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KINETIC MODELS OF COMBUSTION OF KEROSENE AND ITS COMPONENTS

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Modern investigations on creation of kinetic models of combustion of hydrocarbons entering into the composition of kerosene and kerosene as a whole have been analyzed. Certain recommendations on application of these models to calculation of actual gasdynamic flows have been given.

Kerosene is a hydrocarbon fuel widely used in modern aircraft and rocket engines [1]. The necessity of improving the operating efficiency of the engines and of reducing their adverse effect on the atmosphere has aroused considerable recent interest in the understanding of kinetic mechanisms of ignition and combustion of this fuel.

The most efficient approach to solution of problems arising in operation of engines is the development of methods of direct numerical modeling of physicochemical processes that occur in the working medium of a combustion chamber. Practice shows that in the cases where well-tested mathematical models and computational algorithms are used the additional information obtained using numerical modeling compares well with experimental data in reliability and exceeds them in exhaustiveness.

In selecting the level of description of the working medium in the combustion chamber, one must focus primary attention on the kinetic features of the process of combustion. Such an approach implies that kinetic models of this process, which have different degrees of complexity, are involved in the computational scheme modeling the behavior of the medium. In the present work, we have briefly reviewed the state of the art in investigations in the field of construction of kinetic models of combustion of heavy hydrocarbons entering into the composition of kerosene. Also, we have given certain recommendations on application of these models to calculation of actual gasdynamic flows. The work has been carried out within the framework of the AVOGADRO system [2] aimed at solving the problem of information support of scientific investigations in the field of physicochemical gas dynamics.

1. In accordance with the requirements imposed on kerosene by jet aircraft, this fuel must have high energy characteristics, ensure reliable operation of the engine's fuel systems, and be simple to handle, inexpensive, and stable in storage and transportation [3]. Practice has shown that one specification of kerosene is unable to satisfy all the fuel-quality indices. Therefore, several specifications of it have been created, each having certain advantages in operating properties with allowance for the cost and production resources.

Three basic specifications of domestic kerosene — TS-1, RT, and T-6 — are produced at present. TS-1 kerosene is used in both subsonic aircraft and supersonic aircraft with a limited time in flight. RT kerosene, being more thermostable, is admitted for use in thermally stressed engines of airplanes with an increased time in supersonic flight. T-6 kerosene is highly thermostable and has an increased density and a low pressure of saturated vapor. These properties determine its use in high-speed airplanes with a long time in supersonic flight during which a considerable increase in the temperature of the fuel in the airplane tanks is possible because of the aerodynamic heating [3].

The most widespread kerosene in civil aviation abroad is Jet A, which is characterized, unlike TS-1 and RT, by a heavy fractional composition and an elevated temperature of the beginning of crystallization. In military aviation, one uses JP-8 kerosene virtually analogous to Jet A kerosene in properties but with an introduced admixture preventing the formation of ice crystals. In ship-based aircraft, one uses JP-5 kerosene [1].

Middle oil fractions boiling away at a temperature of 140–280°C represent the basic raw material for production of kerosene. As far as the production method is concerned, kerosenes are subdivided into straight-run kerosenes and hydrogenation ones. The first are produced directly from distilled oil fractions without their deep processing,

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TABLE 1. Physicochemical Characteristics of Kerosene

Fuel	Group composition, wt. %			Element composition, wt. %		Q, kJ/kg
	paraffins	naphthenes	arenes	C	H	
T-1	24—42	42—69	14—20	86.2—86.5	13.5—13.7	43 000
TS-1	42—52	30—49	11—21	85.7—85.8	14.0—14.1	43 290
RT	53—58	25—30	12—22	85.8—86.1	13.9—14.2	43 370
T-8	21—50	26—45	14—18	85.8—86.0	13.9—14.1	43 290
T-6	12—20	75—80	3—6	85.4—86.0	13.4—13.6	43 160
T-2	40—43	42—50	14—16	85.5—85.7	14.3—14.5	43 230

whereas the technology of obtaining the second involves such processes as hydraulic cleaning, deep hydration, and hydrocracking. The use of hydrogenation processes makes it possible to obtain high-quality kerosenes and to simultaneously extend the raw-materials production base [3].

More than 98% of kerosene accounts for aliphatic saturated (paraffins), alicyclic (naphthenes), and aromatic (arenes) hydrocarbons. In this connection, carbon and hydrogen are the basic chemical elements of this fuel. Typical representatives of linear paraffins in kerosene are *n*-dodecane (n-$C_{12}H_{26}$) and *n*-tetradecane (n-$C_{14}H_{30}$); paraffins with a branched chain are represented mainly by *iso*-octane (i-C_8H_{18}). Naphthenes are present predominantly in the form of monocyclic compounds, such as cyclohexane (cy-C_6H_{11}) and methyl cyclohexane (CH_3cy–C_6H_{11}) [4]. The content of arenes in kerosene is limited in connection with their increased tendency toward carbonization; the highest concentration is characteristic of toluene (CH_3–C_6H_5) and ethyl benzene (C_2H_5–C_6H_5) [5].

