**UDC 662.758.2:665.7.038**
**https://doi.org/10.15407/kataliz2025.36.086**

# On the mechanism of influence of carbon nanoparticle additives on high-temperature oxidation of diesel fuels

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The problem of increasing the energy efficiency of liquid motor fuels due to ultra-small amounts of nanoparticles is considered. The relationship between the completeness of fuel combustion in engines and the preliminary liquid-phase oxidation of hydrocarbons in atomized droplets is discussed. High-temperature oxidation at 150 °C with air oxygen of model diesel fuel components in a bubble-type reactor was carried out. The effect of carbon spheroidal nanoclusters on the dynamics of changes in the composition of the liquid phase during oxidation under the same conditions of *n*-decane and *n*-dodecane was studied by gas-liquid chromatography. It is shown that the effect of nanoparticles on the conversion of hydrocarbons in a liquid oxidate can vary depending on the proximity of the oxidation process temperature and the boiling point of the liquid. For high-boiling *n*-dodecane (216 °C) under oxidation conditions at 150 °C, the presence of nanoparticles in the solution slows down the change in the composition of the liquid oxidate. When oxidizing a more low-boiling *n*-decane (174 °C), nanocluster additives accelerate the reduction of the initial hydrocarbon content in the liquid mass. The obtained results are explained by the simultaneous interaction of hydrocarbon molecules with oxygen in the liquid-phase and gas-phase reaction regions. Carbon nanoclusters inhibit chain reactions of liquid-phase oxidation in the kinetic mode, but activate gas-phase oxidation by accelerating the diffusion stage. Acceleration of diffusion and evaporation of hydrocarbons from the liquid phase is explained by a change in the supramolecular structure of the solution under the influence of nanoparticles with a decrease in viscosity. It is shown that the non-monotonic nature of the change in the viscosity of *n*-decane from the content of nanoclusters in the solution correlates with the extreme non-monotonic dependence of the energy efficiency of diesel fuel on the concentration of such additives. A possible dependence between the duration of the stages of evaporation of low-boiling components from sprayed droplets and the completeness of combustion of mixed motor fuels is considered.

***Keywords***: energy efficiency of motor fuels, liquid-phase oxidation of hydrocarbons with oxygen, additives to petroleum products, carbon nanoclusters

## *Introduction*

Motor fuels are the most important strategic resources of states. Modern motor fuels are used mainly in liquid form (gasoline, diesel, aviation and rocket fuel), which is due to their high energy intensity and ease of transportation and use.

In connection with the growth of motor fuel consumption and the increase in their negative impact on the environment, an urgent problem of petrochemistry is to increase the energy efficiency of liquid fuels during combustion in engines with a simultaneous reduction in emissions of toxic intermediate products [1].

To increase the energy efficiency of motor fuels, additives (metal oxides, metal complex compounds, nano-sized carbon clusters of various structures) are introduced into them [2]. The presence of minimal concentrations of such additives in fuel compositions increases the rate of interaction of fuel molecules with oxygen in the air and contributes to the conversion of initial reactants into final products ($CO_2$ and $H_2O$) during combustion in power units.

Effect of increasing the energy efficiency of motor fuels is usually explained by the additional additive contribution of the surface energy of nanoparticles to the thermal energy released during the chemical interaction of fuel molecules with oxygen [7-10]. However, this explanation does not take into account the simultaneous increase in heat generation and reduction in emissions of intermediate combustion products. Such a two-factor effect can be ensured only by increasing the completeness of fuel combustion.

According to the hypothesis of the surface energy of nanoparticles as the main additional contribution to heat generation, one would expect a monotonic increase in the magnitude of the effect with increasing the content of additives in the fuel. However, as a rule, the increase in the energy efficiency of fuels under the influence of nanoparticle additions depends on their concentration non-monotonically.

Studies [11, 12] have shown that when adding small amounts of carbon spheroidal nanoclusters to gasoline and diesel fuel, the energy efficiency of fuels increases by 10-20 % with a simultaneous decrease in emissions of intermediate toxic compounds. The greatest effect is observed at the concentration of the components within about $2{\cdot}10^{-4}$ wt. %, and outside this range the magnitude of the effect decreases.

Earlier in [13] we suggested that at low temperatures nanoparticles in the fuel are oxidation inhibitors, and at high temperatures they can change the direction of their action and become initiators of liquid-phase oxidation. Although this point of view allows us to explain the increase in heat release simultaneously with a decrease in emissions of intermediate products, it does not explain the non-monotonic extreme dependence of the energy efficiency of fuels on the concentration of the components.

