JOURNAL OF PROPULSION AND POWER
Vol. 18, No. 5, September–October 2002

Influence of Radical Concentration and Fuel Decomposition on Ignition of Propane/Air Mixture

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A study of hydrocarbon fuel (propane) thermal decomposition was conducted by varying the temperature and pressure of air/fuel mixtures and determining their effect on the degree of fuel decomposition and its attendant product composition. Based on the composition data, the concentrations of low molecular weight components and active radicals were found. Intensification of the combustion process due to an increase in fuel reaction activity resulting from fuel thermal decomposition is demonstrated, and the effect of thermal decomposition resulting in a decrease in ignition delay time is shown. It is also shown that intensification of the fuel/air reaction is possible through the addition of active radicals such as O, OH, and H. The character of the extraequilibrium radical concentrations change, dependent on the conditions of the combustion processes parameters, is determined.

Nomenclature

C = concentration
G = component mass fraction
M = Mach number
P = pressure
T = temperature
t = time
Z = degree of fuel decomposition
ϕ = fuel/air equivalence ratio

Subscripts

a = air
c = combustion
d = decomposition
f = fuel
ind = induction
mix = mixture
q = maximum heat release rate

Introduction

NUMEROUS experimental investigations and computations show that there are serious difficulties with sustaining ignition and efficient combustion of hydrocarbon fuels in devices such as combustion chambers for ground power plants, gas-turbine engines, and ramjet combustors.[1–4]

The static pressure and temperature at the combustor entrance for typical flight trajectories of vehicles powered by airbreathing ramjet engines from $M = 4–8$ are in the range $P = 0.04–0.08$ MPa and $T = 500–950$ K, respectively. Flow velocities V are in the range $0.9–1.6 \times 10^3$ m/s. Consequently, residence times for air/fuel mixtures with combustor lengths of 1–2 m are not more than 1–2 ms. For effective combustor operation under the assumption of diffusion-limited combustion, the value of the induction (self-ignition delay) time t_{ind} must be an order of magnitude or more lower than the residence time.

For example, for stoichiometric ($\phi = 1$) hydrogen/air mixtures, the value of t_{ind} for the flow parameters just listed varies between 10 and 0.1 ms. It is, therefore, not possible to initiate combustion based on self-ignition of these fuel/air mixtures,[5] particularly at the lower flight speeds. Previous evaluations have shown that the self-ignition time delay should not surpass 10–20% of the total combustion time. Thus, for efficient combustion under diffusion or homogeneous combustion mechanisms, t_{ind} should not be more than part of a millisecond. The addition of 20% by weight silane (SiH_4) in hydrogen decreases this value to $t_{\text{ind}} = 0.4–0.05$ ms[1].

For room temperature hydrocarbon fuels, for example, kerosene, the values of t_{ind} increase to 10^2–10 ms, which is unacceptable for fuel self-ignition and efficient fuel/air combustion for these flight conditions. That is why, for high-speed engines, special devices such as plasma jet generators,[6] electric discharge spark plugs,[7] and/or pilot flames using self-igniting components[8] are considered for application. As a rule, these devices only affect the flow locally, and so are installed in regions of flow recirculation (regions of combustion flame stabilization). The local velocity defines the dimensions of the flame stabilization zone along with other flow parameters such as pressure P, temperature T, fuel/air equivalence ratio ϕ, and the physical dimensions of the flame holder. In this case, regimes of residual flames or flame spreading are realized.[8] Consequently, the results of this research could be applied not only to the whole flow in engine, but also to the flow in the flame stabilization zone.

Another ignition and combustion enhancement method is to use a gas generator to prepare the fuel for combustion. Definite success was achieved using gas generator schemes for the combustor operation of high speed airbreathing engines (ABEs).[9,10] However, application of special initiators for ignition, especially with thermal fuel cracking in the presence of water, need to be analyzed from the point of view of propulsion efficiency as a whole.

Presented as Paper 2001-3958 at the 37th Joint Propulsion Conference, Salt Lake City, UT, 8–11 July 2001; received 14 August 2001; revision received 15 May 2002; accepted for publication 20 May 2002.

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Along with the preceding ignition and combustion intensification methods, using the burning of fuel thermally decomposed (cracked) products (FTDP) is another possible ignition and combustion enhancement method because the fuel may be used for cooling of the airframe and engine structural elements. It is expected that these thermal decomposition products are more chemically active than the original fuel because of the increased fuel enthalpy, changing chemical composition, and the presence of active radicals, all of which would intensify the combustion process.[4,11–13]

Another way to increase fuel reaction activity is to saturate the air/fuel mixture with active radicals. This can be achieved, for example, by initiating an energetic discharge into one or both reactant streams. Other approaches include the injection of precombustion products containing high concentrations of radicals, or photochemical method of active-species injection when additional radicals are formed as a result of radiation-induced decomposition of a reagent.

The current analysis will be framed by the effect that these active radical species have on the ignition time delay t_{ind}, without considering the details of how these active species are formed or the mechanism of their injection into the combustion system. In this paper, only one of these effects has been investigated numerically, namely, the impact of the radical concentration in the air/fuel mixture on the characteristic ignition delay time, which specifies the fuel reactivity. Currently, there is a lack of evidence for the matter in question, and, therefore, further research is required.

The present research evaluates, within the framework of existing kinetic schemes, the possible intensification of the ignition and combustion processes by means of an increase in a hydrocarbon fuel's reactivity. The effects of fuel thermal decomposition and potential increases in radical concentration on the ignition-delay time (or other parameters that characterize the combustion process) have been investigated. This includes the influence of the lifetime of the active radicals on the combustion.

Statement of Work and Method of Study

Defining thermal decomposition effects on fuel kinetic activity requires solving two methodical problems. The first is to choose a representative model of the fuel, and the second is to choose a parameter (or parameters) that characterize the ignition and combustion enhancement phenomena.

The model used for the fuel should have the same energetic performance as the actual fuel. In addition, the model fuel nonequilibrium species and radicals, as well as the thermally cracked equilibrium species created during thermal decomposition, must be accurately represented during the analytical investigations. This is provided by the use of modern kinetic modeling schemes.

Information on traditional kerosene-based fuels, which are commonly used in ABEs is not well defined. Although their energetic performance provides good performance for a wide variety of flight vehicles,[3,4,9–11] there are not sufficiently verified chemical kinetics representations of these fuel/air reactions. Consequently, the computed details of the chemical mechanisms for the combustion and thermal decomposition processes, as well as the nonequilibrium kinetics, are not well defined. This same situation exists with the experimental data; the authors publish, as a rule, only information on the degree of gas formation Z (degree of decomposition or cracking) vs fuel temperature and time of heating. There is a rather limited amount of information on gas composition published, due, in part, to the complexity of their measurement in these nonequilibrium cracking processes.[12,13]

Sometimes for simplified evaluation of the gas composition during the decomposition process, equilibrium thermodynamic calculations are used. They permit concentrations of the cracked fuel components to be calculated as a function of the thermodynamic properties for the special case of thermochemical equilibrium, where $Z = 1$ (Refs. 9 and 14). Using such a method to define the gas composition limits its use to define the composition of its reactive features. For that, it is necessary to consider the roles of independent processes during the cracking process and to conduct systematic comparisons of numerical and experimental data.