The hydrocarbon composition of kerosene is dependent on the nature of the petroleum being processed and on the petrochemical processes used in the processing technology. Generalized data on the group and element composition of domestic specifications of kerosene and the mean values of the lower heat of combustion have been tabulated in [3]. Oxygen, sulfur, and nitrogen compounds, including fuel-soluble substances, are present as impurities in kerosene. The content of these impurities is low, but they adversely affect the service properties of the fuel in some cases [6].

Kinetic models of combustion of hydrocarbons entering into the composition of kerosene are developed, on the one hand, by construction of detailed kinetic mechanisms of the process with a large number of elementary stages and possible components of a chemically reacting system [7]. Such models contain a sufficient amount of information for description of a wide range of the phenomena under study. On the other hand, one constructs simplified kinetic models [8] used in calculation of combined gasdynamic flows, when computational difficulties make it impossible to include a detailed kinetic model into consideration [9]. Let us briefly consider certain typical models reflecting these two trends.

2. Detailed kinetic models of combustion of aliphatic saturated hydrocarbons with a normal and branched chain are currently at the stage of development of the structure of the kinetic mechanism of the process for molecules of the starting fuel with a number of C atoms of about 10 or higher in a molecule and at the stage of refinement of the corresponding rate constants of the reactions. The models includes the kinetic mechanisms of combustion in $H_2/O_2/CO$, C_1/C_2, and C_3/C_4 subsystems. The rate constants of the elementary reactions describing the behavior of these systems are based on the results of their direct measurements and have a fairly high degree of reliability [10].

Reactions in the $H_2/O_2/CO$ subsystem are the component part of the basic chain processes of ignition and high-temperature combustion of hydrocarbon fuels. They have been investigated in numerous works by different experimental methods in detail in view of their great significance. A complete kinetic model of combustion in the subsystem contains several tens of reactions and, in a simplified variant, may be reduced to 21 reactions describing the interaction of 10 chemical components [11].

The oxidation of hydrocarbons in the C_1/C_2 subsystem plays a dominant role in combustion of C_n hydrocarbons ($n \geq 3$) because of the formation of methyl (CH_3) and ethyl (C_2H_5) radicals virtually in all the flames. Sufficiently complete kinetic models for this subsystem include about 100 elementary chemical reactions (see, for example, [12]). The C_3/C_4 subsystem contains about 700 elementary stages [13].

Construction of a detailed kinetic mechanism of oxidation of higher terms of the homologous methane series began with the development of simplified models. In one of the first works devoted to the chemistry of combustion of higher alkanes (up to *n*-octane inclusive) [14], the molecules of the starting hydrocarbon initially come into interaction with H, O, and OH. The alkyl radicals formed decompose into smaller alkyl radicals and alkenes (methyl and propene in this case) whose oxidation is described by a detailed kinetic mechanism for the C_1/C_3 subsystem.

Most of the works on investigation of the combustion of heavy hydrocarbons deal with *n*-heptane (n-C_7H_{16}). The reason is that *n*-heptane belongs to standard fuels: the octane number characterizing the quality of gasoline is taken to be zero for it, whereas the cetane number equal to 56 is similar to the corresponding quantity for the standard diesel fuel.

A sufficiently complete detailed kinetic model of oxidation of *n*-heptane (it has been developed in [15]) includes 2450 chemical reactions and 550 components and makes it possible to describe the available experimental data in a wide range of variation of the parameters of the process: p = 0.1–4.2 MPa, T = 550–1700 K, and ϕ = 0.3–1.5. The mechanism of **high-temperature oxidation** of *n*-heptane consists of nine classes of reactions. The basic classes include:

(a) *unimolecular decomposition of the fuel* (initiating stage) to form two alkyl radicals or a heptyl radical and an H atom;

(b) *splitting of the H atom from a fuel molecule* in its interaction with atoms and radicals, which leads to the formation of heptyl radicals and plays an important role at both high and low temperatures;

(c) β *decomposition of the alkyl radical* to form an olefin molecule and a smaller alkyl radical;

(d) *interaction of the alkyl radical with the oxygen molecule* with subsequent decomposition of the adduct formed into olefin and an HO_2 radical.

Branching of the chain in high-temperature oxidation occurs in the reaction $H + O_2 \rightarrow OH + O$.

In the **low-temperature region** ($T \leq 850$ K), high activation energies (27–40 kcal/mole) associated with the β decay of alkyl radicals make the high-temperature part of the mechanism of oxidation of *n*-heptane slower. The most important reactions for alkyl radicals under these conditions become those of their addition to molecular oxygen with subsequent internal splitting of the H atom (H shift), secondary addition of the O_2 molecule, and decomposition of the adduct formed:

$$C_7H_{15} \xrightarrow{O_2} C_7H_{15}O_2 \rightarrow C_7H_{14}O_2H \xrightarrow{O_2} O_2C_7H_{14}O_2H \rightarrow HO_2C_7H_{13}O_2H \rightarrow 2OH + CH_2O + C_5H_{11} + CO\,.$$

This reaction order yields a low-temperature branching of the chain. In most cases, the most important reaction is the first stage (addition of the O_2 molecule to the alkyl radical). The initiating stage represents the splitting of an H atom from a fuel molecule in its interaction with molecular oxygen to form a heptyl radical and an H_2O radical. The low-temperature oxidation of *n*-heptane in the kinetic model of [15] is described by 16 classes of reactions.

