Influence of the Thermodynamic Characteristics of the Combustion Process on Vehicle Emissions in Spark-Ignition Engines

N M Smolenskaya\textsuperscript{a}, V V Smolenskii\textsuperscript{b}
Togliatti State University, Togliatti, Russian Federation
E-mail: \textsuperscript{a}Nata_smolenskaya@mail.ru, \textsuperscript{b}Biktor.cm@mail.ru

Abstract. The paper deals with the influence of the thermodynamic characteristics of the combustion process on toxicity in spark-ignition engines using the example of the UIT-85 single-cylinder unit. The studies were conducted on compressed natural gas and compressed natural gas with the addition of hydrogen gas. Also shown is the relationship of exhaust toxicity with the flame conductivity characteristic, reflecting the intensity of the combustion process in the flame front.

1. Introduction

Thermodynamic characteristics of the combustion process reflect in an integral form all its main manifestations. An analysis of the presence or absence of a relationship between the various thermodynamic characteristics and the main toxic components of the engine exhaust gases shows us how best to influence the workflow to ensure the necessary toxicity reduction. This analysis allows you to better identify those ways of influencing the workflow that will bring the greatest effect of reducing toxicity. This analysis was performed for compressed natural gas and compressed natural gas (CNG) with hydrogen additives. These fuels are currently considered the most likely alternative to liquid hydrocarbon fuels [1,2].

2. Experimental technique

Experimental studies were carried out on a single-cylinder UIT-85 installation (Figure 1a). Include information about the geometric parameters of the engine UIT-85: number of cylinders – 1; working volume – 0.652 liter; compression ratio – 7; diameter of the cylinder – 85 mm; piston stroke – 115 mm; length of connecting rod – 266 mm; rotational speed – 900 rpm; ignition – spark plug, at a fixed ignition advance angle of 13 BTDC for a more visual comparison of the results obtained.

Figure 1. Single-cylinder research unit UIT-85: (a) general view of the installation; (b) combustion chamber with installed sensors.
The portable gas analyzers «META» Avtotest-01.03P and Avtotest-02.03P determined the concentration of toxic components (NO$_x$, CH and CO) in the exhaust gases. The measurement error on the passport of the gas analyzer is 5%. The pressure in the engine cylinder was measured with a Kistler pressure sensor. Local conditions of propagation of the flame front was determined by means of sensors of ionization.

3. Results and Discussion

The most obvious picture of toxicity is given by characteristics not relative (“ppm” or “%”), but absolute [3]. For example, the amount of toxic components in one four-stroke cycle. Therefore, figures 2 and 3a show the toxicity characteristics in mg / cycle when working on CNG and CNG with hydrogen. The characteristics in Figures 2 and 3a are given to better understand the influence of the thermodynamic characteristics of the combustion process on toxicity in spark ignition engines [4,5].

![Figure 2](image1.png)

**Figure 2.** The concentration of toxic components in the exhaust gases for UIT-85 when operating on CNG and CNG with hydrogen: (a) carbon monoxide (CO); (b) nitrogen oxides (NO$_x$).

![Figure 3](image2.png)

**Figure 3.** Characteristics of toxicity and temperature in UIT-85 when operating on CNG and CNG with hydrogen: (a) unburned hydrocarbons (CH); (b) the relationship of the temperature of the end of combustion with the maximum temperature of the cycle.
Also for clarity, Figure 3b shows the linear relationship between the maximum temperature of the cycle and the temperature at the end of the combustion process. These temperatures reflect two main problem points actively influencing the formation of toxic components in the combustion process. Namely: the maximum temperature reflects the maximum rate of oxidative reactions, and the temperature of the end of combustion reflects the thermodynamic conditions at the completion of active oxidative reactions due to the completion of the combustion process.