Published data on thermal cracking of individual hydrocarbons, such as n-pentane, n-heptane, n-octane, etc., gives more detailed information on the equilibrium and nonequilibrium kinetic performance compared to that observed in kerosene thermal cracking. Thanks to the application of free-radical mechanisms of pyrolysis,[14] the calculation of paraffin hydrocarbons' nonequilibrium decomposition becomes possible. The composition of the FTDP and effects of pressure, temperature, and degree decomposition Z on the mass fractions of the mixture's components can, thus, be defined. However, a description of the thermal decomposition using free-radical mechanisms requires special requirements to achieve the accuracy of, and confidence in, the applied kinetic schemes. Because of inaccuracies and shortages of approbation of detailed kinetics schemes, there is a rather large scatter of the global kinetic performance and FTDP composition.[12,14–16]

Taking into account the preceding discussions, propane (C_3H_8) was chosen to represent the kerosene hydrocarbon fuel model. There is a great deal of experience based on the combustion of C_3H_8, and propane's energetic (heat release) performance, in the first approximation, simulates most of the widely used kerosenes.[17–19] Detailed kinetic schemes of propane/air combustion are approbated well and can be found in many publications.[20–24] In this regard, the use of propane as the model fuel permits a methodical and nearly complete analysis of its reaction activity increase to be made when undergoing nonequilibrium thermal cracking. The results obtained will not only represent the individual performance of propane decomposition, but also provide the main tendencies for the thermal decomposition of the more complex hydrocarbons.

As was noted before, the second important issue is the choice of the parameter (or parameters) characterizing any ignition and combustion enhancement due to nonequilibrium chemical kinetics during the fuel thermal cracking process. It is known that in the case of combustion in a well-stirred air/fuel mixture (homogeneous combustion), the reaction is characterized by the ignition time delay t_{ind} and combustion time t_c. Combustion in a nonstirred fuel/air mixture (diffusion controlled combustion) has additional spatial resolution (and concomitant computational) problems, and so this analysis is more difficult. In the framework of this research, only homogeneous combustion was investigated.

In practice, there are some difficulties concerning the definition of t_{ind}. This is because it is defined as the time in a reacting mixture after which combustion becomes appreciable, and this is rather subjective. For example, when t_{ind} is defined in practice, it is the time necessary to visually observe the initiation of an intensive chemical reaction. However, when t_{ind} is analytically computed, it is necessary to define a specific value of the calculated temperature increase, otherwise consistent interpretation of the results is impossible. Also, the definition of t_c is connected with the necessity to take into account additional process performance, for example, the level(s) of heat or kinetic fuel combustion efficiency.

When these circumstances area taken into account, the time to reach the maximum rate of heat release t_q, was chosen as the parameter for evaluation of the fuel and FTDP reaction ability. For this moment of time in a homogeneous combustion process, the maximum rate of temperature increase is calculated. Preliminary calculations of combustion show that the time of maximum heat release is, as expected, between the induction time t_{ind} and combustion time t_c. Thus, this parameter characterizes not only the possibility of self-ignition, but also the possibility to realize, through the combustor (or residence time), intensive combustion. Also, this value is defined rather easily by analyzing the time–temperature dependence.

The first phase of the numerical research is devoted to the definition of both propane thermal decomposition degree Z and the composition of the gaseous mixture under different T and P. In the second phase, the combustion process of the C_3H_8, FTDP and air mixtures are studied.

Processes realized under the thermal decomposition and combustion of fuel and FTDP were calculated under the assumption of a one-dimensional model of the combustion process.[25] This model is based on the assumption that the mixing process (air with fuel and FTDP) is practically instantaneous. In such a way, the homogeneous combustion is modeled and, for this case, all of the characteristic times, t_{ind}, t_q, and t_c, are defined by only the kinetics of the chemical reactions.

The process of fuel thermal decomposition was calculated with the use of mathematical models based on a free-radical mechanism. The presence of such a mechanism during the decomposition process has been demonstrated experimentally.[14] Thus, it is possible to present the correct description of the fuel decomposition and combustion in the framework of the solution of the direct kinetics task. However, it is necessary to provide kinetics for all of the typical reactions, describing the break-up of large molecules and formation, merging, and recombination of radicals.

The following equations describe the combustion and destruction processes, distribution of the reactant concentration, and temperature along the reactor length:

$$U\frac{\mathrm{d}C_i}{\mathrm{d}x} = W_i \tag{1}$$

$$U\frac{\mathrm{d}H}{\mathrm{d}x} = 0 \tag{2}$$

where $t = X/U$ is time, X is coordinate directed along the reactor length, C_i is the ith reactant concentration, $i = 1, \ldots, n$, W_i is the ith reactant formation (or consumption) rate, H is the total mixture enthalpy, n is the total number of reactants, and U is the flow velocity.

Changing of the FTDP composition was calculated with Eq. (1) under the condition of reactant constant temperature, $T_f = \mathrm{const}$. To simulate the combustion process for the original fuel/air mixture with and without additional radicals, the detailed kinetics scheme was applied for hydrocarbons oxidation based on Refs. 22–24, 26, and 27. The scheme comprises 303 reactions between 60 components, including atoms H, O, C, N, and Ar. Constants of elementary reaction rates are adopted mainly from these references. Correction of the rate constants was conducted using the experimental data presented in Ref. 28. In Ref. 28, the ignition delay time behind a normal shock wave for mixtures of $C_3H_8/O_2/Ar$, $CH_4/O_2/Ar$, and others were measured. Thanks to this testing and subsequent correcting, a rather good correlation of the calculated t_i values with the data in Refs. 20 and 28 were obtained along with a good description of the equilibrium concentrations for the combustion products (at $t \to \infty$) in the frame of a one-dimensional mathematical model [Eqs. (1) and (2)]. Also, this correlation verifies that the values of t_q calculated will characterize correctly the process of combustion.