Thus, the question of the mechanism of action of small doses of nanoparticles on the energy release of liquid motor fuels remains open.

*Idea and purpose of the research*

The interaction of hydrocarbons of motor fuels with molecular oxygen occurs sequentially in three temperature ranges.

1. Low temperatures (20-100 °C), at which the fuel is at the stages of storage and supply through the fuel equipment to the reaction volume of the combustion chambers.
2. Stationary high temperatures (100-350 °C), at which the atomized fuel droplets after injection into the working zone of the combustion chamber are gradually heated to the boiling temperatures of the fuel composition components.
3. Non-stationary high temperatures in the range from the boiling temperatures of the fuel components to the flame temperature of 1000-2000 °C. In this case, part of the fuel molecules in the reaction volume is in liquid droplets. These droplets gradually evaporate, and in the gas phase around the liquid droplets (reagent suppliers) combustion occurs.

When considering the combustion of atomized liquid fuel in engines, it is usually assumed [14] that the liquid dispersed phase plays the role of only a supplier of hydrocarbons to the gas phase, in which chemical processes of interaction with oxygen occur with the release of thermal energy.

However, part of the hydrocarbons of the mixed fuel with a wide range of boiling points of the components is stored for a long time at high temperatures in the liquid state until they evaporate. During this time, liquid-phase reactions with dissolved oxygen and the transformation of the initial hydrocarbons into oxygen-containing compounds are possible in the droplets. The primary products of the interaction of hydrocarbon molecules with oxygen are hydroperoxides, which decompose into ketones and aldehydes, and subsequently into stable alcohols and acids [15].

When polar oxidation products accumulate in droplets of liquid hydrocarbons in solution, supramolecular micelle-like spatial structures are formed [16, 17]. These micellar structures block the diffusion and evaporation of hydrocarbon molecules and reduce the completeness of fuel combustion. Due to the encapsulation of the initial fuel molecules in such isolated volumes, hydrocarbons pyrolysis occurs with the formation of carcinogenic polycyclic compounds, carbon monoxide and soot.

In [11, 12, 18] we suggested that nanoadditives introduced in small amounts into liquid fuels prevent the formation of micellar structures in the liquid phase from polar oxidized products by forming a competitive ordered (domain) structure around nanoparticles. When such domain structures occur, the mass transfer and evaporation of hydrocarbon molecules from the liquid into the gas volume may not slow down, but rather accelerate.

A detailed study of liquid-phase transformations of hydrocarbons into oxygen-containing compounds, as well as the influence of introduced terms on the intensity of such transformations depending on the composition of fuels and conditions of the oxidation process, is necessary for understanding the kinetics of reactions and controlling the completeness of combustion of liquid motor fuels in combustion chambers.

Liquid-phase oxidation of hydrocarbons in laboratory conditions is modeled and studied, as a rule, in a closed system, registering the amount of absorbed oxygen or the consumption of the initial hydrocarbon, as well as the accumulation of the main reaction products [16, 17]. Studies of the influence of various additives on the kinetics of oxidation of liquid media are carried out at low temperatures in order to exclude the role of gas-phase interaction processes.

The processes of oxidation of liquids in the transient two-phase regime and the influence of additives on such processes have been studied to a lesser extent.

It is obvious that if nanoparticle additives affect the interaction processes in the gas space, then at the same oxidation temperature of liquid hydrocarbons with different boiling points, the effect of additives on the dynamics of the transformation of the initial reagent will be different.

The contribution of gas-phase reactions to the transformation of the starting product becomes significant for liquids with a boiling point close to the temperature of the oxidation process. At the same time, if the additives of nanoparticles contribute to the acceleration of the evaporation of liquid molecules, then the interaction of hydrocarbons with oxygen in the near-surface gas layer increases. Some of the formed oxygen-containing products have an increased boiling point, they condense and return to the liquid reaction mass. As a result, a faster change in the concentration of the starting reagent in the solution will be recorded than in the absence of additives.

If the boiling point of the oxidizing compound is much higher than the heating temperature of the solution, then the interaction with oxygen under these conditions will occur only in the liquid phase. In such a situation, the introduction of nanoparticles into the solution will either not affect the rate of change in the composition of the liquid phase, or, conversely, may slow down the transformation of the starting substance.

