INFLUENCE OF INTERNAL COMBUSTION CATALYST TO SHORTEN THE IGNITION DELAY

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Abstract: The paper presents a discussion of the combustion processes in the engine piston, in terms of ignition delay. The problem of the physical and chemical ignition delay is discussed and equations which allow the calculation of ignition delay based on the theory of combustion processes are presented. The paper proposes the use of a catalytic coating in the combustion space in order to shorten the ignition delay. The results of studies made on single diesel engine are displayed. Studies have confirmed a significant effect of the catalyst on the combustion process and shortening the ignition delay. Internal combustion catalyst used as a coating made of ZrO2 activated Pt and Rh deposited on engine valves, caused a shortening of ignition delay of about 1 - 3 degrees of crankshaft rotation.

KEY WORDS: INTERNAL CATALYST, IGNITATION, PISTON ENGINE

1. Introduction

Ignition delay, lasting only a few milliseconds, is a fragment in the diesel engine working cycle. Nevertheless, this delay is responsible for conditioning the effectiveness and ecological effects of engine work [1]. If the delay period lasts too long- the combustion goes rapidly (lauqd engine work) and less effective (the toxic components of fumes as well as the fuel consumption are increased). There is known the directly proportional correlation between lasting time of ignition delay period and deterioration of fumes quality, especially when the intensity of incompletely combusted hydrocarbons is concerned (among them mutagenic and carcinogenic multi annular aromatic hydrocarbons), in the exhaust gases in diesel engines [1].

Delay period is longer in diesel engines where the time is counted from the moment of fuel injection and the combustible mixture must be properly prepared during this period.

Physical processes appearing in the cylinder after the fuel injection beginning, are necessary for air- fuel mixture preparation and for the pre ignition chemical reactions initiation. The time interval between the moment of fuel injection and the beginning of chemical chain reaction initiation which causes self ignition is called time of physical ignition delay.

For the physical processes appearing in diesel engines during time of physical ignition delay belong primarily:

- Fuel flow breakup into single drops
- Heating and vapourization of single drops
- Diffusion going in on the limits of fuel and air steams (formation of flammable gas mixture).

The impact on lasting time of chemical and physical ignition delay also have any modification of fuel that feed the engine [1]. Huang, Ren, Jiang, et.al [2] studied the lasting time of ignition period in ZS engine fed by fuel mixtures of diesel type- DMM (Diesel-dimethoxymethane). Those researches indicate the impact of fuel-air mixture on the ignition delay time, especially during the phase of diffusion processes going on [2].

Considering the abovementioned facts, the ignition delay time in injection engines is conditioned by the sum of physical and chemical ignition delay times [3]. It seems impossible to state the clear limit between the ending of physical ignition delay and the beginning of chemical ignition delay. That is why the ignition delay has to be treated as a resultant of normalized physical-chemical processes in which the all transformations- both physical and chemical appear simultaneously. Thus the ignition delay period is the sum of physical and chemical ignition delay[11]:

$$\tau_i = \tau_f + \tau_{ch}$$  \hspace{1cm} (1.1)

The impact on the ignition delay period have various factors which are, primarily, closely related to chemical properties of fuel and the composition of inflammable fuel mixture [1].

On the basics of empirical data and the analysis of kinetic relations Semenow introduced the model for ignition delay period which for fuels coming out from oil is following:

$$\tau_i = \text{const} \left( \frac{T}{p} \right)^{0.5} e^{\frac{E_a}{RT}}$$  \hspace{1cm} (1.2)

Where: p- mixture pressure, T- mixture temperature, E_a activation energy, R-universal gas constant.

After logarithmic calculations of the model, it is visible, that together with the growth of pressure and temperature (exponential function) the delay period decreases [1].

Kavaradze, Zeilinger and Zitzeler [4] made engine researches concerning measurement of ignition time due to the used fuel type, introducing for the first time paradigms for ignition delay of natural fuel and of several synthetic fuel variants.

Thanks to applied research methodology, the results of those researches suggested the validity of the chain theory of ignition. According to the authors of those studies, the presented empirical paradigms can be used for engine fed by particular fuel working stimulation and for prediction of its ecological effects.
For diesel engine with direct fuel injection, which works with the use of classic diesel oil, the suggested paradigm goes as follows:

$$\tau_i = 0.55 p^{-1.3} \exp \left( \frac{4400}{T} \right)$$  \hspace{1cm} (1.3)$$

Where: \( p \) and \( T \) relates to pressure and temperature in the cylinder during the moment of fuel injection.

