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Computer modeling of self-ignition delays of methane-alkane mixtures

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Abstract. The presence of high concentrations of heavy methane homologues with a low detonation resistance makes associated petroleum gases (APG) unsuitable for direct use as fuel for gas piston engines, which constitute the basis of distributed power generation grids in the range up to 5 MW. One of the most informative and demonstrative parameters that determine the detonation characteristics of gas mixtures is the self-ignition delay time. At present, there are no systematic data on the self-ignition delay times of even binary mixtures of methane with its heavier homologues, not to mention more complex compositions typical of APG The paper reports the results of computer simulation of the self-ignition delay times for binary and multiple methane-alkane-air mixtures containing C_2–C_5 alkanes.

1. Introduction

Associated petroleum gases (APG) are mixtures of light, C_1–C_5, and higher alkanes dissolved in oil, which are released from it when pressure drops as oil reaches the ground. In spite of all technological attempts and legislative measures, the utilization of APG remains one of the most complex problems of the modern oil and gas industry [1]. A significant part of the extracted APG can be used just on production sites, including offshore platforms, as a fuel to meet self-demand in heat and energy. Nevertheless, although the main component of APG, as that of natural gas, is methane, the presence of significantly higher concentrations of heavy methane homologues with a low detonation resistance makes APG unsuitable for direct use as fuel for gas piston engines, constitute the basis of a distributed power generation grid in the range up to 5 MW. In addition, the use of such gas leads to enhanced tar and soot formation in the engine, thereby decreasing of its life time [2].

The existing methods of extraction of heavier components from hydrocarbon gases are energy intensive and need complex equipment. They are unprofitable for small-scale power plants with a capacity below 5 MW. Therefore, as more economic and technologically simpler method for decreasing the content of heavier methane homologues in APG, their selective oxidative conversion into lighter and higher-octane compounds has been suggested [2–4]. In this case, both an increase in the methane number MN of the gas and a decrease in its lower caloric value *Q* are achieved [4]. However, the profitability of this and all other methods of extraction or chemical processing of these heavy components decreases sharply with increasing the depth of purification or conversion of these admixtures. Therefore, it is very important to determine the purification depth sufficient to ensure the required detonation resistance.

One of the most informative and demonstrative parameters that determines the detonation characteristics of gas mixtures is their self-ignition delay time. Unfortunately, systematic data on the self-ignition delay time are scarce even for binary mixtures of methane with its heavier homologues, not to mention more complex compositions, typical of real APG. Apart of our preceding works [5–7] on the low-temperature self-ignition of binary mixtures of methane with C_3–C_5 alkanes, it is possible to mention only two recent publications [8, 9].

Recently, we have done a more thorough and systematic experimental investigation on the self-ignition of complex hydrocarbon mixtures, including those modeling real APG. With the use of the method of self-ignition of gas–air mixtures in the Closed Bomb Reactor [10], the self-ignition delay times for stoichiometric compositions of air with binary, triple, and multi-component mixtures of methane with normal alkanes C_2–C_6 (up to 10%) at temperatures of 523÷1000 K and a pressure of 1 atm were measured [11]. It was found that the addition to methane of only 1% of any of C_2–C_6 alkanes decreases its self-ignition delay time by a factor of 2 to 3. Addition of 10% of any of these alkanes makes the self-ignition delay practically indistinguishable from that of the added alkane. Interestingly, ethane addition produces at least the same promoting effect as additions of propane and butane do. In triple and more complex mixtures, the self-ignition delay time is determined by the total sum of added alkanes, being practically independent of their particular fractions within the experimental error.

It would be interesting to reproduce these nontrivial results by computer simulations and to find out whether the available hydrocarbon oxidation models can successfully predict the self-ignition delay times of complex methane-alkane mixtures. Such a possibility would allow estimating the detonation parameters of APG from different sources without performing expensive experimental tests.

