Study of synthesis and combustion of composite fuels based on n-decane and Al nanoparticles

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Abstract. The article is devoted to the analysis of a diffusion combustion of a composite fuel (formed by an addition of non-oxidized aluminum (Al) nanoparticles (NP’s) to n-decane) with oxygen. The process of obtaining Al NP’s consisted of a laser fragmentation of initially large commercially produced NP’s (so called “Alex” with mean diameter is about 450 nm) in the solution of isopropanol. A final size distribution of NP’s was determined by a CPS DC2400 measuring disk centrifuge. The morphology of NP’s was characterized with the Transmission Electron Microscope (TEM) JEM-100C. The measured average diameter of NP’s was about 40 nm. In the final step of a preparation of a composite fuel an isopropanol was exchanged on n-decane. To characterize the composite fuel, diffusion combustion was used in combination with the laser diagnostic technique CARS. Temperature distributions along the x direction were measured at two values of distances from the nozzle. It has been shown that, for the fuel consistent of 0.1% mass concentration of Al NP’s in n-decane, the temperature at the distance equaled 14 mm downstream from the nozzle exit of a burner in the vicinity of the flame front was significantly higher (by 200–300 K) than that upon burning of pure n-decane.

1. Introduction
The use of two-component fuels containing additives of solid combustible components such as Li, Al, Mg, Be along with traditional liquid fuels in the form of hydrocarbon, allows increasing the energy characteristics of fuels and their burning rates [1, 2].

Aluminum seems to be an effective additive to hydrocarbon fuels since it allows raising the temperature of combustion products accelerating the combustion process, accelerating the combustion process, stabilizing the flame and, as a consequence, increasing the specific impulse of the engine.

Of particular interest is the addition of aluminum to hydrocarbon fuels in the form of NP’s (10–100 nm) [3]. This is due to the following reasons.
First, when aluminum is introduced into liquid hydrocarbon fuels in the form of a powder (particle diameter \( d \geq 1 \mu m \)), problems arise with the storage and supply of such fuel to the combustion chamber (sedimentation, increased wear of pumps and clogging of nozzles occurs in a fairly short time).

Secondly, the micro particles do not burn completely, and the smallest (with \( d \approx 5-10 \) nm) particles remain in the combustion products, which are the centers of condensation for \( Al_2O_3 \), which is formed in significant quantities previously in the gas phase. This leads to the appearance (in the combustion products) of rather large (micro) particles consisting of \( Al_2O_3 \), with long times of dynamic and thermal relaxation.

This investigation is part of an integrated approach to studying the properties of composite fuels based on traditional hydrocarbon fuels with additives of nanoscale metals or metalloids. It includes the development of methods for the synthesis of such composites, methods and devices for their combustion, optical methods and equipment for diagnosing thermodynamic parameters that allow verification of the proposed theoretical models and evaluate the efficiency of using composite fuels in practical applications.

The main goal of this study is to obtain comparative information on the temperatures in the flame during the combustion of decane (C\(_{10}\)H\(_{22}\)) and decane with Al NP’s. Such measurements make it possible to directly characterize the differences in the spatial structure of heat release in different zones of the flame. An important aspect in the experimental study of the combustion processes of such fuels containing hydrocarbons and nanoscale components is the use of modern, non-contact methods and systems for diagnosing the parameters and composition of the combustion products of these fuels.

To obtain a composite fuel based on decane and nano sized aluminum particles, it was previously [4] used the method of plasma decomposition of vapors of organometallic compounds (precursor) without oxygen access, followed by sharp cooling (quenching) of the decomposition products with liquid fuel. Both plasma decomposition and mixing / quenching processes are combined in one compact reactor. Trimethylaluminum (\( Al(CH_3)_3 \)) was used as a precursor, which was preliminarily evaporated and then mixed with a plasma-forming gas (argon) and fed into an electric discharge reactor.

2. Experiment
In this work, Al NP’s (as the basis for a composite fuel) were obtained during laser fragmentation of the initial Al nanopowder obtained by explosion of an aluminum wire in a vacuum “Alex” with an average initial size of about 450 nm in organic liquids such as n-decane and isopropyl alcohol [5]. Their physicochemical properties have been studied and the optimal parameters of laser radiation have been selected, which make it possible to achieve the maximum rate of synthesis of nanoparticles. It was found that laser irradiation of aluminum in 95% ethanol leads to the formation of aluminum hydroxide, which is unacceptable for its use as a base for composite fuels. It was also revealed that the use of n-decane as a working fluid under laser action leads to its active decomposition and subsequent evaporation of decomposition products due to plasma impact around NP’s. As a result, isopropyl alcohol, which has a low reactivity and does not contain water, was used as a working fluid. Upon completion of experiments on laser synthesis of Al NP’s in isopropyl alcohol, the latter was replaced by n-decane without changing the concentration and chemical properties of NP’s.