Based on an analysis of this kinetic mechanism, we can single out the basic features of oxidation of higher saturated hydrocarbons. In transformation of the molecules of the starting fuel, we can take, as the first step, their interaction with the active components (O, H, and OH) resulting from the branching of chains. The reaction products (alkyl radicals) either decompose into olefins and smaller alkyl radicals (high-temperature oxidation) or experience a chain of transformations involving intermediate oxygen-containing components (low-temperature region) in interaction with O_2 molecules. Finally, the problem of oxidation of aliphatic hydrocarbons is reduced to the oxidation of lower alkyl radicals (methyl and ethyl) in the $H_2/O_2/CO$ and C_1/C_2 subsystems. This part of the kinetic mechanism is limiting and it is responsible for the similarity of all aliphatic hydrocarbons.

Detailed kinetic models of oxidation of higher (than *n*-heptane) aliphatic saturated hydrocarbons are constructed on the same principle (see, for example, works on modeling of the process of combustion of *iso*-octane (2,2,4-trimethyl pentane) [16, 17], *n*-decane [18], and *n*-hexadecane [19]).

The currently available detailed kinetic models of combustion of aliphatic saturated hydrocarbons fairly well describe numerous experimental data. They include, in particular, the experiments on measuring the temperature and concentrations of the components in turbulent flow reactors [20] and jet-stirred reactors [21], propagation of a premixed laminar flame [22], and two-stage ignition of fuel mixtures in shock tubes [23] and high-speed compressor plants [24].

3. The content of naphthene hydrocarbons in gasoline can attain 80%. Whereas the combustion of aliphatic hydrocarbons has been studied with a sufficient degree of detail, the combustion of naphthenes has received much less attention; the kinetic models of their oxidation are less detailed and call for further refinement.

The mechanism of pyrolysis and combustion of cyclohexane is quite simple as compared to the corresponding mechanism for the higher terms of the aliphatic series due to the high symmetry of its molecule and has been considered in [4] in sufficient detail. Only one cyclohexyl radical (cy-C_6H_{11}) can actually be formed in splitting of an H atom from the starting fuel molecule. The reaction of β decomposition of the cyclohexyl radical at high temperatures opens the ring and forms a linear hexenyl radical. A simplified (quasiglobal) kinetic mechanism of high-temperature oxidation of cyclohexane (this mechanism contains one global stage of β decomposition of the radical cy-C_6H_{11}) has been constructed in [4]. The decomposition products are further oxidized in accordance with a detailed kinetic mechanism. At low and intermediate temperatures, the reaction of addition of the O_2 molecule to the cyclohexyl radical gives rise to a peroxide radical which is further transformed in the chain of reactions:

$$cy\text{-}C_6H_{11} \xrightarrow{O_2} cy\text{-}C_6H_{11}O_2 \rightarrow cy\text{-}C_6H_{10}O_2H \xrightarrow{O_2} cy\text{-}O_2C_6H_{10}O_2H \rightarrow 2OH + CH_2CHO + CH_2CO + C_2H_4 .$$

The second typical representative of the naphthene group in kerosene is methyl cyclohexane. In oxidation of CH_3cy-C_6H_{11}, the splitting of a hydrogen atom from the starting molecule gives rise to five different cyclic radicals C_7H_{13}. In the process of their high-temperature β decomposition, the ring structure is broken to form linear or branched alkenyl radicals, which subsequently decompose into smaller intermediate components. A simplified high-temperature mechanism (proposed in [4]) of pyrolysis of methyl cyclohexane contains two global stages, which sum up different modes of decomposition of CH_3cy-C_6H_{11} and C_7H_{13}. All the products of these stages have been studied and enter into the kinetic schemes of oxidation of aliphatic hydrocarbons (see above). The mechanism can be extended for use in the high-temperature region by including the group of reactions of addition of molecular oxygen to C_7H_{13} to it to form peroxide radicals with their subsequent decomposition (by analogy with the low-temperature mechanism for cy-C_6H_{11}).

The experiments on studying the behavior of fuel mixtures containing cy-C_6H_{12} and CH_3cy-C_6H_{11} are few in number and do not cover the entire range of variation of temperature and pressure. The oxidation of cyclohexane in a rapid compressor plant has been investigated in [25] as applied to the conditions realized in internal combustion engines. The experiments were carried out for stoichiometric mixtures of the fuel with air at pressures of 0.7–0.9 MPa and temperatures of 650–900 K. The results of the measurements carried out have been used in [4] to verify the kinetic mechanism constructed. The combustion of both methyl cyclohexane and their mixtures with toluene has been considered in [26]. A study of such mixtures and the use of the experimental results obtained for construction of kinetic models is the first step on the road to creation of a detailed kinetic model of combustion of kerosene.

4. The concentration of aromatic hydrocarbons in kerosene is no higher than 22%, but for certain types of kerosene this quantity amounts to only several per cent of the total mass of the fuel. Therefore, the kinetics of oxidation of these fuel components does not exert a strong influence on the general dynamics of the chemical process. Arenes are presented in kerosene mainly by toluene and ethyl benzene [5]. The kinetic schemes of oxidation of these components are closely related to the kinetic schemes of oxidation of benzene [27].