Calculation and Analysis of Propane Thermal Decomposition Peculiarities

It is assumed that the propane temperature T_f and pressure P_f are constant; the technical issues associated with defining the fuel state in heat exchanger–reactor were not considered. The calculations show that there is fuel decomposition at fixed values of T_f and P_f as the fuel heating time increases. This is manifested by a decreasing propane mass fraction in the mixture, the appearance of low molecular components, and a decrease in the mixture molecular weight.[12] The dynamics of the decomposition degree Z vs time is presented in Fig. 1 for $T_f = 950$–1300 K with $P = 1$ MPa. Here Z is the mass fraction of C_3H_8 forming low molecular components, and the value of Z is defined as $Z = 1\text{-}G_{\mathrm{C3H8}}$. The range of T_f was chosen to illustrate a case of an extremely fast rate of decomposition and a case with practically zero decomposition. It is proposed that, in a real device, the time of fuel preparation before its burning will not exceed 1 s, and so this time is considered in the calculations, and the results will be reduced by this value. It is proposed that an increase in T_f will provide an increase in the rate of decomposition. One can see in Fig. 1 that the value of $Z > 0.95$ at $T_f = 1300$ K is achieved for time 1–2 ms. For $T_f < 950$ K, there is very little decomposition during the whole period of time (1 s). In Ref. 20, it was noted, based on experimental data,[12] that there is negligible decomposition for $T < 900$ K and a time period of $\sim$1 s. This correlates well with the data in Fig. 1. Analysis of the Z changes with time shows that the gross-kinetic performance is qualitatively the same as for decomposition performance of paraffin hydrocarbons.

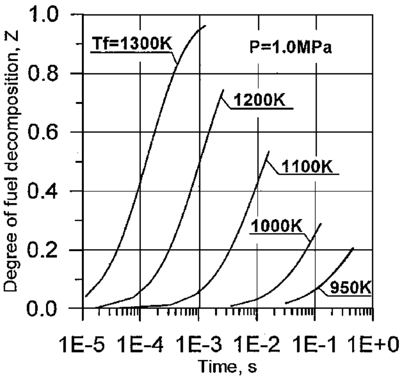

Fig. 1 Propane temperature T_f effect on thermal decomposition degree Z under constant pressure.

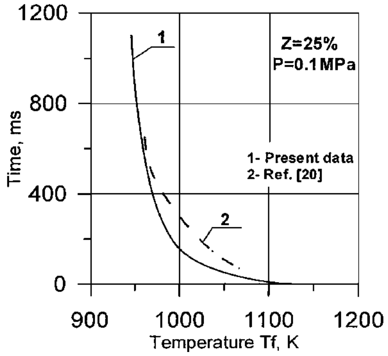

Fig. 2 Propane temperature T_f effect on necessary time for providing definite degree of propane thermal decomposition under pressure P = 0.1 MPa.

Comparison of the calculated data with the data for n-hexadecane decomposition,[15] for example, show it is possible to generalize these dependencies using the expression $1/Z = a \times 1/t + b$. Here, a and b are coefficients; the value of b for the data presented in Fig. 1 is equal to unity, and a is a constant of the reaction rate depending on T according to the exponential law $1/a = k \times \exp(-E/RT)$. Analysis of the Fig. 1 data shows the decomposition process of propane in a wide region of Z could be formally approximated by one-directed reaction of second order of type[29] $C_3H_8 + C_3H_8 \Rightarrow$ destruction products. This type of reaction is typical both for propane and other hydrocarbons having higher contents of carbon. Evaluations of the activation energy and preexponential factor for propane give $E = 266.8$ kJ/mol and $k = 3.4 \times 10^{14}$ 1/s, respectively. These values correlate well with E and k for hydrocarbons inclusive to n-hexadecane.[12]

Thus, the decomposition performance obtained for propane could be considered for other hydrocarbons as well. By the use of the preceding dependencies, it is possible to find the constant of the decomposition reaction rate and, consequently, the Z value. However, in practice, if the kinetics scheme is known, the value of Z could be found rather quickly and accurately under succeeding decomposition conditions.

Based on the Fig. 1 data, it is possible to find the effect of fuel temperature on the time t_z required to establish a definitive degree of Z. In Fig. 2, the influence of T_f on the time required to obtain $Z = 0.25$ at a pressure $P_f = 0.1$ MPa is given. Here, one can see the comparison with the data from Ref. 20. Note that a decrease in T_f sharply increases the decomposition time for the $Z = 25\%$ level. For a practical evaluation, it is possible to accept that a 10% increase in T_f leads to about an order of magnitude decrease in the time needed to achieve a given level of decomposition. It is necessary to emphasize the good correlation in Fig. 2 of the calculated and experimental decomposition times. This argues the validity of the chosen kinetics schemes and the results obtained therefrom. Obviously, under modeling of such a complex processes as fuel decomposition, accuracy of 50–70% is rather acceptable.

Table 1 Required time t_z (milliseconds) for completion of definite fuel decomposition degree Z

Z, %	$P_f = 0.05$, MPa	$P_f = 0.1$, MPa	$P_f = 1.0$, MPa	$P_f = 3.0$, MPa	T_f, K
20	0.1239	0.0865	0.0414	0.0296	1300
40	0.2374	0.1843	0.0946	0.0670	1300
60	0.4222	0.3460	0.1660	0.1376	1300
80	0.8797	0.6977	0.3567	0.3104	1300
20	10.367	7.2363	3.4189	2.4445	1100
40	20.465	16.590	8.8907	6.6680	1100
20	140.58	119.49	69.773	60.815	1000
20	742.56	631.18	427.56	372.40	950

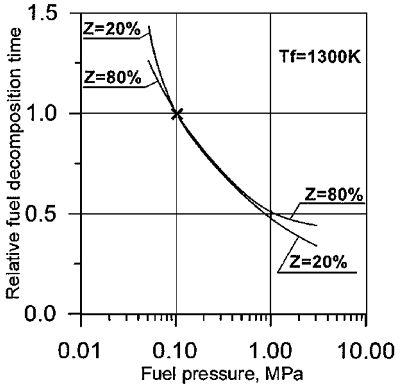

Fig. 3 Pressure effect on relative time of providing fuel decomposition.

In Fig. 3, the effect of pressure on the relative change of time t_z for a fixed value of $T_f = 1300$ K for $Z = 20$ and 80% is presented as a function of pressure. Values of the decomposition time t_z are given in Table 1. Increasing the pressure decreases the decomposition time, and for a wide range of pressures this influence is about the same. There is some difference, for $Z = 20$ and 80% only at very low pressure ($P_f < 0.1$ MPa) and very high pressure ($P_f > 1$ MPa) with the P_f effect being more pronounced at low Z values. There is also some effect at the lower values of T_f. It could be concluded that to provide higher Z levels under the limitations of process time and T_f, it is useful to conduct decomposition at higher pressures.