The technique of laser fragmentation of industrial aluminum nanopowder in isopropyl alcohol has been applied [7]. For this purpose, an Yb fiber laser source was used with wavelength of 1050–1070 nm, pulse duration of 100 ns and repetition rate of pulses of 20 kHz. Isopropyl alcohol also undergoes decomposition into elemental carbon with the simultaneous release of molecular H\(_2\) [6]. However, the percentage of carbon NP’s under laser exposure to isopropanol is significantly lower than from n-decane, and the liquid remains transparent to laser radiation longer. Isopropanol is easily mixed with n-decane, and a colloidal solution of NP’s of Al in it can then be added to n-decane in the required proportion.

After laser fragmentation lasting about 25 min (this time was determined experimentally for the specific conditions of our experiment) the mass distribution of NP’s reaches a stationary condition (depending on their size) and has a clearly pronounced bimodal shape with a first narrow peak corresponding to the size of particles with a diameter of 40 nm and a half-width on half-maximum of 37 nm and a second-wide peak with a maximum around 450 nm (figure 1).
After integration the full mass of all particles with the diameter from 100 nm to 1000 nm is equalled to 155 [abt. units]

Figure 1. The distribution of fragmented particles by mass depending on their size is shown by a black graph (left scale). Red curve (right scale) – integral values of particles by masses depending on their size. It can be seen from the graph that at the end of the fragmentation process, the mass of large-sized particles is 6 times greater than the mass of particles corresponding to the first peak.

Since the sedimentation of large particles occurs at time intervals that are significantly shorter than the sedimentation of small particles belonging to the first peak in figure 1, this made it possible to separate a solution with NP’s with an average diameter of 40 nm from a solution with larger particles with a diameter greater than 100 nm. The morphology of nanoparticles in the final product was determined with the Transmission Electron Microscope (TEM) JEM-100C, the results of which are shown in figure 2. It can be seen from this picture that there are no particles larger than 100 nm in the final product.

Figure 2. TEM images of NP’s after laser fragmentation of industrial Al nano powder in isopropanol. The scale bar denotes 500 nm.

To study the combustion process of synthesized liquid hydrocarbon fuels with the addition of metal and metalloid NP’s, an experimental stand was developed and built, consisting of a special burner and a diagnostic system based on coherent anti-Stokes Raman scattering spectroscopy (CARS).

The created special continuous burner device with an oxygen-free heater-evaporator of liquid fuel and a diffusion type of mixing of fuel and oxidizer (oxygen or air) makes it possible to obtain stable laminar flames with a stationary and well-defined geometry of the flame front. This, in turn, makes it possible to register changes in the parameters of the flame during the combustion of both pure and combined fuels with sufficient accuracy. The burner structure is shown schematically in figure 3.
Figure 3. Diagram of the burner and the relative position of the laser beams in the flame: 1 – oxidizer flow, 2 – fuel flow, 3 – nitrogen flow, 4 – fuel injector, 5 – evaporator housing, 6 – heater of the evaporator, 7 – burner body, 8 – flame front, 9 – CARS radiation beam (473 nm), 10 – CARS pumping beams in planar BOXCARS geometry (532 nm, 532 nm, 607 nm). The axes of the used coordinate system are drawn. The vertical arrow at the bottom of the flame shows the possibility of moving the evaporator with the nozzle along the Z axis inside the burner housing relative to the focal region of the laser beams.

The developed and adapted to the burner laser system for diagnosing the temperature and composition of the main components of the reacting gas mixture based on CARS spectroscopy (part of the general laser diagnostic system) makes it possible to study in detail the spatial distributions of the parameters of the reacting flows with high spatial resolution. The scheme of the CARS spectrometer is shown in figure 4.

The CARS spectrometer consists of a repetitively pulsed nanosecond Nd$^{3+}$: YAG laser with a crystal for second harmonic generation (10 Hz, 10 ns, 532 nm), a modeless broadband dye laser pumped by it, a system of mirrors and lenses, a spectrograph equipped with a gated optical multichannel analyzer, a pulse delayed generator and a computer. A small part of the second harmonic radiation of the Nd$^{3+}$: YAG laser is used in the CARS process, and the rest of green laser power is used to pump the generator and amplifier of the dye laser. In particular, radiation with a wavelength of 607 nm and a spectral width of 200 cm$^{-1}$ is used to record CARS spectra of N$_2$ molecules. The optical scheme of convergence of the pump beams ensures the alignment of laser pulses in time and matching of the positions and sizes of each of the pump beams in the focal area. The CARS radiation (473 nm) passed through the interference filter from the probed volume is delivered to the spectrograph by using a multimode optical fiber. An optical multichannel analyzer synchronized with a Nd$^{3+}$: YAG laser pulses records the CARS spectrum in each laser pulse. The high spatial resolution of measurements is determined by the size of the intersection region of the focused pump beams crossing in the planar BOXCARS scheme. These dimensions can be characterized by the confocal parameter $b$ and the transverse size of the waist area $2w_0$, which, when the beams were focused by a lens with a focal length $f = 300$ mm, were $b = 2$ mm and $2w_0 = 0.025$ mm.
The range of measured values in CARS thermometry is limited from above by the values at which the dissociation of molecules selected as test occurs and lies in the range 3500–4000 K. Calibration measurements showed that the relative value of the random measurement error is 3.6%. This value characterizes the temperature measurement error in a time equal to the duration of one laser pulse (10 ns). With an increase in the measurement time to 1 s (averaging at 10 laser pulses with a repetition rate of 10 Hz), the relative value of the random error decreases to 1.2%. The relative value of the systematic error is 0.5%.