The high-temperature oxidation of benzene is initiated as a result of the breaking of the C–H bond in interaction of C_6H_6 with H and O atoms and OH radicals to form the phenyl radical C_6H_5. A competitive process is the formation of phenol in interaction of the starting fuel molecule with O and OH, and the basic channel of further transformation of phenyl radicals is their decomposition to disrupt the ring structure and to form n-C_3H_3 radicals and acetylene molecules [28].

The most active link in a toluene molecule is the methyl group. Therefore, the basic channel of initiation of the reaction of oxidation of toluene is the separation of an H atom from the methyl group in interaction of the starting toluene molecule with H and O atoms and OH radicals to form the radical $C_6H_5CH_2$, which forms the radical C_6H_5O in interaction with O atoms. The end products of the chain of transformation of the C_6H_5O radical are acetylene and CO. The competitive process consists in disintegrating the toluene molecule into the radicals C_6H_5 and CH_3, which gives rise to benzene and methane molecules [29]. A detailed kinetic model of high-temperature oxidation of n-propyl benzene (n-C_3H_7-C_6H_5) entering into the composition of certain kerosenes has been developed in [30]. The kinetic parameters of the model were obtained by comparison of the calculated and measured concentration profiles in a jet-stirred reactor at $p = 1$ MPa, $T = 900–1250$ K, and $\phi = 0.5–1.5$.

As has been noted above, aromatic hydrocarbons are the basic source of condensed carbon in the combustion products of kerosene. Therefore, the problem of formation of polycyclic aromatic hydrocarbons and soot has received much attention in works on investigation of the high-temperature transformation of arenes. The kinetic models including the formation of these components have been reviewed in [31, 32]. Experimental works on study of the behavior of a chemically reacting system in oxidation of aromatic hydrocarbons are quite numerous. They, in particular, contain the results of measurements of the concentration profiles of the basic components in high-temperature oxidation of benzene, toluene, and ethyl benzene in a turbulent flow reactor [33] and in propagation of a pre-mixed laminar flame [34].

5. The existing kinetic models of combustion of kerosene roughly follow the above models of combustion of its basic components. A kinetic model of high-temperature combustion of Jet A1 kerosene has been proposed in [35]; in this model, the transformation of the molecules of the starting fuel in its interaction with molecular oxygen is described by one global reaction

$$C_{11}H_{22} + 0.75O_2 \rightarrow 2.18C_2H_4 + 1.5CO + 1.005H_2 + 0.8C_3H_6 + 0.55CH_4 + 0.21C_4H_8 + 0.11i\text{-}C_4H_8 ,$$

and the oxidation of the reaction products is modeled by a detailed kinetic mechanism for the subsystem C_1/C_4. The stoichiometry of the global reaction and the numerical values of the parameters of its rate $w = 2.8 \cdot 10^{15}$ $[C_{11}H_{22}]$ $[O_2]^{0.8}$ exp $(-22{,}650/T)$ were determined by matching the calculation results to the experimental data obtained in a jet-stirred reactor at $T = 873–1033$ K, $p = 0.1$ MPa, $\phi = 0.2–1.5$, and an initial concentration of the fuel of 0.1%.

A mixture of *n*-decane and *n*-propyl cyclohexane has been used in [36] for modeling of the high-temperature combustion of Jet A1 kerosene. This kinetic model is based on a more detailed kinetic mechanism of transformation of fuel molecules, which includes the initiating stage, the stage of continuation of the chain (splitting of an H atom in interaction of a fuel molecule with atoms and radicals), and the global stage of decomposition of the radicals formed at the previous stage.

In the kinetic model of combustion of JP-8 kerosene [37], the starting fuel is presented in the form of a mixture of dodecane, tetradecane, *iso*-octane, methyl cyclohexane, *m*-xylol, and tetralin. The kinetic parameters of the model have been determined from a comparison of the calculated and experimental data on combustion of pure components of the mixture.

The kinetic model of high-temperature combustion of JP-10 kerosene whose basic component is *exo*-tetrahydrodicyclopentadiene ($C_{10}H_{16}$) has been developed in [38]. The model contains 13 global stages describing the process of disintegration of the molecules of the starting fuel into smaller hydrocarbon components and a detailed kinetic mechanism for the C_1/C_3 subsystem. It quite well describes experimental data [39] on measurement of the concentration profile of OH and the delay time of ignition τ in the JP-10/O_2/Ar mixture behind the reflected shock wave at $p = 0.1–0.9$ MPa, $T = 1200–1700$ K, and $\phi = 0.5–1.5$.

In the kinetic model [40] used for description of the formation of polycyclic aromatic hydrocarbons and soot in combustion of kerosene, the starting fuel is presented in the form of a mixture of *n*-decane (80%) and toluene (20%). The model has been constructed based on a detailed kinetic mechanism of combustion of kerosene [41] and contains 1015 elementary chemical reactions and 140 components. The fields of temperature and concentrations of the components in diffusion combustion of the kerosene/air mixture in a confined turbulent jet have been calculated using this model.