Side by side with the t_z, the composition of FTDP is an important performance parameter. As was mentioned before, low molecular weight components appear during the decomposition process. Within the modeling of thermal decomposition, the quantity of reacting components is defined by the type of accepted kinetics scheme. In our case, the quantity of such components was equal to 60. For analysis, it is enough to consider three groups of components. The first one involves components whose concentration could characterize the gross performance of the mixture and, partly, its conventional molecular weight. The second group involves the more chemically active components. The third is the active radicals in the mixture.

Results from these calculations show that the total performance of the decomposition process (and products) is defined by the following five decomposition components: propylene (C_3H_6), ethylene (C_2H_4), acetylene (C_2H_2), methane (CH_4), and hydrogen (H_2). The total concentration of these components for the considered regimes while taking into account the concrete degree of decomposition Z is more than 98%, and, consequently, there is a change in the conventional molecular weight. From comparison of the data in Ref. 20 with the present calculations, the same composition of decomposition products except acetylene is observed. Besides, the list of main components given in Ref. 20 is essentially the same both for propane and butane.

In Fig. 4, the effect of Z on mass fractions of the aforementioned components is presented. For illustration, two of the more important regimes of thermal decomposition were chosen. In the first, the values of T_f and P_f are close to maximums used in the calculations. In the second regime, they were close to the average values of T_f and P_f. Mass fractions of hydrogen and H radical for all of the investigated regimes at $Z = 25\%$ are given in Table 2. As seen in Fig. 4, changes of the main component concentrations reflect phase character. During the first decomposition phase at $Z < 60$–70%, a sharp increase of propylene is observed. Concentrations of another mixture components are very small, and it is possible to propose that propane transformed into the intermediate product (propylene). As was shown before, this process looks like a single reaction of second order. In the second phase, when the degree of decomposition is large and concentration of initial components small, formation of low molecular components in the mixture resulted in decreases in both the initial and intermediate components. Consequently, it is possible that this nonmonotonic character, along with the Z concentration such as for the propylene change, will be observed for another carbon containing specie (such as C_2H_4 or C_2H_2). However, this process will proceed only under very high ($Z > 95\%$) decomposition degrees, under which it is difficult to obtain high accuracy in the calculations. This is a result of the peculiarities of the code algorithm at large Z, which requires significant increases in calculation time without a decrease in accuracy at a given integration step. Definition of the decomposition products composition for $Z \rightarrow 1$ should be conducted in the framework of special numerical research.

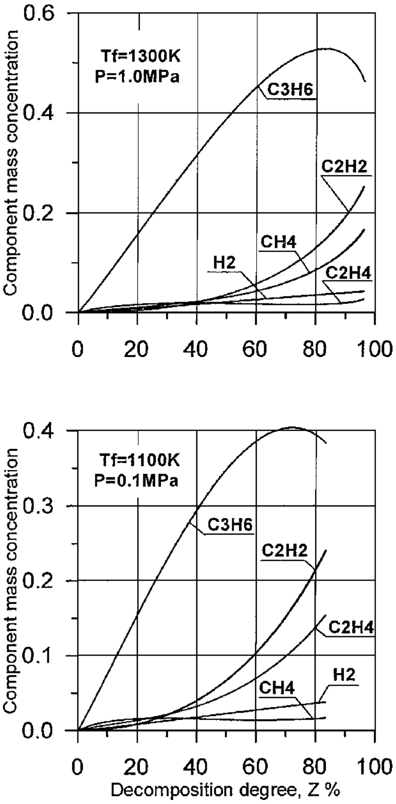

Fig. 4 Effect of fuel decomposition degree on gaseous component decomposition concentrations.

Analysis of the Table 2 data shows that an increase in the H_2 and H product mass fraction results from temperature increases. Moreover, the increase in H_2 concentration is small, but the growth of the H radical is equal to approximately four orders of magnitude. The pressure effect is rather small, especially at $T_f = 1300$ K. At low temperature, it is possible to increase the H_2 concentration, but the absolute value of H_2 in the decomposed products is very low, not more than 3–4%, even at Z close to one. The concentration of H also is very low. Thus, it is difficult to propose large benefits in the increase of reactive activity of decomposition products in comparison with the initial fuel without special fuel heating preparations.

Note that, in general, the effect of Z on the low molecular weight components is nonlinear, especially for such species as acetylene and methane. This is important when the operation process is organized in technical devices.

Table 2 Mass fractions of H_2 and H in propane decomposition products ($Z = 25\%$) at P_f = variable (Megapascal) and T_f = variable

	$T_{f,} K$				
Product	1300	1200	1100	1000	950
			$P_f = 3{,}0$		
H_2	9980×10^{-3}	1044×10^{-2}	9650×10^{-3}	6540×10^{-3}	3346×10^{-3}
H	1158×10^{-7}	1960×10^{-8}	2259×10^{-9}	1603×10^{-10}	3491×10^{-11}
			$P_f = 1{,}0$		
H_2	9736×10^{-3}	1019×10^{-2}	1000×10^{-2}	8640×10^{-3}	6371×10^{-3}
H	2654×10^{-7}	4411×10^{-8}	5083×10^{-9}	3607×10^{-10}	7731×10^{-11}
			$P_f = 0{,}1$		
H_2	1069×10^{-2}	1048×10^{-2}	1028×10^{-2}	1026×10^{-2}	9974×10^{-3}
H	1290×10^{-6}	1943×10^{-7}	2596×10^{-8}	2029×10^{-9}	4508×10^{-10}
			$P_f = 0{,}05$		
H_2	1059×10^{-2}	1038×10^{-2}	1018×10^{-2}	1016×10^{-2}	9881×10^{-3}
H	2061×10^{-6}	3104×10^{-7}	4148×10^{-8}	4117×10^{-9}	7202×10^{-10}

The model of the process used (again with other models, for example, that of Ref. 20) does not take into account coke formation during thermal decomposition. However, according to the thermodynamic calculations at $\phi \to \infty$, the mass fraction of condensed carbon can be up to 60–70%. This means that the increase in the reactivity of the decomposed products at Z increases is accompanied by the formation of condensed carbon. Some this carbon will enter into the combustor, but the main part of C will stay in the heat reactor, resulting in heat exchanger coking and a worsening of fuel energetic (heat absorption or cracking) performance. A study of coke formation is not a task of our research, but it is desirable to evaluate its effect on the energetic performance of practical devices in the future.

Effect of Fuel Thermal Decomposition on Enhancement of Its Reactive Activity

Combustion of propane and thermal decomposition products were calculated with the use of the same mathematical models (1) and (2) and kinetics schemes that were applied in the first section of this paper. It is known that the reactive ability of air/fuel or air/FTDP mixtures is characterized by the level of energy activation of the total combustion reaction. Definition of this parameter is based on calculation of the fuel ignition delay time. In this research, the time to obtain the maximum rate of heat release t_q, which was considered earlier, was accepted as such a parameter.