When analyzing the experimental data, it was found that both temperatures considered have an impact on the toxicity of exhaust gases. Figures 4 and 5a show graphs for those temperatures whose effect is more linear. Assessing the relationship of carbon monoxide (CO) toxicity with the temperature of the end of combustion (Figure 4a), we note that for mixtures rich in oxygen, the amount of CO is minimal. For mixtures with a small lack of oxygen, an increase in CO toxicity is observed, but it is associated with a lack of oxygen, and no significant temperature effect was detected. The same applies to mixtures with a significant lack of oxygen, where there is an increase in CO toxicity with decreasing temperature. The decrease in temperature occurs due to an excessive decrease in the rate of heat generation when the mixture is enriched with fuel, starting with excess air coefficients less than 0.9. The toxicity of nitrogen oxides (NO\textsubscript{x}) is more influenced by the maximum temperature in the engine cylinder (Figure 4b). Here the effect of temperature is obvious. So for mixtures with an excess of oxygen, the main mechanism for the formation of NO\textsubscript{x} is a thermal mechanism, which, according to many authors, accounts for more than 90% of NO\textsubscript{x} in exhaust gases [6,7]. We see that this assumption also holds in our results. NO\textsubscript{x} toxicity has a maximum for mixtures with an excess of oxygen in the region of the air excess factor of 1.05 – 1.1, where the temperature corresponds to 2900 – 2950K. Then there is a drop in temperature, which leads to a decrease in NO\textsubscript{x}. At maximum cycle temperatures of 2600K and below, or 2450K and below, a sharp decrease in the effect of temperature on NO\textsubscript{x} toxicity is observed for the temperature of the end of combustion [8,9]. This effect suggests that starting from a maximum temperature of 2600K and 2450K for the temperature of the end of combustion, the amount of thermal NO\textsubscript{x} decreases sharply, and a significant contribution is made by the NO\textsubscript{x} formation mechanism in the flame front (fast NO\textsubscript{x}) [9,10]. This mechanism is practically the only one in the combustion of a mixture with a significant lack of oxygen. This is observed for mixtures with an air excess ratio less than 0.94. NO\textsubscript{x} formed in the flame front is affected by the rate of chemical reactions and their energy intensity, which is reflected by an increase in NO\textsubscript{x} with increasing combustion temperature. It should also be noted that both mechanisms have approximately equally affecting the formation of NO\textsubscript{x} in mixtures with a slight lack of oxygen [10]. The formation of NO\textsubscript{x} is determined by the temperature characteristics and the amount of oxygen, and the chemical composition of the fuel has no fundamental effect on the formation of NO\textsubscript{x}.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure4.png}
\caption{The relationship of temperature with toxic components in the exhaust gases: (a) the connection of carbon monoxide (CO) with the temperature of the end of combustion; (b) the relationship of nitrogen oxides (NO\textsubscript{x}) with the maximum temperature cycle.}
\end{figure}
Consider the effect of temperature on the formation conditions of unburned hydrocarbons (CH) in an engine cylinder (Figure 5a). From figure 5a, it can be seen that CH is practically independent of temperature during combustion. Their content is more dependent on the adequacy of oxygen for complete combustion and reduction of the total amount of burning hydrocarbons due to the replacement of hydrocarbon fuel (natural gas) with hydrogen, which is completely burned, taking oxygen with it. Therefore, for mixtures with a significant lack of oxygen, we cannot see a decrease in toxicity due to a lower CNG concentration with the addition of hydrogen. Considering the mechanisms of formation of CH in the engine cylinder, they mainly emit the mechanism of formation of CH in volume due to lack of oxygen or with a significant reduction in the rate of combustion. This leads to the breakthrough of unburned CH into the zone of combustion products, where oxidation processes are much less active. This mechanism, in addition to the composition of the mixture, is also reflected in the temperature of the combustion process [11]. It is seen that in our case, the combustion temperature exceeds 2400K. Therefore, a significant reduction in the rate of combustion in the studies was not observed. The second mechanism of CH formation is the mechanism associated with the breaking of the burning chains in the vicinity of the walls. Due to the active reduction of the temperature of the mixture at the wall due to heat sink into the wall [11]. The same mechanism takes place when the flame is attenuated in clamped volumes, which is, in our case, the area between the piston and the cylinder to the first compression ring. In our case, the design of the engine in the process of experiments has not changed. Therefore, we will not be able to track the effect of this mechanism. Consider the influence of the area of the walls of the combustion chamber at the moment of the end of combustion on the CH toxicity (Figure 5b). Figure 5b clearly shows the significance of increasing the wall area with an increase in the duration of the combustion process for CH toxicity. Taking into account that when working on mixtures with an excess of oxygen, we have complete combustion in the flame front. Therefore, the main source of CH will be the near-wall frozen layer, an increase in the area of which linearly affects the toxicity of CH. With a lack of oxygen, we also observe a linear relationship between the toxicity of CH and the area of the wall layer at the end of the combustion process. The obtained linear dependences show that CH formed in the volume due to the lack of oxygen is added to CH remaining in the wall layer. The influence of the fuel composition is determined only by the fact that the rate of combustion increases with the addition of hydrogen. This leads to a decrease in the area of the near-wall layer. No other toxicity reduction factors with the addition of hydrogen in CNG were detected during detailed thermodynamic analysis of the combustion process. This shows that although the addition of hydrogen and reduces the concentration of hydrocarbon fuels, in the process of combustion, hydrogen is completely burned taking oxygen. A more slowly burning hydrocarbon fuel, with a lack of oxygen in the mixture, it is also not enough. This leads to the fact that behind the flame front the amount of bulk hydrocarbons is determined by the general lack of oxygen and does not depend on the proportion of hydrogen in the fuel. Thus, we can say that hydrogen as a chemical element does not have an activating effect on the formation of the toxic components in question. Its influence affects the thermodynamic characteristics of the combustion process, which affect the conditions for the formation of toxic components.
Figure 5. The relationship of unburned hydrocarbons (CH) with the characteristics of the end of combustion: (a) the temperature of the end of combustion; (b) wall area at the end of combustion.