The number of experimental and theoretical works on combustion of different specifications of kerosene is small, on the whole. At the present time, there is no detailed kinetic model of the process that involves the oxidation of all the basic components of kerosene. Nonetheless, the use of model mixtures similar to those considered above makes it possible to predict the dynamics of the processes and to evaluate a number of side effects.

6. The combustion of hydrocarbon fuels, in particular, kerosene, in different combustion chambers represents a combination of complex interrelated physicochemical processes to describe which one uses all kinds of gasdynamic and kinetic models. The kinetic model of the process, which is a part of a more general gasdynamic model, must be extremely simplified, on the one hand, and quite accurately model the behavior of a chemically reacting system, on the

other. The reduction of the kinetic mechanism to one or several gross stages is ideal in some cases, even if such an approximation acts in a very narrow range of variation of the parameters of the process.

The objective of simplification of a detailed kinetic mechanism is to determine the degree of importance of the individual stages of the process in question and to construct the hierarchy of these stages from the preassigned criteria. The optimum (skeleton) kinetic mechanism adequately describing a chemically reacting system from the viewpoint of determination of the values of a certain assigned functional F dependent on the concentration of the components and the gasdynamic variables (temperature, pressure, gas velocity, etc.) is determined as the minimum subset of the detailed kinetic mechanism that satisfies the condition $\left|F_{\mathrm{opt}}/F_{\mathrm{full}} - 1\right| \le \varepsilon$ [42]. The methods of local (global) analysis of sensitivity, comparison of the velocities of the stages, and others (see, for example, [43]) are used to quantitatively evaluate the degree of importance of the individual stages of a complex chemical reaction.

The optimum kinetic mechanism (presented in [44]) of combustion of *n*-heptane contains 56 reactions and makes it possible to describe experiments on two-stage ignition of a fuel and data on measuring the composition of a chemically reacting system in an ideal-displacement reactor. A simplified version of the mechanism, which consists of 30 reactions, quite well reproduces the temperature dependence of the delay time of ignition at p = 0.1–10 MPa for nearly stoichiometric conditions.

The optimum kinetic mechanism of oxidation of a mixture of standard fuels (*n*-heptane and *iso*-octane) [45] includes 55 reactions and 32 components. Using it, one satisfactorily models the process of high- and low-temperature ignition of the mixture in a rapid compressor plant, as the octane number changes from 0 to 100.

The procedure of construction of the optimum kinetic mechanism does not remove the problem of rigidity of a system of kinetic equations; this problem is associated with the presence of active intermediate components, whose concentrations rapidly reach the quasistationary level and then slowly change in the course of the process, in the chemically reacting system. Therefore, the approximations of quasistationary concentrations and rapid chemical reactions are used for further simplification of the mechanism of the process in question and for construction of a reduced kinetic model.

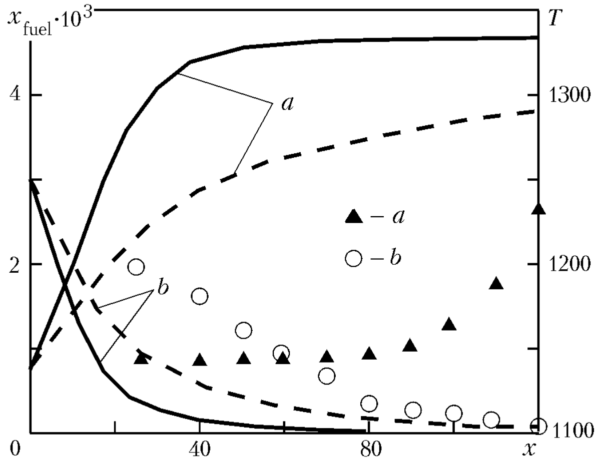
Two reduced kinetic models of ignition of *n*-heptane as applied to different temperature regimes have been obtained in [44] based on the algebraic transformation of a system of kinetic equations for the optimum mechanism of combustion of this fuel. In a low-temperature regime, the process is described by four global reactions, whereas for the regime of intermediate and high temperatures the kinetic model contains nine global reactions. The reaction rates are written in the form of the linear combinations of corresponding rates of the optimum mechanism. Most of the intermediate components (including OH radicals) are in the steady state, and their concentrations are expressed by the concentrations of the basic components and the rate constants of the elementary reactions of the optimum mechanism.

A reduced kinetic model of high-temperature ignition of hydrocarbon fuels has been developed in [46]. It contains 19 reactions and 17 chemical components and well describes the temperature dependence of the ignition-delay time for *n*-heptane, *iso*-octane, and *n*-decane.

The recent improvements in computer technologies have stimulated the creation of different computational procedures for automatic generation of reduced kinetic models. They include, in particular, the ILDM (Intrinsic Low-Dimensional Manifolds) method [47] used in [48] for reduction of the kinetic mechanism of combustion of higher hydrocarbons and the CSP (Computational Singular Perturbation) procedure [49]. Sufficiently detailed reviews of numerical methods of construction of reduced kinetic models have been given in [8, 9].

7. The above-considered detailed and simplified kinetic models of combustion of the hydrocarbon components of kerosene contain a lot of elementary reactions and chemical components the description of whose behavior requires that a large number of the corresponding kinetic equations be solved. These equations are rigid, as a rule, and require special computational procedures. On the other hand, both the rate constants of elementary reactions and the reactions themselves that are available in the literature are not reliably established; therefore, they can be the source of large errors.