This paper reports the results of computer simulations of the self-ignition delay time for binary and complex methane-alkane-air mixtures containing C_2–C_6 alkanes. The simulations were carried out using the NUI Galway kinetic scheme [12], which has demonstrated the ability to successfully describe low-temperature combustion processes. The model includes 293 chemical components and 3152 elementary stages and incorporates sub models for oxidation of hydrogen, carbon monoxide, and C_1–C_5 alkanes [13]. It was used in the Calorimetric Bomb Reactor (CBR, V, Q = const) implementation. The results were found to compare favorably with the data obtained from task-specific experiments performed in the Closed Bomb Reactor [11].

2. Kinetic modeling of the self-ignition delay time for binary methane-alkane mixtures

Along with experiment, the kinetic modeling of complex chemical processes long ago became an indispensable investigation tool. Although, there are a number of published detailed kinetic models with high predictive possibilities for capable of efficiently simulating the oxidation of methane at temperatures below 1000 K [14], there are practically no reliable and verified kinetic models for the oxidation of heavier alkanes in this temperature range. In the present study, simulations were performed using the NUI Galway kinetic model [12], which, however, is restricted to C_1–C_5 hydrocarbons.

Figures 1–3 compare experimental results and kinetics model predictions for the self-ignition delay times of stoichiometric mixtures of methane with ethane, propane and n-butane additions in air [15].

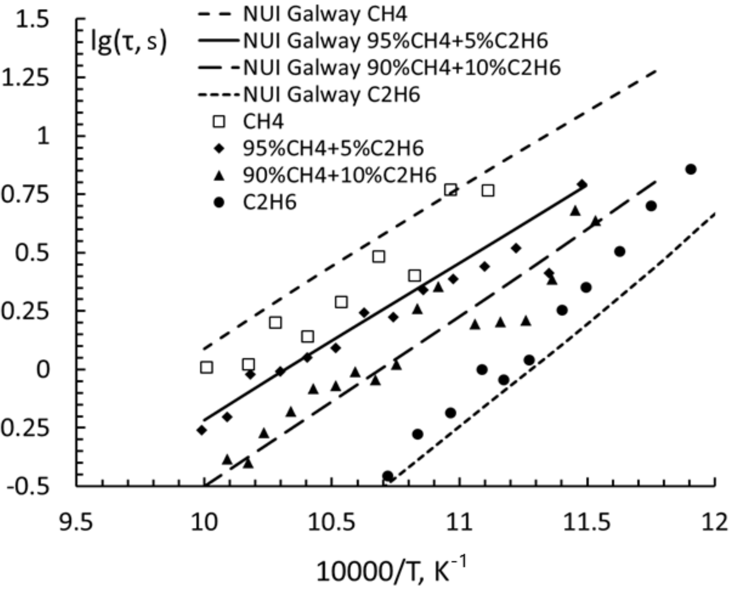

Figure 1. Temperature dependence of the self-ignition delay times of stoichiometric methane-air and ethane-air mixtures and binary mixtures of methane with 5% and 10% ethane additives in air. Symbols and lines represent, respectively, experimental data and the results of calculations by the NUI Galway mechanism. $P_0 = 1$ atm.

