

Prediction of multi-component effects on ignition delay of oxygenated diesel fuel blends

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The quasi-stationary (Q-S), spherically symmetric combustion of the isolated multi-component droplets of oxygenated diesel fuel has been modelled using a variable mechanism, which has been developed and validated against several independent data sets. The composition of three-component motor fuel, consisting of fossil diesel (DF), rapeseed oil methyl ester (hereinafter RME; B100) and dehydrated ethyl alcohol (DEA), closing to DF by its ignition delay characteristic is established. Numerical simulation results show that in contrast to RME, the additive of dehydrated ethyl alcohol to DF/RME blend tends to increase a time of ignition delay. Striving for improving of the combustion process strained by bigger volumes of fossil diesel being replaced by oxygenated biofuels to meet ecological behavior and economical independence on imported fuels, as well as simultaneously omitting any regulatory adjustment, leads to combining of dehydrated ethyl alcohol and rapeseed oil methyl ester to compound the conventional diesel fuel.

Keywords: Multi-component effects, Ignition delay, Fuel droplet, Biofuel combustion, Quasi-stationary combustion, Combustion modelling

Fuel ignition delay (hereinafter ID) and its effects on combustion stability and pollutant formation is a key aspect of research in current engines and fuels. During the delay period, the injected fuel undergoes complex physical and chemical processes such as atomization, evaporation, mix up and preliminary chemical reaction. Ignition takes place after the preparation and reaction of the fuel-air mixture and leads to fast exothermic reaction¹. Namasivayam *et al.*² concluded that the emissions of particulate matter and nitrogen oxides remain the main hurdle in the complete exploitation of compression-ignition engines. Despite many experimental trials, sustaining the fact that use of biodiesel and dehydrated ethyl alcohol in diesel engines results in substantial reductions of unburned hydrocarbons, carbon monoxide and particulate matter, most studies have shown that bio-based fuels result in an increase in NO_x emissions with respect to petroleum diesel³⁻⁷. The complete mechanism behind the NO_x increase from biofuels of the first-generation is not completely understood but evidence suggests that it is caused by differences in both the physical properties and the chemical oxidation mechanisms

between alternative fuels of biological origin and petroleum diesel^{3,7}. Marchese *et al.*³ emphasizes, that poor understanding of above mentioned parameters is limiting development of ASTM specifications for alternative fuel blends and additional research is required. Citing Szko and Schaeffer⁸, Namasivayam *et al.*^{2,4} as well as Korakianitis *et al.*⁵, such approach produces energy carriers for multi-fuel and multi-product strategies, where flexibility is a key target, allied to other co-benefits, especially those related to the increased use of renewable energy sources.

Admittedly, the research into ignition characteristics similitude could not be accomplished by the combustion device tests alone, not taking into consideration physical-chemical processes involved⁹. Hereby, to be on the safe side while discussing the thermal processes within the combustion of the multi-component blends of oxygenated diesel fuel, we've concluded to readjust a complicated mechanisms of the mathematical theory of combustion based quasi-stationary (Q-S) models of hydrocarbon fuel droplet combustion¹⁰⁻¹² to meet an easy accessible possibility for the primary studies of the multi-component effects on the motor fuel ignition delay^{9,13}.

However, the cause and effect relationships implicit in the test results are often hard to

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interpreting, thus making it difficult to establish strategies that carry-over from one design iteration to the next through experimentation alone^{1,9,13}. On the other hand, modeling approaches, although less precise in predicting the outcome of a specific test, can effectively isolate one variable at a time and point out trends and causes¹.