The aim of this work is to experimentally assess the influence of nanoparticles on the dynamics of changes in the composition of the liquid phase during high-temperature two-phase oxidation mode of low and middle distillate components of diesel fuel under the same temperature conditions. Analysis of the obtained experimental results will allow us to consider the possible effect of the introduced nanoparticles on the diffusion stage and evaporation of hydrocarbon molecules from the liquid phase into the gas reaction volume during the combustion of multicomponent fuels.

### *Materials and conditions of experiment*

Structurally similar alkane components of diesel fuels: *n*-decane and *n*-dodecane were chosen as model liquid media with different boiling temperatures. The boiling point of *n*-decane (174 °C) is close to the temperature at which oxidation was carried out (150 °C). The boiling point of *n*-dodecane (216 °C) is significantly higher than the temperature of the oxidation process. In the selected compounds manufactured by Merks (brand h), the content of the main component was not less than 99.6 wt. %.

The oxidation of selected individual compounds and compounds with nanoparticle additives with molecular oxygen was carried out in a bubbling glass reactor in an air flow with a flow rate of 10 l/h. The reactor was equipped with a heating system, thermocouple and sampling ports, and a reflux condenser for returning liquid products to the mass undergoing oxidation. At regular intervals, without interrupting the oxidation process, liquid samples were prepared and the composition of the liquid-phase oxidation product was analyzed chromatographically.

Gas chromatographic analysis of oxidation products was performed on an Agilent Technologies 7890A chromatograph with a flame ionization detector using a 60 m long, 0.320 mm internal diameter quartz capillary column with a medium-polar cyanopropylmethylsilicone (6 % cyanopropyl, 94 % methylpolysiloxane) stationary phase DB-624 UI (layer thickness 1.8 μm) in the isothermal mode. Helium was used as a carrier gas at a flow rate of 2.0 ml/min. The analysis temperature was 210 °C. The evaporator temperature was 260 °C, the detector temperature was 250 °C. Samples were introduced into the column with a 10 μl microsyringe. Sample volume: 0.4-0.6 μl. The results were processed using the ChemStation analytical program.

Samples of alkane solutions with carbon nanoparticles were prepared as follows. Carbon nanoclusters were obtained by high-frequency discharge-pulse synthesis using a light hydrocarbon fraction of propane-butane as the starting material [13]. To increase the solubility and stability of the solutions, carbon nanoclusters were brominated in excess liquid bromine at 20 °C for 72 h. The residual bromine was driven off in vacuum at room temperature. Isolation of nanoparticles from the synthesis product and their size fractionation were carried out by extraction in absolute ethanol. The average size of the extracted nanoparticles, which was estimated by electron and atomic force microscopy methods, was 10-15 nm [13].

Solutions of nanoparticles in alkanes were prepared using an ultrasonic low-frequency (22 kHz ± 10 kHz) disperser. From the obtained stable solution with the maximum concentration of nanoparticles, solutions with a lower concentration required for the study were prepared by adding calculated amounts of hydrocarbons.

For each sample, repeated oxidation experiments were carried out under similar conditions. Deviations in the content of specific products in the liquid mass under similar oxidation conditions did not exceed ± 5 %. Studies of the effect of carbon nanocluster additives on increasing the saturated vapor pressure of fuel were carried out using commercial gasoline A-95.

### *Results and discussion*

Fig. 1 shows the results of the study of the conversion over time of pure *n*-dodecane and *n*-dodecane with the addition of $1 \cdot 10^{-4}$ wt. % carbon nanoclusters during high-temperature oxidation with air oxygen.

At the initial stage of oxidation, a weakly pronounced induction period was observed for the studied substances. The time of slow change in the concentration of the starting *n*-dodecane did not exceed 20 min. Perhaps such a small value of the induction period was associated with the presence of peroxide compounds in the starting product.

After 3 hours of oxidation, the decrease in the content of the starting reagent in the liquid mass for pure *n*-dodecane was 14 %, and when oxidizing *n*-dodecane with the addition of nanoparticles, the conversion was 12 %. Thus, the addition of nanoparticles in this case weakly inhibits the process of liquid-phase oxidation.