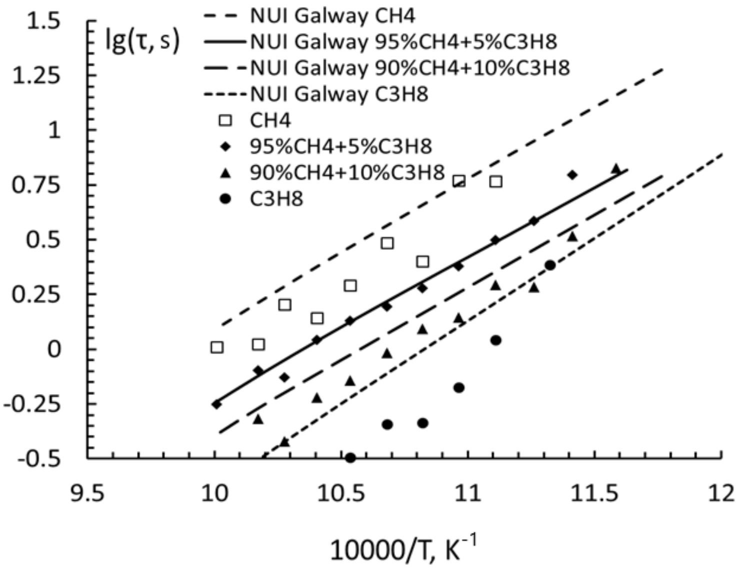

Figure 2. Temperature dependence of the self-ignition delay times of stoichiometric methane-air and propane-air mixtures and binary mixtures of methane with 5% and 10% propane additives in air. Symbols are experimental results, whereas lines are calculations within the framework of the NUI Galway mechanism. $P_0 = 1$ atm.

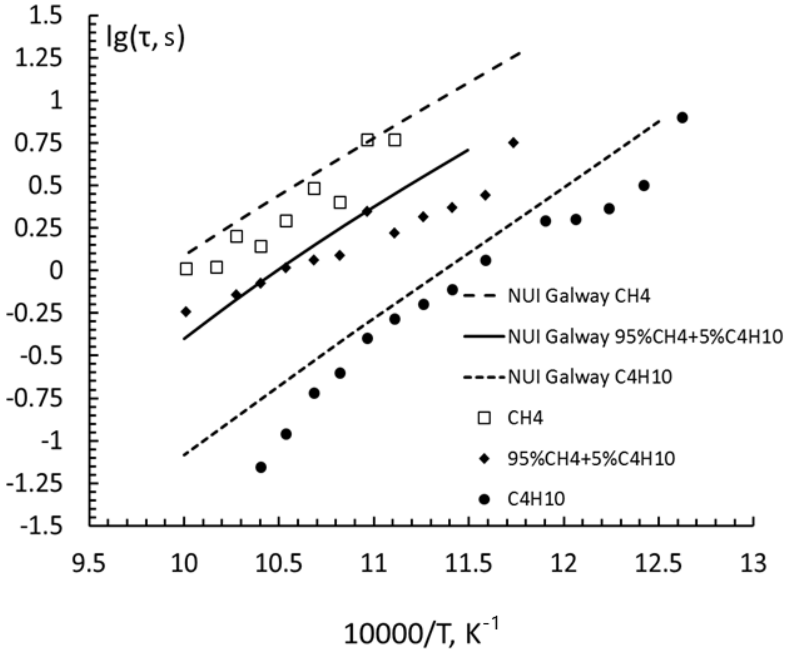

Figure 3. Temperature dependence of the self-ignition delay times of stoichiometric methane-air and *n*-butane-air mixtures and binary mixtures of methane with 5% *n*-butane in air. Symbols and lines are respectively experimental results and calculations by the NUI Galway mechanism. $P_0 = 1$ atm..

As it can be seen, calculated values of the self-ignition delay times of stoichiometric methane-alkane-air mixtures agree well with experimental data for temperatures below 1000 K. Therefore, we believe that it is possible to use NUI Galway mechanism for analysis of experimental data on the self-ignition of binary methane-alkane mixtures.

The calculations were performed for α_j,

$$\alpha_j = \frac{X_{jF}}{\sum_{jF}^{L} X_{jF}} \tag{1}$$

– the fraction of the *j*th alkane in the fuel, where X_j is the mole fraction of the *j*th component in the gas mixture, L is the number of paraffin hydrocarbons in the fuel. The index *jF* attributes the *j*th component to paraffin hydrocarbons.