Due to the fact that in present diesel engines the recirculation of fumes is used, for the paradigm (1) there has been added empirically assigned \( K \) factor. The value of this factor is determined according to recirculation ratio. Thus the paradigm is:

$$\tau_i = 0.55 K p^{-1.3} \exp \left( \frac{4400}{T} \right)$$  \hspace{1cm} (1.4)$$

Where: \( K = 0.9 z^{0.99} \) for \( z = 5 \text{ – } 40\% \)  \hspace{1cm} (1.5)$$

From the abovementioned paradigm it follows that the temperature in the cylinder during the fuel injection moment is inversely proportional to lasting time of ignition delay. The higher the temperature is, the shorter ignition delay time is. Because this relation decreases exponentially, thus even slight prevailing temperature increase in the cylinder during injection should result in noticeable effects of shortening ignition delay.

William and Schmidt [5], while analyzing parameters of ignition initiation during the researches concerning catalytic oxidation of higher alkenes with the use of rhodium as an active factor, noticed that introduction of even small amount of catalyst in reactor simulating the prevailing engine conditions (with certain limits concerning the actual engine conditions, for the case of reactor constructed by the authors the adiabatic processes are present) results in high efficiency in limiting those compound emission. One of the authors’ suggestion is the thesis that the active factor introduced into combustion space causes the beginning of complicated chain reactions causing, at the same time, the shortening of chemical ignition time delay and therefore, the lasting time of adverse processes producing toxic, organic carbon compound is minimized.

According to literature [1,4,5,6] it is possible to conclude that the modification of engine combustion space based on introduction of active factor (catalyst), may, with high probability, cause the shortening of chemical ignition delay through declining activation energy of pre ignition reactions.

2. Internal combustion catalyst

The notion of internal combustion catalyst is understood by the authors as the fragment or entirety of walls creating the combustion space of internal combustion engine or the element of this space, e.g. valve, glow pug, which were covered with ceramic coating that composes catalytic substance media which is also soaked with this substance and activated. Internal catalysts, known in literature, were made through activation (ion implantation) of the wall surface combustion space or through introduction of catalytic active material such as platinum tube or wire into this space.

Trials of using internal catalyst, which were described in literature, indicated its positive influence on the combustion process. However, it should be emphasized that the basis of the effectiveness of the catalysts process is the large amplification of the catalytic space and relatively high catalyst temperature. For platinum, high effectiveness is noticed over the temperature of 500K.

In literature, the presented solutions are characterized by relatively low catalyst temperature and low amplification of space.

The offered solution based on using the ceramic coating as media, according to coating property, causes quick obtainment of higher coating temperature, and thus higher effectiveness of the catalyst working.

The catalyst placed inside combustion space may work in several combustion stages:

a) in the phase of preparing inflammable mixture-cracking processes of injected fuel,

b) in the pre fiery phase- shortening ignition delay,

c) in the combustion period- the increase of combustion speed

d) in the afterburner period- combustion of hydroxides in the boundary layer, afterburning of CO and NO\(_x\) reduction.

According to its kind, size and catalyst placement as well as load and rotary speed of engine, the effectiveness of catalyst working may change in the particular stages. It should be expected, however, that the adverse working may appear in e.g. NO\(_x\) increase or fumes smokes increase.

Offered by the authors, internal catalyst of combustion is made in the form of ceramic coating deposited on the element surface or combustion chamber wall. After depositing, the coating is polished in order to obtain even gage and then it is activated by precious metals with catalytic properties- in this case rhodium and platinum. After depositing of precious metals the coating faces calculations and reduction processes. It may be predicted, that the most beneficially is making the active coating on the surface of piston combustion chamber. From the technical points, according to the present negative experiences connected with incommensurate durability of coating made on pistons, it has been decided to make the coating on the surface of valve mushrooms.

![Fig. 2.1. Scheme of internal combustion catalyst.](image-url)
As it has been mentioned, the necessary condition of catalyst working is possibly large surface on which the catalytic material is deposited and its high temperature over 250°C.

In the case of internal combustion catalyst, according to the present experiences, it has been decided to use the coating made of zirconium oxide, partially stabilized by yttrium (PSZ), as the media. Yttrium stabilization prevents the adverse changes in the structure and the yttrium participation is of 8-20% of weight.

Ceramic media of catalyst should be characterized by fine bed adhesiveness, temperature shock resistance, aggressive environment (chemical and gas corrosion) resistance and the catalytic activation sensibility (large surface amplification, porosity).

3. Research location and measurement methods.

For the purpose of engine research, the portion of valves with ceramic covering and platinum active coating and with ceramic covering and platinum and rhodium activation. The gage of ceramic coating was of 0,3 mm. The coating was deposited with ZrO₂8Y₂O₃ on the base of MCrAlY with the gage of 100 µm.

The valves were mounted to stationary single cylinder SB3.1 engine made based on SW680 engine elements.