In Fig. 5, results of the t_q calculations for stoichiometric ($\phi = 1$) fuel/air mixtures at $P = 0.05$ MPa vs the value of $1000/T$ are presented, where T is initial mixture temperature. The four regimes of decomposition given in Fig. 5 were chosen to analyze the reactivity based on changes in the decomposition products for differing T_f and Z at constant $P = 1$ MPa. Note that the dependence t_q $(1000/T)$ is nearly linear, and any incoherence of the activation energy for these limiting reactions does not vary by more than 20%. In the case of hydrogen combustion, the activation energy is different for regions of low and high temperatures, with the main phase change at $T \approx 1000$ K (Ref. 5). Data presented on the decomposition products show the increase of reactive ability defined mainly by Z, but due slightly to the decomposition process temperature as well.

Curves 1–4 in Fig. 5 show decreases in the activation energy required under transition from propane to decomposed products of 3.2, 4.9, 9.4, and 12.2%, respectively, for the four example cases presented for a t_q of 1 ms. These are rather small in comparison with these same effects using hydrogen fuel. The increase in the FTDP reaction ability in comparison to when hydrogen is used, based on average values of activation energy, is equal to 20–25%.

More computation verification of the reaction ability increase is given in Fig. 6, where ratios of the t_q values for the initial hydrocarbon fuel and FTDP at combustion are presented. These data were obtained for the same regimes as those given in Fig. 5. The temperature of the mixture was changed by changing the air temperature, with the FTDP temperature being either $T_f = 1000$ or 1200 K.

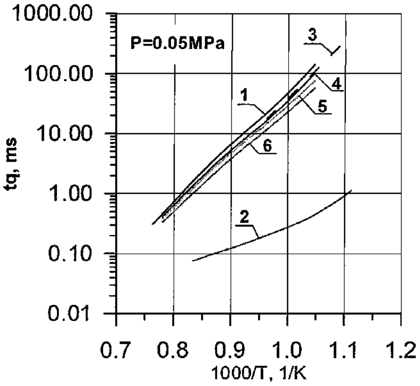

Fig. 5 Effect of stoichiometric air/fuel mixture temperature on time corresponding to maximal heat release rate at combustion: 1) C_3H_8, 2) H_2, and 3–6) products of fuel decomposition at $P = 1$ MPa and different T_f; 3) $T_f = 1000$ K, $Z = 25\%$; 4) $T_f = 1200$ K, $Z = 25\%$; 5) $T_f = 1200$ K, $Z = 50\%$, and 6) $T_f = 1200$ K, $Z = 75\%$.

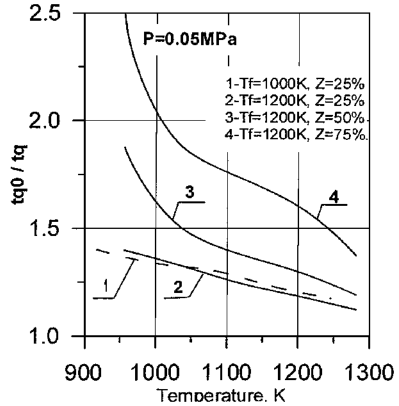

Fig. 6 Effect of air/fuel mixture temperature on decrease of time corresponding to maximal heat release rate at combustion of C_3H_8 decomposition products under $P = 1.0$ MPa.

First, Note that the effect of FTDP is more pronounced at low temperatures. For example, for $T_{\text{mix}} < 1000$ K, the decrease in t_q is approximately 2.5–3 times that of the reference value. At $T_{\text{mix}} > 1300$ K, this effect is less pronounced and, even at large Z, is not more than 20–30%. Also note that the effect of T_f on t_q is small. The data in Figs. 5 and 6 show that characteristics of t_q and t_{q0}/t_q are about the same vs mixture temperature T_{mix}.

Evaluations of the benefits of these ignition enhancements for high-speed ABE performance were also performed. In Fig. 7, the effect of air and fuel temperatures T_a and T_f on the ignition time

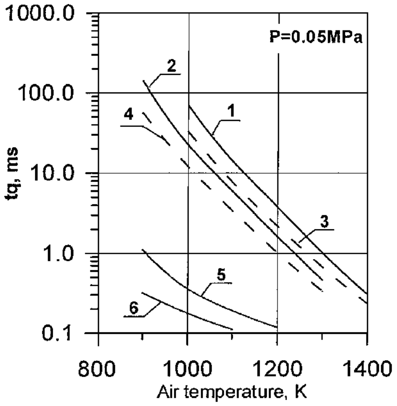

Fig. 7 Effect of air temperature on time corresponding to maximal heat release rate at stoichiometric combustion of air/propane mixture, products of its decomposition and hydrogen: 1 and 2) propane, 1) T_f = 900 K and 2) T_f = 900 K; 3 and 4) products of C_3H_8 thermal decomposition at Z = 75%, 3) T_f = 900 K and 4) T_f = 1200 K; and 5 and 6) hydrogen, 5) T_f = 900 K and 6) T_f = 1200 K.

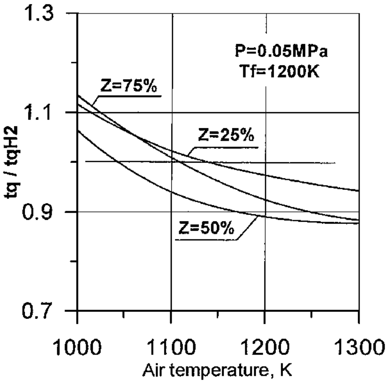

Fig. 8 Effect of air temperature on time ratio of maximal heat release rate at combustion of C_3H_8 thermal decomposition products (t_q) and of C_3H_8/H_2 mixture (t_qH_2).

t_q under conditions $P = 0.05$ MPa, $T_f = 900$ and 1200 K, and $Z = 75\%$ is presented. It could be concluded that the increase of T_a for all regimes results in decrease of t_q as T_{mix} is increased. Also note a rather small decrease of t_q in the case of FTDP combustion. Here, the data on hydrogen combustion are also presented for the same conditions as for the propane. Comparison of these t_q values show again the negligible effects of FTDP application in comparison with propane use.

Thus, it is possible to conclude that combustion organization under the self-ignition concept is possible only for a rather narrow region of referenced parameters (partly, at high T_a). Changing the propane to FTDP at low T_a does not permit effective combustion to be organized in the limits of the available fuel residence times. However, increasing the hydrogen concentration in the FTDP, for example, by fuel conversion in the presence of water,[9] could provide combustion enhancement.