The concept of a global kinetic mechanism makes it possible to significantly simplify the kinetic model of the process and, when the selection of the order of global chemical reactions and the corresponding rate constants is appropriate, is capable of giving a satisfactory description of rather complex gasdynamic problems. The basis for this concept is the representation of a chemical process in the form of several successive and partially overlapping gross stages, whose kinetic parameters are determined from a comparison of the calculation and experimental results.



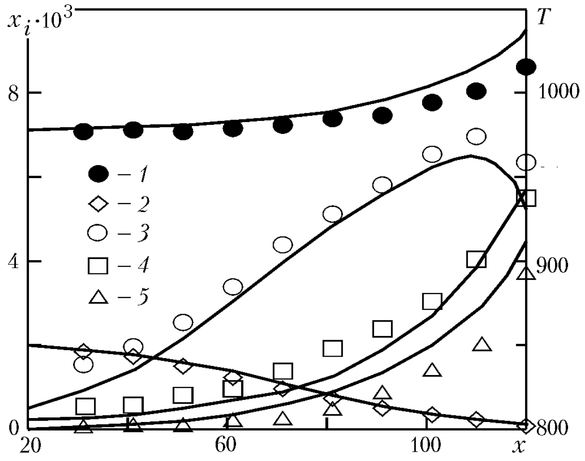


Fig. 1. Change in the temperature T (a) and the mole fraction of the fuel x_{fuel} (b) as a function of the coordinate x in combustion of C_3H_8 propane in a turbulent flow reactor. Points, experimental data of [52], solid and dashed curves, calculation according to the two-stage mechanism [50] and the 6/5 mechanism [51] respectively. T, K; x, cm.

Fig. 2. Change in the temperature T (1) and the mole fractions of the components x_i (2–5) as a function of the coordinate x in combustion of the $C_8H_{18}/O_2/N_2$ mixture in a turbulent flow reactor: 2) C_8H_{18}; 3) C_2H_4; 4) H_2O; 5) CO. Points, experimental data of [52]; curves, results of the present calculation. T, K; x, cm.

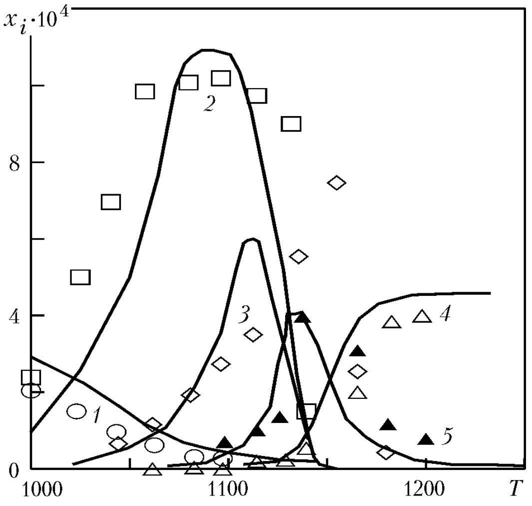
A single-stage global kinetic mechanism is the simplest and most convenient for numerical modeling. This mechanism considers the oxidation process as that directly converting the reagents (C_nH_m and O_2) into the reaction products (CO_2 and H_2O) without formation of intermediate hydrocarbon components [50].

The next step on the road to construction of a simplified model of combustion of a hydrocarbon fuel is the introduction of a two-stage global kinetic mechanism which separates a strongly exothermic oxidation of CO to CO_2 from a less exothermic oxidation of the starting hydrocarbon fuel from CO to H_2O [50]. Adjacent to this group of models are empirical models of combustion of paraffin hydrocarbons with a number of C atoms of 1 to 14; these models have been proposed in [51] and have been recommended as the initial approximation for modeling of turbulent combustion. Nonetheless, since the kinetic parameters of these models have been determined from a comparison of the calculated and measured velocities of propagation of a premixed laminar flame, they do not describe the dynamics of the combustion in turbulent flow reactors and jet-stirred reactors and the experiments on ignition of fuel mixtures in shock tubs and rapid compressor plants.

Figure 1 compares the calculated and experimental data on measurement of the temperature and concentration of the starting fuel in combustion of propane with the use of the two-stage kinetic mechanism [50] and the 6/5 mechanism [51]. The computations have been carried out as applied to the conditions of combustion of the stoichiometric mixture $C_3H_6/O_2/N_2$ in a turbulent adiabatic flow reactor [52]. The thermodynamic characteristics of the components from [53] have been used for calculation of a change in the medium's temperature. As is clear from the figure, the global combustion mechanisms optimized in [50, 51] as applied to the conditions of propagation of a laminar flame yield a too rapid growth in the temperature in turbulent combustion and a sharp decrease in the molecular concentration of the starting hydrocarbon.