When analyzing the factors affecting the toxicity of CH, the dependence of the amount of CH in the exhaust gases with energy introduced with the fuel into the engine cylinder was detected (figure 6a). The results obtained in Figure 6a correlate well with the conclusions made above. Thus, an increase in the energy introduced into the cylinder with fuel with a lack of oxygen leads to a linear increase in the toxicity of CH. However, there is no separation of the results due to the addition of hydrogen to CNG [12]. This confirms the statement that hydrogen is completely burned, and the entire lack of oxygen falls on CNG. Therefore, the influence of the type of fuel in figure 6a for mixtures with a lack of oxygen was not detected. For mixtures with an excess of oxygen, a decrease in CH toxicity is due to faster burning in a smaller volume, which leads to the obtained results.

In addition to analyzing the influence of the thermodynamic characteristics of the combustion process on the toxicity of exhaust gases, an assessment was made of the possibility of determining the toxicity of exhaust gases of a spark-ignition engine using the flame conductivity characteristics. The main characteristic of the electrical conductivity of the flame is the magnitude of the amplitude of the ion current signal. The greatest correlation was shown by the amplitude of the ion current from the sensor installed 80 mm from the spark plug. In Figure 1b, it is designated as a electrical conductivity sensor 2. The best correlation of electrical conductivity on the sensor remote from the spark plug is explained by the fact that it is the characteristics of the completion of combustion that largely determine the toxicity of exhaust gases. Therefore, the comparison is made exactly by the electrical conductivity sensor 2. A comparison of the toxicity characteristics with the magnitude of the ion current signal amplitude is shown in Figures 6a, 7a, and 7b. Let us begin the analysis of the relationship between toxicity and electrical conductivity from Figure 6a, which shows CH toxicity. It may be noted that there is a clear correlation between CH toxicity and the amplitude of the ion current signal for mixtures that do not have an oxygen deficiency. At the same time, combustion with a lack of oxygen occurs at high rates of combustion, which leads to an increase in the ion current. But oxygen deficiency increases the amount of bulk CH, thereby making monitoring of CH toxicity over the signal amplitude for these compounds not possible.
Figure 6. The relationship of CH toxicity to the characteristics of the combustion process: (a) the relationship with the energy introduced into the cylinder with the fuel; (b) a relationship with the electrical conductivity of the flame at the end of the main phase of the combustion process.