Additional calculations were carried out to determine the effects of the presence of hydrogen on the reactive ability of mixtures of gases, that is, for FTDP at $P = 0.05$ MPa and $T_a = 1000$–1300 K. The decomposition process was assumed to occur at $P = 1$ MPa and $T_f = 1200$ K, with $Z = 25$, 50, and 75%. The resulting values of $t_q/t_{q\mathrm{H2}}$ are shown in Fig. 8. The purpose of these calculations is to find $t_{q\mathrm{H2}}$ values for FTDP, in which all of the hydrocarbon species are replaced by propane, but hydrogen is conserved. In each case (new mixture composition), the stoichiometric coefficient L, equal to its value in the initial mixture, was found by changing the nitrogen concentration. Based on the results shown in Fig. 8, it is possible to conclude that hydrogen presence does not explain the increase of the FTDP reactivity, and so the values of $t_q/t_{q\mathrm{H2}}$ are <1. Nevertheless, for rough estimations, it is possible to use the hydrogen concentration in the FTDP to obtain the efficiency of thermal decomposition and to choose conditions under which the hydrogen concentration will be at a maximum. Analysis of the data in Fig. 8 shows a decrease in $t_q/t_{q\mathrm{H2}}$ at T_a increases. This result can be explained by the behavior of $t_{q\mathrm{H2}}$. At low T_a, the values of $t_{q\mathrm{H2}}$ are lower, but at high T_a, they are greater than the real values t_q. Hence, when we have an increase in T_a or T_{mix}, the concentration of radicals is increased during the preflame stage, and their role becomes decisive during the combustion process.

Table 3 Relative value of FTDP specific efficiency $\Delta(RT)_d$ increase vs Z

	$[(RT)_d - (RT)_0]/(RT)_0$, %	
Z, %	$T_a = 900$ K	$T_a = 1200$ K
25	0.642	0.581
50	1.418	1.280
75	2.238	2.024

It is useful to determine the increase in FTDP/air mixture specific efficiency with air temperature and Z increases. It is explained by the formation of low molecular weight components in the mixture and by increasing equilibrium temperatures of the FTDP/air combustion process. Data for these calculations are given in Table 3 for stoichiometric mixtures in a combustor with $P = 0.05$ MPa and two values of T_a ($T_f = 1200$ K and $P = 1.0$ MPa) with fixed thermal decomposition conditions of $Z = 25$, 50, and 75%.

Here, the propane specific efficiency $(RT)_0$ was taken as a base level. Note that the increase of FDTP is more for larger Z and for low T_a. In general, an increase of $(RT)_d$ does not surpass 3% and is explained mainly by the hydrogen appearance during fuel decomposition.

In summary, a wide parametric database of pressure, temperature T_a, and equivalence ratio coefficient ϕ effects was calculated based on this operation process, and these effects are summarized hereafter:

1) An increase in air temperature has greater effects on decreasing the combustion process time and enhances the organization of combustion based on self-ignition principles. The relative effects of FTDP use is more pronounced at low T_a.

2) An increase of pressure decreases the combustion process time. This can be argued with numerical and experimental research. It is explained by the second order of limited combustion reaction for the considered fuel. Process time dependence vs pressure is approximately the same when Z is varied. The effects of pressure on t_q for H_2 and C_3H_8 are different. For example, in the case of hydrogen, $t_q \sim P^{-1}$; however, for propane, dependence $t_q(P)$ is also decreased when the pressure increases. This decrease is almost linear. Another aspect of the pressure influence on fuel decomposition was discussed in the first section, which shows a favorable effect of pressure decrease on H_2 and H concentrations.

3) Decreasing the equivalence ratio ϕ from 1.0 to 0.4 causes a decrease of t_q both for propane (30%) and FTDP (20%). This is confirmed qualitatively by the results[20] for the combustion of propane and n-butane.

Effects of Initial Radical Concentration on Characteristic Ignition Time of Fuel/Air Mixture

It was shown earlier that fuel thermal decomposition ($Z \leq 75$–80%) has only a small influence on the reactivity of fuel/air mixtures. It was also shown that the low level of active radical concentrations (RC) formed during the decomposition process, given in Table 2, resulted in only a small increase in combustion intensification. Thus, it is expedient to consider the effect of significant RC increases on combustion intensification. It is important to have information on the required level of radicals formed by special devices because this level will define the value of necessary energy input to enhance the combustion intensification. For example, in Ref. 30, additional RCs

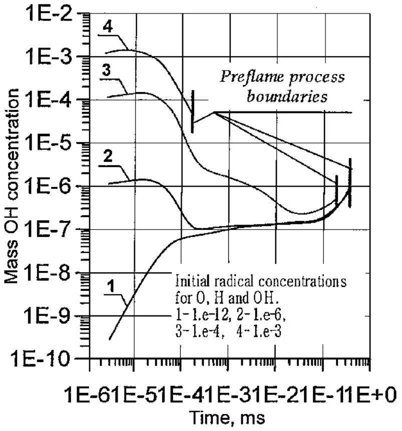

Fig. 9 OH mass fraction vs time through the preflame stage, stoichiometric air/fuel mixture: $P = 0.05$ MPa, $T_f = 900$ K, and $T_a = 1300$ K.

were provided using a torch plasma generator of 1.2-kW power at a hydrogen/air mixture rate 10–15 g/s.

The effect of the initial RC on self-ignition time is investigated in the frame of the same equation system as thus used in Eqs. (1) and (2). The way that this concentration increase is generated is not considered here. Calculations for air/propane mixtures show that RCs upstream of the combustion front region is very high, when the combustion temperature of the homogenous mixture is close to its equilibrium value. For the initial stage (before the flame front) and at the moment of equilibrium state (behind the front), the radical and intermediate product concentrations are very low in comparison with the their maximum values. For simplicity, the effect of the initial RC level of each specie was considered, that is, the effects of O, H, and OH in the mixture on the preflame process in combustor. The radical OH was chosen to generalize the behavior of all active species within the combustor because the radical OH is a more reliable mark for characterizing the flame front location than the other radicals listed.

Figure 9 shows the time history for the OH RC along the combustor length under conditions of $P = 0.05$ MPa using propane and air with temperatures equal to 900 and 1300 K, respectively. The time period corresponding to the preflame region of homogenous mixture combustion is presented when changes in the initial T_{mix} are small. The initial level of RC was varied in the limits of 10^{-12}–10^{-3}. The minimum value RC and its maximum correspond to the practical absence of RC and to the RC in the flame front. The data in Fig. 9 show that an increase of the initial RC from 10^{-12} up to 10^{-6} does not effect the duration of the preflame process. The position of the preflame stage boundary, after which the change in the initial T_{mix} can no longer be considered small ($\Delta T_{\text{mix}} \leq 1\%$), is constant. The behavior of RC changes in the preflame stage ($t < 10^{-4}$ ms) for these cases are very different. At a 10^{-12} initial value for the RC, we observe a monotonic increase in the RC up to ignition of the fuel/air mixture. In the case when RC $= 10^{-6}$ or more, the changes of RC are not monotonic. First, the RC decreases, striving for the equilibrium level corresponding to the mixture state. Only after that does the RC begin to grow during the progress of combustion. Increases of the initial RC from 10^{-6} up to 10^{-4} result in a decrease of the preflame process duration by 2–2.5 times. A sharp fall in the preflame process duration by 2–3 orders of magnitude is observed at an initial RC up to 10^{-3}. Thus, effective intensification of the combustion process takes place when the RC increases. However, the initial RC concentration should be at a level close to that at the flame front. In this case, the scheme of combustion organization based on self-ignition principles is transformed into the scheme that is used for pilot flames for ignition enhancement and sustainment.