The calculations with the use of the kinetic model [12] confirmed the conclusion drawn from experimental results in [11] that the self-ignition delay time of stoichiometric methane-propane-air mixtures at a pressure of 1 atm and temperatures of $800 \le T(\text{K}) \le 1000$ can exceed that of methane-ethane-air mixtures, all other things being equal. This tendency holds over a larger part of this temperature interval if the fractions of ethane and propane are identical. At the same time, calculations show that, at T = 800 K, the self-ignition delay time for methane-ethane mixtures is longer. Figure 4 demonstrates the temperature dependence of the self-ignition delay time for stoichiometric methane-ethane-air and methane-propane-air mixtures at $800 \le T(\text{K}) \le 1000$ and atmospheric pressure for $\alpha_{C_3H_8} = \alpha_{C_2H_6}$.

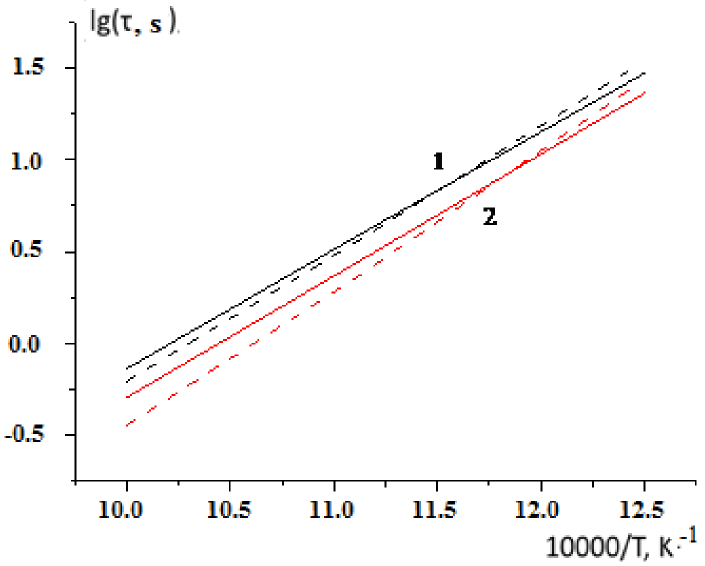

Figure 4. Calculated temperature dependence of the self-ignition delay for stoichiometric methane-ethane-air (dashed lines) and methane-propane-air (solid lines) mixtures at $P = 1$ atm and (1) $\alpha_{C_3H_8} = \alpha_{C_2H_6} = 5\%$ and (2) $\alpha_{C_3H_8} = \alpha_{C_2H_6} = 10\%$

The results obtained show that due to the difference in the activation energies of the self-ignition delay time of the different alkanes, their relative influence on the self-ignition of methane can change and be different in various temperature ranges. This result is very important from the practical point of view, since it shows that the relative influence of various alkanes on the detonation behavior of natural gas and APG can depend on the particular type of engine and the regime of its operation.

3. Kinetic modeling of the self-ignition delay times of triple mixtures of alkanes

Based on a comparison of experimental data on self-ignition delays, the authors of [11] have drawn an unexpected conclusion, very important from the practical point of view, that, in the first approximation, the effects of C_2–C_5 alkanes, individually or in any combination, on the self-ignition delay time of methane are very similar. Moreover, it was concluded that the added hydrocarbons influence each other so as to decrease the self-ignition delay time below the level provided by each of them individually (synergetic effect). Nevertheless, taking into account the spread of the experimental data in [11], this hypothesis needed theoretical justification.

The kinetic modeling demonstrated satisfactory agreement with the experimental results for triple methane-ethane-propane, methane-ethane-butane, and methane-ethane-pentane mixtures. What is more, the modeling has confirmed the existence of a weak synergetic effect for the self-ignition delay time at similar concentrations of heavier alkanes added to methane. As an example, the Figure 5 compares the calculated and experimental results on the self-ignition delay time for CH_4–C_2H_6–C_4H_{10}–air stoichiometric mixtures at an initial temperature of 900 K, atmospheric pressure, and $\alpha_{C_2H_6} + \alpha_{C_4H_{10}} = 10\%$, $\alpha_{CH_4} = 90\%$. Similar results were obtained when propane in the mixture was substituted by butane or pentane.