For the association of NO\textsubscript{x} toxicity with the amplitude of the ion current signal (Figure 7a), a greater correlation is observed than with CH toxicity. So there is a clear correlation in the zone of mixtures with an excess of oxygen, where the thermal mechanism of NO\textsubscript{x} formation dominates. The characteristics of NO\textsubscript{x} toxicity in the zone of mixtures with a significant lack of oxygen are also well correlated, where the mechanism of NO\textsubscript{x} formation in the flame front is the main one. In the zone of excess air coefficients of 0.94 – 0.99, the electrical conductivity of the flame is at its maximum and varies slightly with the addition of hydrogen to CNG, which makes it difficult to assess toxicity in this range for all toxic components studied.

Considering the connection of CO toxicity with the amplitude of the ion current signal (Figure 7b), we can note the possibility of correlation only for mixtures with air excess factors less than 0.94. Since in the zone of excess air coefficient of 0.94 – 0.99, the correlation is difficult for the previously noted reasons. And in the zone of mixtures with an air excess factor of more than 1, CO toxicity has minimal values and varies by the level of gas analyzer error. Thus, an analysis of CO toxicity by flame conduction has no practical meaning.

Figure 7. Relation of toxicity with flame electrical conductivity characteristics at the end of the main phase of the combustion process: (a) connection with nitrogen oxides (NO\textsubscript{x}); (b) association with carbon monoxide (CO).
The results showed the significance of thermodynamic analysis to assess the potential for reducing toxicity of the main toxic components. The analysis showed that the perceived decrease in toxicity attributed to the properties of hydrogen activating the combustion process is not entirely correct. Hydrogen, as shown by thermodynamic analysis, leads to a change in combustion conditions. This results in an increase in temperature and a decrease in the surface layer at the end of combustion. At the same time, the data obtained suggests that having achieved the same thermodynamic characteristics by changing the degree of compression and the ignition timing, we obtain the same changes in toxicity as with the addition of hydrogen. Thus, hydrogen affects toxicity only within the framework of changes in the thermodynamic characteristics of the combustion process and is not a catalyst for the formation of toxic components. An analysis of the possibilities of regulating toxicity by the amplitude of the ion current in the flame front revealed some regularities. So, by the amplitude of the ion current, it is possible to effectively evaluate toxicities for NOx and CH in the area of mixtures with an excess air coefficient of more than 1, as well as toxicity for NOx in the area of mixtures with an air excess factor less than 0.94.

4. Conclusion

1. The effect of temperature in the combustion process on the mechanisms of the formation of NOx and CO is shown, taking into account the ratio of air to fuel.
2. It was found that by temperature and wall area at the end of the completion of combustion, it is possible to evaluate CH toxicity, taking into account the air-to-fuel ratio.
3. It was revealed that hydrogen has a significant effect on the thermodynamic characteristics of the combustion process, thereby affecting the engine's toxicity for CH, NOx, and CO. In this case, the effect of replacing the main hydrocarbon fuel to reduce toxicity as a consequence of a decrease in the concentration of hydrocarbon fuel in the engine cylinder was not detected. On the contrary, it is shown that the addition of hydrogen in CNG under the same thermodynamic conditions does not affect the toxicity of CH in the parietal layer or in the concentration of CH behind the flame front with the same lack of oxygen.
4. An assessment of the possibility of determining toxic components by the amplitude of the ion current showed the possibility of this approach in assessing toxicity of NOx and CH in the area of mixtures with an excess air coefficient of more than 1, as well as toxicity for NOx in the area of mixtures with an excess air factor of less than 0.94.

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