Further analysis of OH concentration changes (Fig. 10) shows that the RC at the flame front is approximately constant, in spite of the preflame process time becoming much shorter at large initial values of RC. This result is very important from a practical point of view because it offers the possibility of conducting calculations of the combustion process under simulation of a practical operational process that does not require taking into account mixture satiation by additional radicals. The second important conclusion is based on the initial RC's inability to affect the characteristic ignition time, except for the case when this initial concentration corresponds with the RC at the flame front. This same conclusion was obtained in Ref. 30, where it was shown that the ignition delay time of hydrogen/air mixtures depends strongly on RCs of O and N in the mixture.

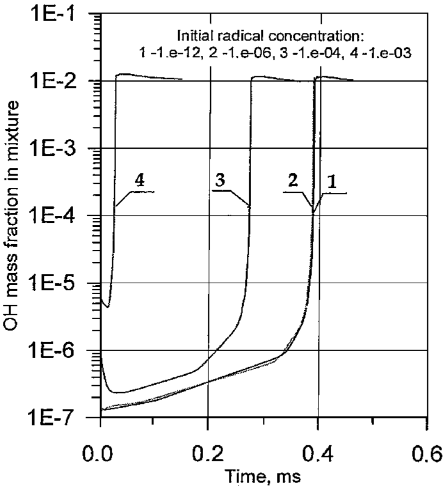

Fig. 10 OH mass fraction vs time combustion of stoichiometric air/fuel mixture: $P = 0.05$ MPa, $T_f = 900$ K, and $T_a = 1300$ K.

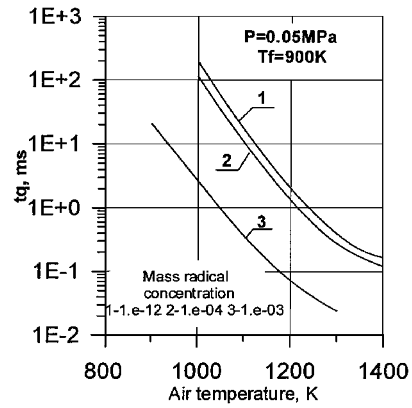

Fig. 11 Effect of air temperature on time corresponding to maximal heat release rate at combustion of stoichiometric propane/air mixture under different radical concentration levels.

Two principal conclusions following from the results of Ref. 30 are as follows:

1) The addition of radicals into the reactive mixture provides both the decrease of preflame process time and the increase of combustion normal velocity.

2) In the frame of the kinetics scheme applied in Ref. 30, the strong effect of the O radical is rather clear, but the effect of the N radical on combustion requires more careful analysis.

As applied to the actual operation of high speed ABEs ($P = 0.05$ MPa, $T_f = 900$ K), the influence of the initial RC on t_q under variable T_a was considered. Results from these calculations are presented in Fig. 11. Note that the character of the radical influence on combustion intensification is the same for the whole temperature region, as was shown earlier (Fig. 9). The initial RC strongly effects time t_q if its values are close to the RC in the flame front. Thus, for example, an increase in mass RC in a fuel/air mixture up to 10^{-3} results in a decrease in ignition delay time by an order of 1.5.

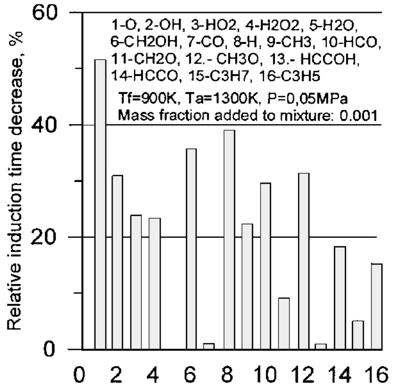

Fig. 12 Comparative estimation for an effect of extra components added to mixture on induction time decrease under combustion of stoichiometric air/fuel mixture.

As was noted earlier, the amount of different radicals and intermediate species formed during the combustion process are limited by the kinetics scheme possibilities. The effects of individual radicals (and some species added to the mixture) on t_q are given in Fig. 12. The efficiency of the radical addition was characterized by a decrease in t_q with respect to the fuel without such an additive. Stoichiometric mixtures of propane/air at the combustion conditions listed in Fig. 12 were also considered. Mass fractions of species were the same for all variants and were equal to 10^{-3}. From the data in Fig. 12, it follows that the radical O has the strongest effect on time t_q. It is followed by the radicals (in order of significance with respect to influence on the combustion process) H, OH, CH_2OH, HCO, and CH_3O. Other additives have almost no effect on ignition time delay.

Note that the efficiency of radical addition is more favorable for the FTDP in comparison with the initial fuel. For example, the increase of initial mass RC in the mixture up to the level of 10^{-3} at $T_a = 1000$ K and $Z = 0.3$ results in a decrease of t_q by more than two orders of magnitude. This is explained by the presence of the active radicals in the FTDP and progressive chain chemical reaction mechanisms in the mixture under the conditions of a partly reacting mixture.

Evaluation of Radical Concentrations in Gaseous Mixtures Under Different Initial Conditions

As was shown before, the input of radicals is a very effective way of achieving combustion intensification. However, in practice, it is necessary to choose correctly the place where the radicals should be put into the combustor. Intensive gasdynamic computations will eventually be required to solve for the gasdynamic flow properties, degree of mixing, etc. Nevertheless, in the framework of Eqs. (1) and (2), it is possible to evaluate the kinetics part of the problem and, consequently, to demonstrate the possibility of reaching the combustion zone by the use of radicals.

First, a comparative evaluation of the extra radicals' influence on decreasing the maximum heat release rate time t_q at their forming in either the air or gaseous fuel ducts was performed. Conditions for these calculations were $T_a = T_f$ and $P = 0.05$ MPa, with stoichiometric mixtures and O, OH, and H radicals chosen as the most effective ones. The resulting analysis shows that the addition of radicals into the fuel is less effective than the addition of radicals into the air. This could be explained in the case of the same initial RC, but different initial RCs in the mixture. Comparison of the combustion intensification by radical saturation of air or by a premixed stoichiometric mixture shows only small differences. In general, the intensification depends mainly on the RC under equivalent conditions.