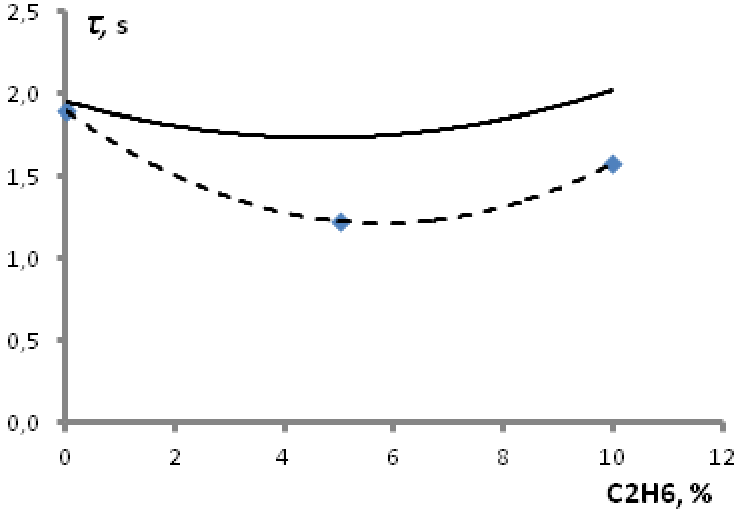

Figure 5. Dependence of the self-ignition delay time for CH_4–C_2H_6–C_4H_{10}–air stoichiometric mixtures on the concentration of ethane at $T = 900$ K and $P = 1$ atm. The solid line represents the results of kinetic simulations, and symbols and the dashed line represent experimental results from [11].

4. Analytical calculation of the self-ignition delay time for binary and triple methane-alkane-air mixtures

Given that rapid analytical analysis or even rough preliminary estimation of the detonation parameters of complex hydrocarbon mixtures are great practical significance; this possibility was examined for binary and triple methane-alkane-air mixtures. An expression for the self-ignition delay time of binary methane-alkane mixtures at atmospheric pressure was obtained for temperatures of $800 \leq T_0(K) \leq 100$ and mole fractions of added alkane of $0.01 \leq \alpha_{C_nH_{2n+2}} 0.2$ $(n > 1)$ in the form

$$\tau = A \exp\left(\frac{B}{T_0}\right) \gamma X^{\nu} \tag{2}$$

where A=3.46·10^{-7} s and B=1.52·10^{4} K. At $\alpha_{C_nH_{2n+2}} \leq 0.01$, expression (2) becomes much more complicated. The values of coefficients γ and ν depend on the initial temperature and number of carbon atoms n in the alkane molecule (Table 1). Only for propane, these coefficients are independent of T_0.

Table 1. Coefficients in expression (2) for the self-ignition delay of binary methane-alkane-air mixtures at $P = 1$ atm.

n[a]	$T_0 = 800$ K	$T_0 = 850$ K	$T_0 = 900$ K	$T_0 = 1000$ K
2	$\gamma = 0.1$ $\nu = -0.303$	$\gamma = 0.0456$ $\nu = -0.422$	$\gamma = 0.0247$ $\nu = -0.52$	$\gamma = 0.01133$ $\nu = -0.642$
3	$\gamma = 0.455$ $\nu = -0.428$	$\gamma = 0.455$ $\nu = -0.428$	$\gamma = 0.455$ $\nu = -0428$	$\gamma = 0.455$ $\nu = -0.428$
4	$\gamma = 0.0332$ $\nu = -0.453$	$\gamma = 0.0259$ $\nu = -0.497$	$\gamma = 0.0205$ $\nu = -0.525$	$\gamma = 0.0129$ $\nu = -0.569$
5	$\gamma = 0.0161$ $\nu = -0.535$	$\gamma = 0.00751$ $\nu = -0.653$	$\gamma = 0.00431$ $\nu = -0.747$	$\gamma = 0.00259$ $\nu = -0.832$

[a] n is the number of carbon atoms n in the alkane molecule.