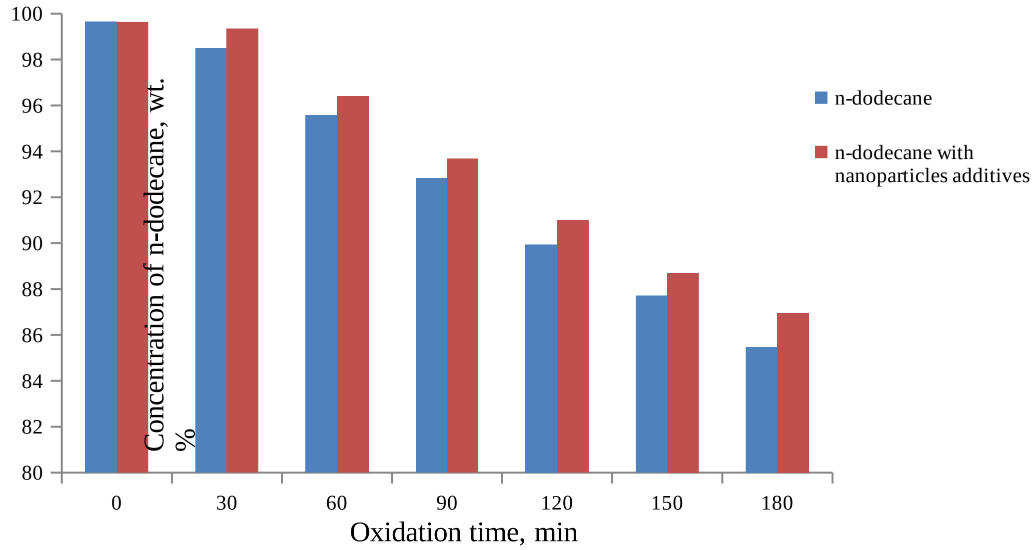

**Fig. 1.** Dynamics of changes in content of starting alkane in liquid phase during high-temperature oxidation (150 °C) with air oxygen: pure *n*-dodecane and with addition of $1\cdot10^{-4}$ wt. % carbon nanoclusters

The results of changes in the concentration of the starting hydrocarbon in the liquid reaction mass for pure *n*-decane and *n*-decane with the addition of $1\cdot10^{-4}$ wt. % carbon nanoclusters during oxidation under similar conditions are shown in Fig. 2. At the initial stage of this process a slow development of the reaction is observed. The duration of this induction period (corresponding to the accumulation of hydroperoxides) was about 90 min, after which autoacceleration occurs due to the decomposition of hydroperoxides with the formation of oxygen-containing compounds in the oxidate.

The sequence of formation of oxidation products of *n*-decane is described by the scheme:

*n*-decane → hydroperoxides → ketones → alcohols and acids

After 3 hours of oxidation, the change in the concentration of *n*-decane in the solution was less than during the oxidation of *n*-dodecane during the same time. For pure *n*-decane without nanoparticle additives, the conversion of the starting reagent was only 1.8 %, and for the solution with nanoparticles - about 5 %.

After 5 hours of oxidation, the conversion of pure alkane was 4.8 %, and for alkanes with nanoclusters, the conversion value was significantly higher and was 19.3 %. Thus, during the oxidation of a hydrocarbon whose boiling point is close to the process temperature, the presence of nanoparticles accelerates the conversion of the starting reagent in the liquid mass.

According to the results of gas chromatography of the oxidates, the main oxidation products were $C_{10}$ secondary alcohols and isomeric ketones with different placement of the carbonyl group in the hydrocarbon skeletal chain. Among other oxygenates, a small amount of $C_1$-$C_9$ aliphatic acids and aldehydes was detected. When the oxidation process was prolonged for more than 2.5 hours, higher-boiling compounds (esters with a boiling point above 260 °C) were recorded in the oxidation products.

