

Experimental test carried out on real SI 4-stroke engine feeding with oxygen enriched mixture gave results of exhaust gas emission, which could be explain by theoretical consideration or by modelling and simulation of combustion process. Simulations were carried out by using two tools: CFD model and 0-dimensional extended chemical model. The results obtained from both gave almost the same dependencies for three analyzed cases with oxygen-enriched mixture. The presented work concerns only to the charge devoid of nitrogen however with high EGR ratio and with stoichiometric conditions in relation to oxygen. Advance angle of ignition was extended at lower value of oxygen mass ratio in the fresh charge.

1. The engine filled with high EGR ratio requires significantly much more oxygen in order to oxidize CO being in exhaust gases.
2. Higher amount of $CO_2$ and lower amount of CO delivered to the cylinder by EGR system causes the same relations after combustion process.
3. Change of molar concentration or mass fraction of CO and $CO_2$ during combustion process is dependent on running of dissociation process (forward and reverse reaction).
4. Higher initial mass fraction of oxygen causes higher cylinder pressure and also internal work.
5. Pre-exponential factor should be increased during simulation process when oxygen mass
fraction has lower value and advance angle of ignition is increased.

6. Rapid change of pressure and temperature occurs during kinetic reactions, where a sudden change of CO molar concentration takes place.

7. After combustion of assumed mixtures one comes to existence a big amount hydrogen which was not measured during experimental tests.

This work is based on experimental investigations done within the confines of Research Project financed by Research Scientific Committee.

Nomenclature/Skróty i oznaczenia

- EGR - Exhaust Gas Recirculation/recyrkulacja gazów spalinowych
- CFD - Computational Fluid Dynamics/dynamika płynów w obliczeniach
- CA - crank angle/kąt obrotu wału korbowego
- BTDC - before top dead centre/przed górnym martwym położeniem tłoka GMP
- ATDC - after top dead centre/ po górnym martwym położeniu tłoka GMP

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