The engine was loaded with rotational current Hennan-Froude brake which provides the stability of rotations and full range of load.

For the measurement of fumes components URAS 10E no 3.200418.2 analyzer, 4-gas Infralift 4000 and Infralift T4393/2238 analyzers, as well as the NOₓ CLD type by Pierburg Co. analyzer in the final phase of researches were assigned.

The usage of fuel was measured by volumetric meter with the compliance of fuel density.

For the measurement of air usage, the system including reservoirs equalizing the air ripple and the double flange ISO system with the measurement of clypeal pressure, were used.

The measurements of pressure in the combustion chamber were carried out for:
- Different conditions of engine working: three different speeds (1200, 1400 and 1600 rotations/minute) with different loads and three different angles of the beginning of fuel squeezing 20, 23 and 27 °OWK,
- Different construction modifications: “basic” condition-engine in standard version (from producer), ceramic in the combustion chamber and platinum as catalyst, ceramic activated by platinum and rhodium.

About the diagram accuracy, concerning the changes of indicated pressure and its position towards reference point i.e. external turn, several measurement aspects are deciding. Among them there are: sensor calibration methodology (static and/or dynamic), whole measurement line calibration, the location of pressure sensor in the combustion chamber, type of signal filtration, the frequency of sampling, accuracy of defined location of external piston turn (GMP).

In the presented studies, sensor calibration has been made with accuracy of ± 0,01 MPa, but for the whole measurement line calibration the amplifier, oscilloscope and 18 bits measurement computer card were applied. For those devices the accuracy of ± 0,01 MPa for the measurement extend of 0÷5 MPa and ± 0,03 MPa for measurement extend of 0÷10 MPa were used. This diversity results from transformation of measurement impulses on the pressure value during different signals amplification in the amplifier and oscilloscope.

The measurements of pressure in the combustion chamber were carried out for:

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4. Research results

Disposing of actual pressure processes it was possible to indicate the values of angles of the combustion beginning – table 4.1.

**Table 4.1. Angles of combustion beginning for different conditions of engine working**

<table>
<thead>
<tr>
<th>Angle of the beginning of fuel squeezing °OWK before GMP</th>
<th>Combustion beginning, °OWK before GMP</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1200 rot/min</td>
</tr>
<tr>
<td>Basic condition with catalyst</td>
<td>Basic condition with catalyst</td>
</tr>
<tr>
<td>-20</td>
<td>- 1,10</td>
</tr>
<tr>
<td>-23</td>
<td>- 3,24</td>
</tr>
<tr>
<td>-27</td>
<td>-11,00</td>
</tr>
</tbody>
</table>

From the data presented in the table above, it follows that in the case of external catalyst using, the combustion process begins earlier than in the engine of basic condition.

The combustion beginning is also a function of engine rotation speed and together with its increase, the combustion beginning moves towards external turn (GMP).

In the table 4.2 there were correlated values of pressures increase in the combustion phase for different conditions of engine working.

**Table 4.2. Pressure increase dp/dα in the combustion phase for different conditions of engine working.**

<table>
<thead>
<tr>
<th>Angle of the injection timing [°CA]</th>
<th>dp/dα, MPa/°OWK</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>1200 min⁻¹</td>
</tr>
<tr>
<td>Basic condition with catalyst</td>
<td>Basic condition with catalyst</td>
</tr>
<tr>
<td>-20</td>
<td>0,43</td>
</tr>
<tr>
<td>-23</td>
<td>0,29</td>
</tr>
<tr>
<td>-27</td>
<td>0,64</td>
</tr>
</tbody>
</table>

The abovementioned research material indicates that, for the angles of squeezing beginnings of 20 and 23 degrees before the external turn the value dp/dα are higher for the engine working conditions with internal catalyst than those for the basic conditions. Only for 27 degrees angle and the speed of 1200 and 1400 rotations/minute diverse relationship was observed. The lack of clear tendency may be explained by the chance of angle optimum in the squeezing beginning for the engine with catalyst and thus, it is necessary to work out further researches towards optimizing engine regulations.

5. Conclusions

From what has been presented it follows that the use of internal combustion catalyst shortens the ignition delay of about 1 to 3 degrees of crankshaft rotation. Shortening of ignition delay essentially influences the improvements of engine working parameters, especially in the aspect of using fuels with variable composition and properties like biofuels. The use of internal catalyst decreases engine sensitivity to fuel properties, which allows to use fuels of lower quality that usually show increased angle of ignition delay, without adverse impact on combustion process and harmful fumes components emission.

6. Literature

4. KAVTARADZE R., ZEILINGER K., ZITZLER G.: Ignition delay in a diesel engine utilizing different fuels; High Temperature, Vol.43, No.6, 2005, pp. 951-960,