In the literature, hardly any data are available at present on the ignition delay for a number of advanced fuels, and the known results relate to conventional fuels alone. In addition, experimental investigations of the period of ignition delay are usually performed using a special simulating (more often than not, transparent) bomb of constant volume. It is obvious that, in such cases, the experiment (including the visual observation of the ignition process) turns out to be simpler and is associated with lower material costs¹⁴. While talking about the numerical simulation, one could be said briefly – until recently, mostly complicated models for calculation of ignition delay have been used^{1,10-12,15-20}. Due to a wide spectrum of variable parameters a single component fuels were target of researches^{1,17,19,20}. However, droplet size and fuel chemistry are all functions of fuel composition and vaporization rates^{1,17}. Multi-component effects were not considered to be serious for reasons that commercial fuel blends are highly refined and lie within narrow specification ranges, and requirements of combustor efficiency and emission are generally stringent^{17,19}. Thus, recent developments in design of combustion devices and fuel formulation indicate that multi-component effects will become progressively more important in the utilization of liquid biofuels^{9,13,21}. Bio-based fuels of the first-generation have different combustion characteristics as well as various ranges of the boiling points^{9,19}. The widely differing physical and chemical properties of these blends necessitate consideration of multi-component effects in an essential way^{9,13,19,21}.

It is desirable, that a diesel fuel spray injected into combustion chamber consisted of the droplets with their radii variable from 5 to 50 μm ²². Numerical simulations of the fuel drops of such a small radius have never been performed before, because obtained findings cannot be validated using a single droplet technique but only spray visualization method alone^{1,17,19,20}. Because of the above mentioned, the practical significance of newly deduced formula presented in this paper, firstly been examined by calculations of *n*-octane droplet of radius 1 mm as

well as compared to the laboratory and theoretic findings obtained by other authors^{1,10-12,17,19,20} before the simulation into multi-component effects on ID.

In the light of those facts, the ability of the ignition model to predict an effect of the admixed bio-additives to the diesel fuel on the point of ignition was carried-out under described above conditions. At the discussion stage with an intention to draw an inference about the certain multi-component combustible compound ignition properties, thermal-physical characteristics and its feasibility to use as a fuel, hereunder described Q-S model can fully or in partly replace an expensive laboratory tests, requiring stringent and difficult controls. Ignition delay calculations can also draw a clear view about the multi-component fuel combustion peculiarities thus avoiding the preconceived performing of possibly unnecessary modifications of combustion devices and allowing increase a quantity of oxygenates in diesel fuel at the same time.

Mathematical Formulation

Ignition delay time equation derived from rearrangements of Q-S combustion theory for *n*-octane droplet

A droplet of liquid fuel with radius r_0 placed in heated stationary oxidising environment with its gas temperature T_∞ was analysed (Fig. 1).

To simplify the solution the most commonly applied approximations were used: fuel vapour does not burn up to the point of ignition, Nusselt criterion

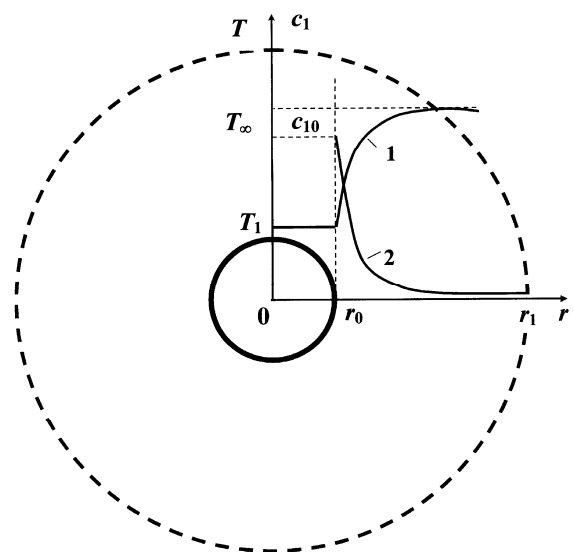


Fig. 1– Liquid hydrocarbon fuel drop ignition scheme: (1) temperature distribution in space $T(r)$; (2) distribution of fuel-vapour concentration around droplet $c_1(r)$. Dotted line indicates zone where chemical reaction starts (separating fuel vapour from oxidizer)

is equal to 2 ($Nu=2$), time of thermal and concentration relaxations around the droplet is very short (Q-S approximation), Lewis criterion is equal to 1 ($Le=1$), i.e., temperature and concentration fields are similar, all physical values do not depend on temperature and droplet temperature within the distance of all radius is stable at any time moment used^{1,10-12,17,19,20}.