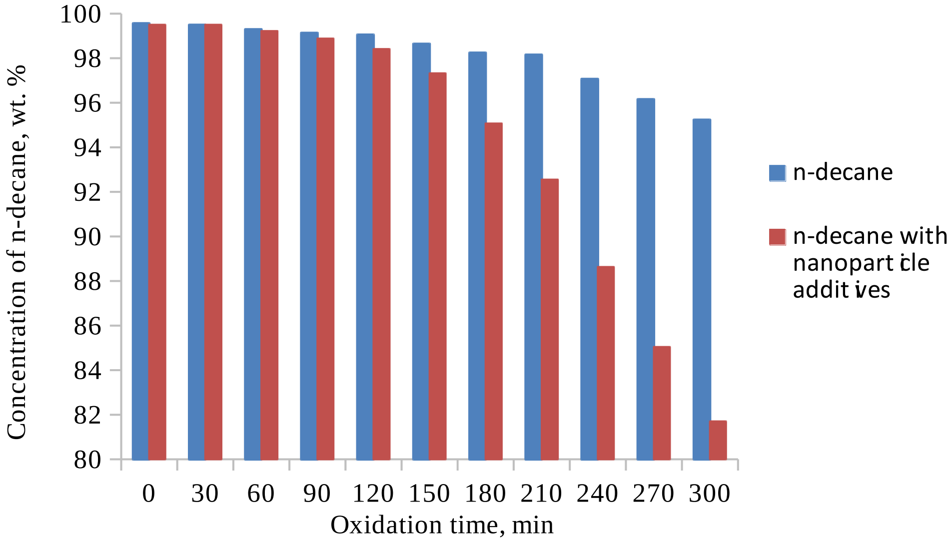

**Fig. 2.** Dynamics of changes in content of starting alkane in liquid phase during high-temperature oxidation (150 °C) with air oxygen at a flow rate of 10 l/h: pure *n*-decane and with addition of carbon nanoclusters

Different directions of action of nanocluster additives on the oxidation of selected alkanes should be explained by an additional contribution to the conversion of liquid oxidates of gas-phase reactions.

When oxidizing hydrocarbons, the boiling point of which is close to the process temperature, the introduction of nanoclusters into the oxidized composition contributes to the acceleration of the conversion of the starting compound. This increase in oxygen-containing products in the liquid oxidate with nanoparticles is due to the intensification of the interaction processes in the gas reaction zone. Alcohols and esters that arise in the upper gas layer have higher boiling points than the original alkanes (for example, the boiling point of *n*-decane is 174 °C, and *n*-decyl alcohol is 231 °C). Therefore, high-boiling oxidation products condense and return to the liquid phase, and their accumulation in the oxidate leads to a decrease in the relative content of original *n*-decane in the liquid mass. According to the law of active masses, the rate of a chemical reaction is proportional to the concentrations of reactants in stoichiometric degrees. At low temperatures, far from the boiling point of the hydrocarbon liquid, the content of hydrocarbon molecules in the gas phase is insignificant and the interaction with oxygen occurs only in liquid-phase volumes. At temperatures close to the boiling point of the liquid, the content of hydrocarbons in the gas region increases, where there is an excess of oxygen molecules. The reaction zone of interaction of hydrocarbons with oxygen shifts to the air region adjacent to the surface of liquid-phase volumes [18, 19].

Indeed, as can be seen from the results presented in Fig. 3, the introduction of carbon nanoparticles into liquid hydrocarbon fuels contributes to an increase in the saturated vapor pressure of such liquids. This effect confirms the assumption that nanoparticle additives accelerate the diffusion of hydrocarbon molecules from the bulk layers of the liquid to the surface and the evaporation of such molecules. The rate and degree of conversion of hydrocarbon molecules in near-surface gas regions are limited by the diffusion of molecules from the liquid volumes and the removal of reaction products from these reaction regions.

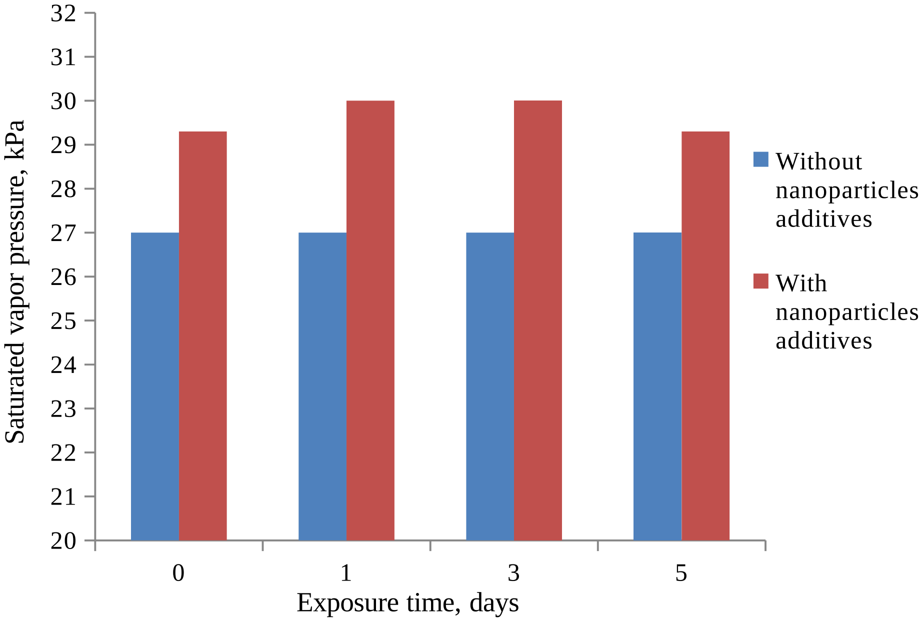

**Fig. 3.** Increase in saturated vapor pressure of commercial gasoline A-95 with addition of $2 \cdot 10^{-4}$ wt. % carbon spheroidal nanoclusters (measurements were carried out on a Reid device at a temperature of 37.8 °C). The error in determining the pressure value is less than 0.1 kPa

The removal of oxidation products from the interphase regions occurs in two opposite directions - the most easily boiling ones enter the air space, and products with elevated boiling points (higher alcohols, ketones, acids) return to the liquid phase.