A more realistic global kinetic model of combustion of hydrocarbons, which involves the transformation of the starting hydrocarbon to smaller intermediate hydrocarbon components at the initial stage of the combustion, has been proposed in [52]. The general scheme of the process of combustion is written in the form of four gross reactions:

$$C_nH_m \to \frac{n}{2} C_2H_4 + \left(\frac{m}{2} - n\right) H_2 , \qquad (1)$$



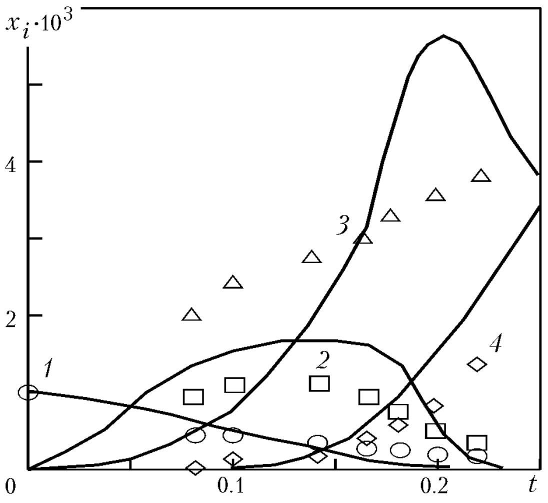


Fig. 3. Mole fractions of the components x_i vs. temperature of the process T in combustion of the n-$C_{16}H_{34}/O_2/N_2$ mixture in a jet-stirred reactor: 1) $C_{16}H_{34}$; 2) C_2H_4; 3) H_2; 4) $CO_2/10$; 5) $CO/10$. Points, experimental data of [19]; curves, results of the present calculation. T, K.

Fig. 4. Dynamics of change in the mole fractions of the components x_i in combustion of C_3H_7cy-C_6H_{11} in a jet-stirred reactor: 1) C_3H_7cy-C_6H_{11}; 2) C_2H_4; 3) CO; 4) CO_2. Points, experimental data of [36]; curves, results of the present calculation. t, sec.

$$C_2H_4 + O_2 \to 2CO + 2H_2\,, \tag{2}$$

$$H_2 + \frac{1}{2}O_2 \to H_2O\,, \tag{3}$$

$$CO + \frac{1}{2}O_2 \to CO_2\,, \tag{4}$$

where the component C_2H_4 represents a combination of all the intermediate hydrocarbon components (mainly olefins) formed in the process of combustion. Since the element composition of kerosene is usually taken to be equal to the arbitrary element composition C = 85 and H = 15 wt. % in heat-engineering calculations, the first reaction of the kinetic scheme of combustion of kerosene is written in the form $C_{10}H_{20} \to 5C_2H_4$. Based on the processing of numerous experimental data, the following expressions have been obtained in [52] for the rates of the corresponding reactions:

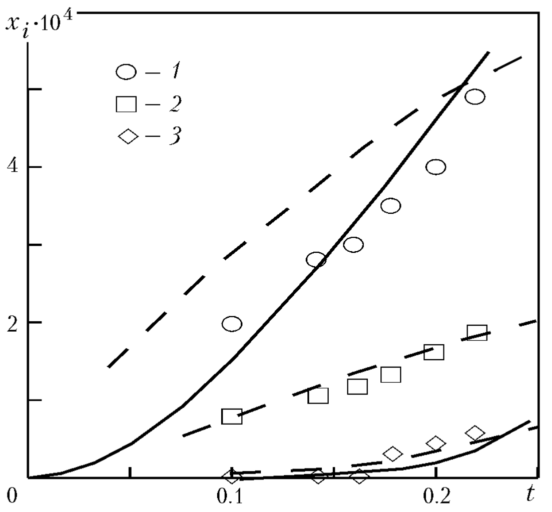
$$w_1 = 2.09 \cdot 10^{17} \exp(-24962/T)\,[C_nH_m]^{0.5}\,[O_2]^{1.07}\,[C_2H_4]^{0.40}\,,$$

$$w_2 = 5.01 \cdot 10^{14} \exp(-25164/T)\,[C_2H_4]^{0.90}\,[O_2]^{1.18}\,[C_nH_m]^{-0.37}\,,$$

$$w_3 = 3.31 \cdot 10^{13} \exp(-20634/T)\,[H_2]^{0.85}\,[O_2]^{1.42}\,[C_2H_4]^{-0.56}\,,$$

$$w_4 = 4.00 \cdot 10^{14} \exp(-20131/T)\,[CO]^{1.0}\,[H_2O]^{0.5}\,[O_2]^{0.25}\,.$$

It is proposed that the correction factor $S = \min\{7.93\exp(-2.4\phi);\,1\}$ be introduced into the dependence for w_4. The initial concentration of C_2H_4 in the expression for w_1 is set to be 10^4 times lower than the initial concentration of the fuel.