The expression for the self-ignition delay time of methane-alkane 2-alkane 3-air triple mixtures is given by

$$\tau = A\exp\left(\frac{B}{T_0}\right)\gamma(X_{F2} + X_{F3})^{\nu} \tag{3}$$

where X_{F2}и X_{F3} are the mole fractions of alkane 2 and alkane 3 in the triple mixture. The parameters A and B are the same as specified above, with the parameters γ and ν defined as

$$\gamma = 0.5 * \left[\frac{X_{F2}}{(X_{F2})_b}\gamma_{F2}(T_0) + \frac{X_{F3}}{(X_{F3})_b}\gamma_{F3}(T_0)\right] \tag{4}$$

$$\gamma = 0.5 * \left[\frac{X_{F2}}{(X_{F2})_b}\nu_{F2}(T_0) + \frac{X_{F3}}{(X_{F3})_b}\nu_{F3}(T_0)\right] \tag{5}$$

where $(X_{Fj})_b$ is the mole fraction of the jth alkane in the methane-alkane j-air mixture at the same value of α_j as in the triple mixture. The values of $\gamma_{Fj}(T_0)$ and $\nu_{Fj}(T_0)$ are listed in Table 1 for the particular hydrocarbon at temperature T_0.

Figure 6 demonstrates a satisfactory agreement between the dependences of the self-ignition delay time for methane-ethane-propane-air mixtures on the concentration of added ethane as calculated by the reduced kinetic model and by expression (3).

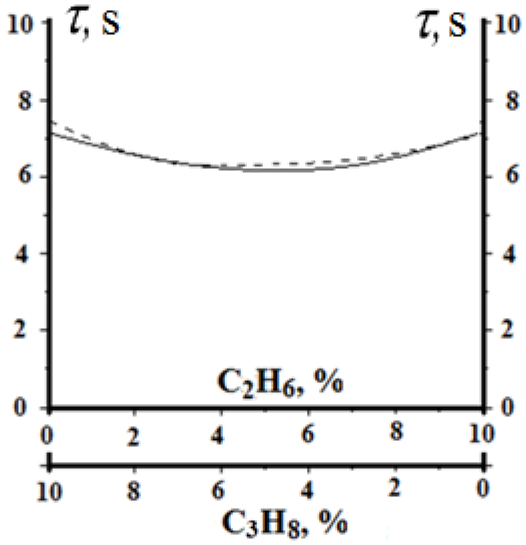

Figure 6. Dependences of the self-ignition delay time for methane-ethane-propane-air mixtures on the concentration of added ethane, as calculated by kinetic model (solid line) and by expression (3) (dashed line) at $\alpha_{CH4} = 0.9$, $\alpha_{C3H8} = 0.1$, $T_0 = 850$ K, and $P = 1$ atm.

5. Conclusions

The results of computer simulations of the self-ignition delay times of binary and complex methane-alkane-air mixtures with C_2–C_5 alkanes shows that the most elaborated kinetic models, specially adjusted for describing the oxidation of light alkanes at moderate temperatures, closely reproduce the self-ignition delay times of complex mixtures of light alkanes.

The kinetic modeling confirmed the existence of a weak synergetic effect for the self-ignition delay time at similar concentrations of two heavier alkanes added to methane.

It was demonstrated that, due to the difference in the activation energy of self-ignition delay for different alkanes, their relative influence on the self-ignition of methane varies, being different in different temperature ranges. This result shows that the relative influence of various alkanes on the detonation behavior of natural gas and APG can depend on the type of engine and the regime of its operation.

6. Acknowledgments

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