Let us consider the possible impact on the completeness of fuel combustion in engines of the effect of increasing the diffusion rate and evaporation of hydrocarbon molecules from liquid droplets under the action of nanoparticles. As a rule, liquid motor fuels are multicomponent mixtures with a fairly wide range of boiling points of components. The evaporation of droplets of a multicomponent composition in a heated gas stream has been little studied both experimentally and theoretically [21-23].

When describing the evaporation of droplets of multicomponent mixtures, the approximation of continuous thermodynamics or a more accurate discrete-component approach is used [24, 25].

In the discrete-component approach to modeling the evaporation of multicomponent liquid droplets in a heated gas environment, a system of (n+1) heat and mass transfer equations is considered, written separately for each component, where n is the number of component compounds of the mixed fuel. Even for binary mixtures, the exact solution of such systems of equations is quite laborious, but the results of the computational experiment allow us to conclude that the course of evaporation of mixed fuels differs from the evaporation of droplets of monofuel by the appearance of certain features. In work [26], based on the discrete-component approach to describing heat and mass transfer processes, numerical modeling of the evaporation process of droplets of lower alcohols - ethanol, butanol and their binary mixtures - was carried out. The evaporation of fuel mixture droplets of different initial composition with an initial size of 2 mm at different component ratios in air heated to temperatures of 160-400 °C was considered.

The specific curves of changes in the characteristics of the drop over time during evaporation depend on the composition, initial droplet size, and bulk temperature of the heated gas. However, a common fact is that in the case of drops of binary mixtures of alcohols, the evaporation of molecules of different components is not realized simultaneously and continuously, but selectively component by component. At the same time, changes in the temperature, size, and composition of the drops of the studied fuels during evaporation occur stepwise and discretely (Fig. 4) [26].

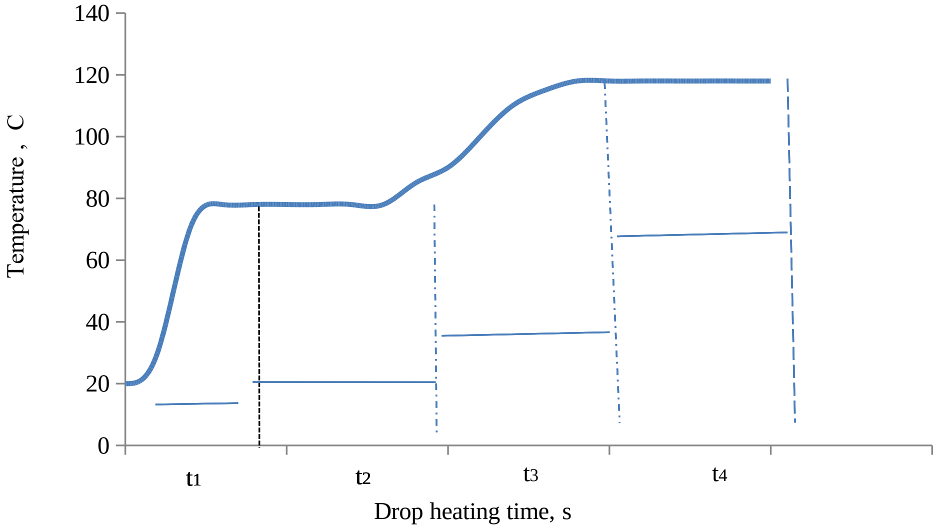

**Fig. 4.** Characteristic curve of drop temperature changes during evaporation of a model two-component fuel mixture (40 % ethanol + 60 % butanol) in a heated gas volume according to [26]: $t_1$ and $t_3$ – duration of drop heating stages, $t_2$ and $t_4$ – duration of drop evaporation stages

Initially, the drop temperature increases to the boiling point of the most low-boiling component without loss of mass and reduction in drop size. Then, when the boiling point of the low-boiling component is reached, the drop temperature stabilizes, and for some time this component evaporates with a decrease in drop size. During the evaporation time, the drop temperature is maintained constant due to the “conditioning effect” - heat removal for evaporation of the low-boiling component of the mixture.