Measurements of the concentrations of $\text{N}_2$ and $\text{O}_2$ molecules in a cold stream show that the experiment allows to obtain detailed information on their distribution in the mixing region of the combustible mixture and oxidizer flows and, in particular, to observe the diffusion of air oxygen - the nitrogen stream with decane vapors in, and nitrogen out. Since the vapor-gas mixture of decane with nitrogen, created in the evaporator of the burner before mixing with the oxidizer, is homogeneous, the spatial distribution of nitrogen molecules should correspond to the distribution of decane molecules. Analysis of the results of measurements in a cold stream in the direction perpendicular to the flow axis shows the symmetry of the distributions of the $\text{N}_2$ and $\text{O}_2$ concentrations relative to the stream axis, as well as an increase in the $\text{O}_2$ concentration inside the stream and the $\text{N}_2$ concentration at the stream periphery as the distance from the nozzle increases due to diffusion.

3. Results
The diffusion combustion of a synthesized combined fuel consisting of n-decane and Al NP’s has been studied experimentally. Two-dimensional spatial profiles of temperature were studied directly in the combustion zone. A comparative analysis of the parameters of the reacting mixture during the combustion of pure decane and decane containing different amounts of metal NP’s has been carried out. The most characteristic difference is as follows. In the case of combustion of decane with Al NP’s, the temperature values are systematically higher and repeat the profile of the values measured for pure decane. In the areas of the flame front, the temperature difference for the two types of fuels increases with an increase in the distance downstream from the nozzle exit and at a distance of $Z = 14$ mm reaches its maximum value equal to 300 K at a mass concentration of Al NP’s equal to 0.1%. Also, the combustion temperature of pure decane is 2200 K, and the combustion temperature of decane with Al reaches 2500 K. The experimental CARS spectrum and the corresponding calculated spectrum for a given point of the flame in the combustion of decane with Al are shown in figure 5.

Figure 4. A scheme of the CARS spectrometer: YAG – Nd$^{3+}$: YAG pumping laser, G – generator and A – dye laser amplifier, T1,2 – telescopes, L1 and L2 – focusing and collimating lenses, B – burner, F – narrow-band interference filter, C1 and C2 – radiation input and output devices, WG – optical fiber, GS – spectrograph, OMA – optical multichannel analyzer, DG – delayed pulse generator.
The temperature determined from treating the experimental CARS spectrum is equal 2550K.

**Figure 5.** An example of a procedure for determining temperature based on CARS spectra. The black line is the experimental spectrum. The red line is the calculated spectrum with temperature 2500 K. The blue line is the difference spectrum that characterizes the accuracy of the fit.

The temperature distribution over the flame cross section at a distance of $Z = 14$ mm from the nozzle exit is shown in figure 6. With a further increase in $Z$ downstream, the difference in the temperatures of the two fuels decreases monotonically, which is apparently due to the fact that at distances greater than 14 mm in the peripheral region of the stream, the bulk of the fuel (both pure and with Al NP’s) burns out. The difference in temperatures during the combustion of decane with and without Al stabilizes and amounts to 100–120 K, which is apparently due to the somewhat higher specific heat release of decane with Al.

**Figure 6.** Temperature profile in the flame along the X axis of the flow at a distance $Z = 14$ mm from the nozzle exit during combustion of decane and decane with Al NP’s (0.1%).
Measurements of the transverse profiles of the gas temperature directly in the flame at various distances from the nozzle exit during the combustion of pure decane vapor showed the possibility of obtaining a detailed picture of spatial temperature changes, determining the position of the flame front and monitoring its changes with the increase in distance from the nozzle exit.

4. Conclusion
This article presents the results of research aimed at developing the synthesis of composite fuel based on decane and Al nanoparticles, studying the features of its combustion in a specially designed combustion device using laser diagnostic methods. A characteristic feature of the developed approach to the synthesis of nanoparticles is laser fragmentation of Al nanopowder in organic liquids. This method makes it possible to obtain non-oxidized nanoparticles directly in liquid hydrocarbon fuel.

The created experimental stand, consisting of a combustion device and diagnostic tools based on CARS and LIF, demonstrated the ability to obtain detailed information on the spatial distribution of the concentrations of oxidizer molecules, fuel and gas temperatures in the flame. This information makes it possible to trace and characterize the differences in the spatial structure of the composition and heat release in different zones of the flame.

The obtained measurements are supposed to be used to verify the proposed theoretical models, simulate kinetic and dynamic processes in the flow of a reacting mixture, and evaluate the efficiency of using the developed composite fuels for practical applications.

It should be noted that the complexity of the combustion processes of nanoparticles, even in such a simple form of flame, requires additional research to clarify the effect of evaporation of nanoparticles, secondary reactions, clustering of combustion products, etc.

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