Based on the data in Fig. 9, it is important to note two results as applied to this section's tasks:

1) Self-ignition under the considered levels of air and fuel temperatures is realized even at a very low RC level.

2) At high RC, first a sharp decrease along the ignition time is realized, which is limited by the process of radicals creation during the preflame phase. It follows that the radical creation processes are most important during the preflame phase.

The state of the mixture [temperature T (900–1200 K), pressure P (0.05–0.5 MPa), and fuel/air equivalence ratio ϕ (0.7–0.1)] on RC was also characterized. The initial RC of O, OH, and H is accepted as equal to 10^{-3}. Based on results of the calculations, it is possible to conclude that the RC in the mixture always decreases, approaching the equilibrium value at the given state of the gaseous mixture. This process takes only parts of a millisecond. During this process, the RC decreases and becomes equal to intermediate stationary state values, and, if self-ignition is possible under these conditions, an RC increase is then observed. For all considered mixture states, the equilibrium active RCs are much lower than the initial level. Hence, in the case of low intensive preflame processes, the positive effect caused by the input of radicals will decrease as a mixture of low RC is supplied to the combustor.

The effect of mixture temperature and pressure on OH concentration vs time is presented in Fig. 13 at $\phi = 0.1$. At a constant pressure $P = 0.05$ MPa, a decrease of temperature causes a sharp increase in the preflame process duration (Fig. 13a). Variation of pressure at $T = 1200$ K (Fig. 13b) does not have a noticeable effect on the preflame process duration. However, the intensity of radical creation at low pressures is increased.

The effect of ϕ on radical OH, O, and H concentrations is presented in Fig. 14 for $P = 0.05$ MPa and $T_{\mathrm{mix}} = 1200$ K. The duration of the preflame process is decreased for the leaner mixtures, and the creation of radicals is slowed because of combustion. The behavior of the O and H radicals is qualitatively the same. A more accurate analysis is possible when all radicals are taken into account.

Thus it is possible to conclude, at the considered conditions, that Rcs are not constant and mostly depend on the temperature of the air/fuel mixture. Also, the position of any radical source should be chosen to be immediately before the combustion zone if the mixture temperature at the combustor entrance does not exceed 1000–1100 K. This will prevent a decrease in the radical

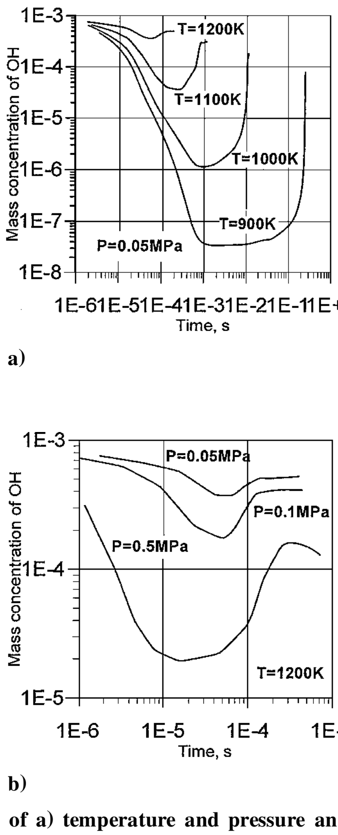

Fig. 13 Effect of a) temperature and pressure and b) temperature on change of OH concentration from superequilibrium level for air/propane mixture at fuel/ air equivalence ratio $\phi = 1.0$.

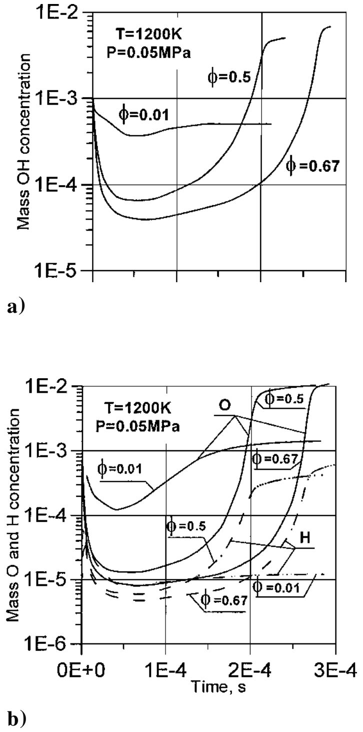

Fig. 14 Changes of a) mass OH concentration and mass O and H concentration and b) mass OH concentration vs fuel/air equivalence ratio ϕ.

concentration from initial superequilibrium level. If T_{mix} or T_a is large (>1200 K), then the position of radical source will be limited by the kinetics performance of the preflame process, but not the initial level of RC. At the same time, an increase in T_{mix} will accelerate combustion even without any added radicals, and the combustion zone can be attached to the radical source in spite of its productivity.

Conclusions

Numerical research of the thermal decomposition process of propane in the frame of one-dimensional mathematical models under parameters $T = 900$–1400 K and $P = 0.05$–3 MPa demonstrates the following:

1) Thermal decomposition takes place at $T \geq 900$–950 K with the products of composition consisting mainly of C_3H_6, C_2H_4, C_2H_2, CH_4, and H_2 depending on P, T, and the degree of decomposition Z. Increases in pressure provide an acceleration of the decomposition.

2) Mass fractions of more reactive H_2 species and H radicals, which comprise the majority of radicals in the FTDP, do not exceed $(3$–$4) \times 10^{-2}$ and 2×10^{-6}, respectively, for the considered values of Z and process parameters.

3) The reactivity of C_3H_8 thermal decomposition products is greater than that of pure C_3H_8, and, for example, at $T < 1000$ K, the reference time t_q is less by anywhere from two to three times in comparison with C_3H_8 fuel. Increases in specific efficiency $\Delta(RT)_d$ in the case of thermal decomposition products does not exceed 2–3%.

4) The addition of radicals to the original fuel (C_3H_8) or to the thermal decomposition products has a strong effect on the self-ignition time in comparison with the time for the original fuel if the RCs injected are comparable with the flame front RCs. In this case, the decrease in t_{ind} can be reduced by from one to two orders of magnitude in comparison with the original fuel.

5) Injection of active radicals into the air provide a greater effect at the same fuel/air equivalence ratios compared with the case when radicals are injected into the fuel. The initial RC is not conserved, but reaches an equilibrium state corresponding to the thermodynamic properties of the flow with subsequent changes in RC defined by the kinetics of the preflame phase of combustion.

Acknowledgments

This work was supported by the John Hopkins University Contract and Russian Fund of Fundamental Researches, Grant 01-01-00910. The authors are sincerely grateful to I. Gomzyakova for her help and assistance in preparation and processing the numerical data.

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