It is evident, that ignition process begins at point $r = r_1$, where speed of a chemical reaction exceeds its maximum $W(T)$. A second-order chemical reaction of fuel oxidation can be written as:

$$W = k_0 \cdot c_1 \cdot c_2 \exp\left(-\frac{E}{R \cdot T}\right) \quad \dots (1)$$

Fuel-vapour concentration reliance on temperature is a function also depending on time. While a distance to droplet surface recedes to infinity, fuel-vapour temperature T remains high however concentration as well as partial pressure are of the low values. Around the droplet surface—on the contrary vapour temperature is not high enough. We continually made an assumption that until the ignition vapour of the droplet and oxidizer are mixing in the correct stoichiometric amounts thus forming the end products of chemical reaction. Coordinates of the evaporating droplet ignition point could be established from the common solution of two-equation system:

$$\frac{\partial W}{\partial r} = 0 \quad \dots (2)$$

$$p_1 = \varphi \cdot p_2 \quad \dots (3)$$

Differentiating an equation of chemical reaction rate (Eq. 1) and taking as advantage an expression of the stoichiometric ratio (Eq. 3) we derive a sum of two components. The first one could be established from the partial pressure around the droplet and the second one – from the distribution of vapour temperature^{1,10-12,19,20}:

$$2 \cdot p_1 \cdot \frac{k_0}{\phi} \cdot \exp\left(-\frac{E}{R \cdot T}\right) \frac{\partial p_1}{\partial r} + p_1^2 \cdot \frac{E}{R \cdot T^2} \cdot \frac{k_0}{\phi} \cdot \exp\left(-\frac{E}{R \cdot T}\right) \frac{\partial T}{\partial r} = 0 \quad \dots (4)$$

or

$$\frac{2 \cdot \partial p_1}{p_1 \cdot \partial r} + \frac{E \cdot \partial T}{R \cdot T^2 \cdot \partial r} = 0 \quad \dots (5)$$

In the Q-S state analysis the time dependent terms become zero and the boundary conditions are imposed on the basis of negligible liquid-phase reaction within the droplet and completion of chemical reaction at the outer boundary.

The conservation equations are in an exact form but because of the boundary conditions and the form of expression for chemical reaction rate, analytic solutions of the equations are not possible¹⁰⁻¹². Consequently the major assumption of an “infinitely rapid chemical reaction rate” is made, that is, the chemical reaction rate is not controlling the rate of droplet disappearance in any way¹⁷. Usually this assumption is coupled with the use of a simplified chemical reaction of the type Fuel + Oxygen → Products, although of course the same result is obtained for any chemical mechanism and could be used for a two-stage mechanism, e.g., infinite rate combustion of a hydrocarbon fuel to carbon monoxide followed by afterburning¹⁷.

In this model the flame zone, as a consequence of the infinite rate assumption, is of infinitesimal thickness and would thus be represented by a surface rather than an extended reaction zone. Generally it is necessary to assure that the fuel and oxidant diffuse to the reaction zone in stoichiometric proportions and again, as a consequence of the infinite reaction rate assumption, their concentrations become zero at the reaction interface¹⁷. When these approximations are made an analytic solution may be obtained. The forms of the final equations depend upon the exact method of solution:

$$\frac{r_1}{r_0} = \frac{\left(1 - \frac{T_0}{T_\infty}\right) \cdot \exp\left(\frac{3 \cdot \lambda^{gas} \cdot \tau_{ign}}{\rho \cdot c_p^{liq} \cdot r_0^2}\right)}{1 - \frac{E}{4 \cdot R \cdot T_\infty} \cdot \left(\sqrt{1 + \frac{8 \cdot R \cdot T_\infty}{E}} - 1\right)} \quad \dots (6)$$