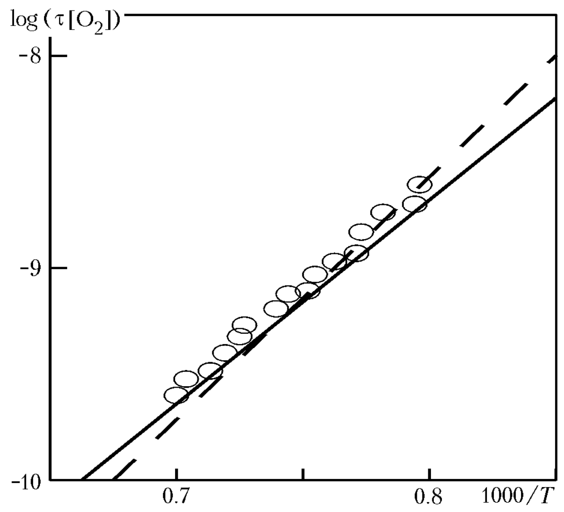


Fig. 5. Dynamics of change in the mole fractions of the components x_i in combustion of Jet A1 kerosene in a jet-stirred reactor: 1) C_2H_4; 2) C_3H_6; 3) CO. Points, experimental data of [35]; solid and dashed curves, results of the present calculation and of that according to the model of [35]. *t*, sec.

Fig. 6. Ignition-delay time τ vs. temperature in the JP-10 kerosene/O_2/Ar mixture behind a reflected shock wave. Points, experimental data of [39]; solid curve, results of the present calculation; dashed curve, data of calculation according to the model of [38]. τ [O_2], sec·mole/cm^3; *T*, K.

To evaluate the suitability of this model for numerical modeling of the process of combustion of hydrocarbons entering into the composition of kerosene and kerosene as a whole, in the present work, we have carried out a series of experiments and have compared the results obtained to the available experimental data. Figure 2 shows the behavior of the concentrations of the basic components and the temperature of the process in combustion of the 0.2 vol. % C_8H_{18} + 13.6 vol. % O_2 + 86.2 vol. % N_2 mixture in a turbulent flow reactor [52] (reactor diameter 20 cm, initial flow rate of the gas 0.73 mole/sec, initial temperature 978 K, and p = 0.1 MPa). As is clear from the figure, the calculation results obtained using the global kinetic model describe the measurement data quite well.

The results of modeling of the process of combustion of *n*-hexane in a jet-stirred reactor and their comparison to experimental data [19] are given in Fig. 3. The starting mixture contains 0.03 vol. % $C_{16}H_{34}$, 0.735 vol. % O_2, and 99.235 vol. % N_2. The time of the process is equal to 0.07 sec; p = 0.1 MPa, and ϕ = 1.0. An analysis of the figure shows that it is possible to attain a satisfactory description of the process using the global kinetic model in question.

Figure 4 compares the calculated and experimental data [36] on combustion of *n*-propyl cyclohexane in the 0.1 vol. % C_3H_7cy-C_6H_{11} + 6.75 vol. % O_2 + 93.15 vol. % N_2 mixture in a jet-stirred reactor at p = 0.1 MPa and T = 1020 K. Quite a satisfactory agreement between the results of numerical modeling of the combustion and the measurement data is observed. It is noteworthy that the behavior of the calculated $x_i = x_i(t)$ curves in the case in question is substantially dependent on the temperature of the process: its change of ten degrees leads to a pronounced shift of the maxima of the concentration curves for C_2H_4, CO, and CO_2. It can be inferred that the selection of the parameters of a global kinetic model is quite accurate [52].

Figure 5 shows the behavior of the concentration curves $x_i = x_i(t)$ (calculated using the global kinetic model [52]) in stoichiometric combustion of a mixture of JET A1 (0.1 vol. %) kerosene with O_2 and N_2 in a jet-stirred reactor at p = 0.1 MPa and T = 973 K and compares them to experimental data [35]. Just as in the previous case, the behavior of the calculated curves is strongly dependent on the temperature of the process.

Figure 6 compares the results of calculation of the delay time of ignition τ in a mixture of JP-10 kerosene (0.00218 vol. %), O_2, and Ar to the measured values of this quantity behind a reflected shock wave at p = 0.3 MPa, T = 1200–1700 K, and ϕ = 0.75 [39]. Also, the figure shows the results of calculation using the model of [38] (dashed curve). It is seen that the calculation according to the global kinetic model yields more accurate results.

CONCLUSIONS

1. A brief analysis of the state of the art in investigations on creation of kinetic models of combustion of heavy hydrocarbons has shown that, at the present time, there is no detailed kinetic mechanism of combustion of kerosene that contains information sufficient for description of a wide range of the phenomena studied. In this connection, the determining role in modeling the physicochemical processes in combustion chambers operating with kerosene is reserved by empirical and semiempirical combustion models describing the behavior of a chemically reacting system in narrow ranges of variation of the parameters of the process.

2. We have selected the most realistic global kinetic model involving the transformation of the molecules of the starting fuel to smaller intermediate hydrocarbon components at the initial stage of the process of combustion. To evaluate the suitability of the model for numerical modeling of the combustion of hydrocarbons entering into the composition of kerosene and kerosene as a whole we have carried out a series of calculations and have compared the results obtained to the available experimental data.

NOTATION

[A], concentration of the component A, mole/cm^3; F, functional; p, pressure, Pa; Q, lower heat of combustion, kJ/kg; S, correction factor; T, temperature, K; t, time, sec; w, reaction rate, mole/(cm^3·sec); x_i, mole fractions of the components; x, coordinate along the reactor axis, cm; ε, error; ϕ, excess-fuel coefficient; τ, ignition-delay time, sec. Subscripts: fuel, fuel; full, total; opt, optimum.

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