Changes in time of the temperature of drops of the fuel mixture evaporating in a heated environment, with different initial ratios of mass fractions of the components, other things being equal, are qualitatively similar. All mixtures considered in [26] are characterized by relatively short time intervals of droplet heating. The duration of the entire process of such discrete stepwise evaporation of the droplet, as the concentration of components with a lower phase transition temperature increases, is increasingly determined by the kinetics of evaporation of the most volatile component. Thus, the duration of the stay of high-boiling components in a liquid droplet (and therefore, the degree and depth of their liquid-phase conversion during reactions with oxygen dissolved in the liquid) is determined by the duration of the evaporation time of low-boiling components.

Due to the multicomponent nature of the fractional composition of gasoline and diesel motor fuels (the boiling points of diesel fuel components are within 160-360 °C), the process of their heating and evaporation in the heated gas volume of the combustion chambers proceeds in multiple discrete jumps with short, but finite in duration, individual stages.

If the diffusion rate of low-boiling hydrocarbon molecules in the liquid increases, then the duration of their evaporation time decreases. At the same time, accordingly, for higher-boiling components, the residence time in the liquid is reduced and the possibility of interaction with oxygen in the drop decreases. This means that the accumulation of oxidized intermediate products in liquid oxidates decreases.

And, conversely, with a decrease in the diffusion rate of low-boiling molecules in droplets, the duration of the evaporation time of such components increases. Accordingly, the time for the implementation of chemical reactions of the liquid-phase interaction of higher-boiling molecules with oxygen inside the droplets increases. In such a situation, when a sufficient amount of polar products accumulates in the droplets and they form micelles, pyrolysis of the highest boiling fuel components occurs inside the liquid droplets, with the appearance of resinous carcinogenic products and unburned carbon (soot) in the emissions.

The discrete stepwise nature of the evaporation of components in multicomponent liquid fuel droplets should have the greatest impact on the completeness of combustion of high-boiling motor fuels (diesel and jet). Therefore, reducing the characteristic evaporation time of light components using nanoparticle additives can be an effective resource for increasing the energy efficiency of such fuels.

The results of studies of the influence of various additives on the evaporation rate of liquid substances are quite contradictory. For the studied media (water, alcohols, petroleum products) and various nanoparticles [27-29], both acceleration and inhibition of diffusion and evaporation were found. In addition, the direction of the action of additives on these processes may also depend on the concentration of the additives.

In the general case, the mass transfer coefficient D in a liquid according to the Stokes-Einstein equation [30] depends on the viscosity of the medium as follows: $D = kT/6\pi \cdot \mu \cdot a$, where $k$ is the Boltzmann constant, $T$ - temperature, $\mu$ - dynamic viscosity of liquid, $a$ - characteristic size (hydrodynamic radius) of diffusing particle. From this relation it follows that the speed of movement of fuel molecules from the liquid to the gas region is inversely proportional to the viscosity of liquid phase.

Viscosity is a characteristic of the energy of intermolecular interactions in a liquid. Therefore, any factors that change the intermolecular interaction (structure formation or destruction of structures) and are accompanied by a change in viscosity affect the mass transfer and evaporation of molecules from the bulk layers of the liquid.

Let us consider how the viscosity of a hydrocarbon liquid changes when small amounts of carbon nanoparticles are added to it. Fig. 5 shows the dependence of the viscosity of *n*-decane on the content of carbon nanoclusters additives. As follows from the obtained data, the introduction of carbon nanoclusters into *n*-decane in an amount of $10^{-4}$ wt. % reduces the viscosity of the solution by approximately 10 %. Beyond this concentration of nanoclusters, the viscosity changes are less significant, and with an increase in the content of nanoparticles in the alkane above $10^{-3}$ wt. %, the viscosity of the solution begins to increase.

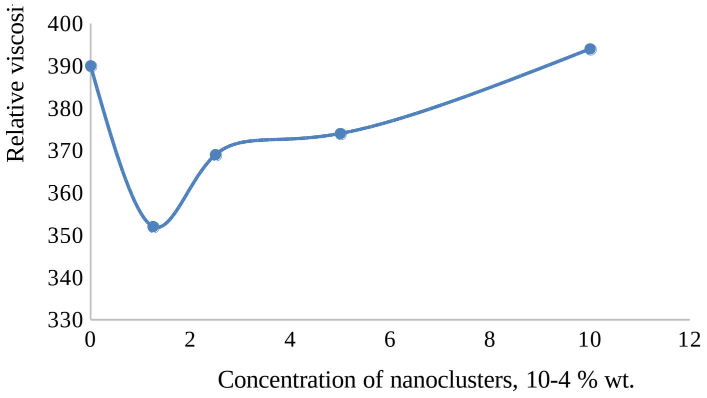

**Fig. 5.** Dependence of *n*-decane viscosity on concentration of carbon nanoclusters

According to the results of engine tests on a diesel engine in [12] it was shown that the introduction of carbon nanoclusters into diesel fuel allows for a 10-20 % increase in the energy efficiency of the fuel during combustion in engines. At the same time, the maximum increase in energy efficiency under the influence of nanoparticle additives was observed at their concentration in the fuel of about $10^{-4}$ wt. %. Beyond this value of the additive content in fuels, magnitude of the effect decreased. Thus, the energy efficiency of the fuel during combustion changes with a change in the content of nanoparticles symbatically with a change in the viscosity of the hydrocarbon liquid (Fig. 5).

## *Conclusions*

Adding ultra-small amounts of nanoparticles to liquid multicomponent motor fuels increases the completeness of combustion and energy efficiency of fuels. The article proposes a non-trivial approach to explaining the mechanism of this effect. The negative impact on the completeness of combustion of multicomponent liquid fuels of the discrete selective nature of evaporation from liquid droplets of components with different boiling points is considered. Long-term evaporation of low-boiling ingredients from liquid fuel droplets restrains the temperature increase and extends the duration of the existence of a liquid drop in a heated gas volume. Such a delay in the evaporation of high-boiling molecules contributes to liquid-phase reactions of their oxidation and an increase in the concentration of intermediate toxic products during fuel combustion. Nanoparticle additives allow accelerating the diffusion of molecules in the liquid phase and reducing the duration of the stages of evaporation of low-boiling components of the mixed fuel. Reducing the evaporation time of light components reduces the time for liquid-phase reactions of high-boiling hydrocarbons with oxygen and prevents the formation of intermediate conversion products in the volume of liquid droplets.

### *Acknowledgements*

The authors express their gratitude to Academician of the NAS of Ukraine A.G. Naumovets for interest and support of research in this area.

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*Надійшла до редакції 21.08.2025*

# Про механізм впливу добавок карбонових наночастинок на високотемпературне окиснення дизельних палив

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Розглянуто проблему підвищення енергетичної ефективності рідких моторних палив за рахунок надмалих кількостей наночастинок. Обговорюється взаємозв’язок між повнотою згоряння палив у двигунах і попереднім рідкофазним окисненням вуглеводнів у розпилених краплях. Проведено високотемпературне окиснення при 150 °С киснем повітря модельних компонентів дизельних палив в реакторі барботажного типу. Методом газорідинної хроматографії вивчено вплив вуглецевих сфероїдальних нанокластерів на динаміку зміни складу рідкої фази під час окиснення за однакових умов *н*-декану та *н*-додекану. Показано, що вплив наночастинок на перетворення вуглеводнів у рідкому оксидаті може бути різним залежно від близькості температури процесу окиснення та температури кипіння рідини. Для висококиплячого *н*-додекану (216 °С) в умовах окиснення при 150 °С наявність наночастинок в розчині уповільнює зміну складу рідкого оксидату. При окисненні більш легкокиплячого *н*-декану (174 °С) добавки нанокластерів прискорюють зменшення вмісту вихідного вуглеводню в рідкій масі. Отримані результати пояснюються одночасною взаємодією молекул вуглеводнів з киснем в рідкофазній і газофазній реакційних областях. Вуглецеві нанокластери гальмують ланцюгові реакції рідкофазного окиснення в кінетичному режимі, але активують газофазне окиснення за рахунок прискорення стадії дифузії. Прискорення дифузії і випаровування вуглеводнів з рідкої фази пояснюється зміною супрамолекулярної структури розчину під впливом наночастинок зі зменшенням в’язкості. Показано, що немонотонний характер зміни в’язкості *н*-декану від вмісту нанокластерів у розчині корелює з екстремальною немонотонною залежністю енергетичної ефективності дизельного палива від концентрації таких добавок. Розглянуто можливу залежність між тривалістю стадій випаровування легкокиплячих компонентів з розпилених крапель і повнотою згоряння сумішевих моторних палив.

***Ключові слова:*** енергетична ефективність моторних палив, рідкофазне окиснення вуглеводнів киснем, добавки до нафтопродуктів, карбонові нанокластери