On the assumption that $t \rightarrow 0$, a distance from the ignition point (r_1 / r_0) could be written as follows:

$$\frac{r_1}{r_0} = \frac{\left(1 - \frac{T_0}{T_\infty}\right)}{1 - \frac{E}{4 \cdot R \cdot T_\infty} \cdot \left(\sqrt{1 + \frac{8 \cdot R \cdot T_\infty}{E}} - 1\right)} \quad \dots (7)$$

On the basis of Eqs (3) and (7):

$$\frac{r_1}{r_0} \cdot \exp\left(\frac{L}{R \cdot T_1} - \frac{L}{R \cdot T_b}\right) = \frac{1}{\phi} + 1 \quad \dots (8)$$

Ignition delay depends upon both the distance from the ignition point (r_1/r_0) as well as temperature of the droplet surface at the moment of ignition T_1 ¹⁰⁻¹²:

$$T_1 = T_\infty - (T_\infty - T_0) \cdot \exp\left(-\frac{3 \cdot \lambda^{gas} \cdot \tau_{ign}}{\rho \cdot c_p^{liq} \cdot r_0^2}\right) \quad \dots (9)$$

Appreciating this, a fact that τ_{ign} serves as a foundation of the Eq. (9) could be maintained:

$$\frac{L}{R \cdot T_\infty \cdot (1-Y)} + \ln\left(\frac{Y}{1 - \frac{T_0}{T_\infty}}\right) = \ln\left(\frac{1}{\phi} + 1\right) + \frac{L}{R \cdot T_b} \quad \dots (10)$$

$$\text{Where, } Y = \left(1 - \frac{T_0}{T_\infty}\right) \cdot \exp\left(-\frac{3 \cdot \lambda^{gas} \cdot \tau_{ign}}{\rho \cdot c_p^{liq} \cdot r_0^2}\right)$$

Therefore, seizing comparable occasions of the classical theory of combustion based Q-S droplet ignition models^{1,10-12,19,20} we've derived a basic expression for the calculations of ignition delay of hydrocarbon fuels:

$$\tau_{ign} = \frac{\rho \cdot c_p^{liq} \cdot r_0^2}{3 \cdot \lambda^{gas}} \times \left(1 - \frac{1}{\theta_0} \cdot \frac{\left(1 - \frac{T_0}{T_\infty} - \frac{R \cdot T_b}{L} \ln \frac{\phi \cdot E \cdot \theta_0}{R \cdot T_\infty}\right)}{\left(1 - \frac{R \cdot T_b}{L} \ln \frac{\phi \cdot E \cdot \theta_0}{R \cdot T_\infty}\right)}\right) \quad \dots (11)$$

Derivation of the simplified algebraic expression: Validation of the Q-S model

The research into dominance of the proceeded parameters based on the further mathematical rearrangements was performed by using pure hydrocarbon fuel (*n*-octane) motivating that it is one of the most investigated type of fuel^{1,23-27}. While making an attest that

$$\frac{R \cdot T_b}{L} \ln \frac{\phi \cdot E \cdot \theta_0}{R \cdot T_\infty} \ll 1,$$

Eq. (11) can be written as:

$$\tau_{ign} = \frac{\rho \cdot c_p^{liq} \cdot r_0^2}{3 \cdot \lambda^{gas}} \left(\frac{T_b - T_0}{T_\infty - T_0}\right) \quad \dots (12)$$

Calculation can be done more precisely and simplified, if we leave exponential dependence $Y(\tau_{ign})$ out, which is used in mathematical rearrangements, by drawing Eq. (10):

$$\tau_{ign} = \frac{\rho \cdot c_p^{liq} \cdot r_0^2}{3 \cdot \lambda^{gas}} \ln\left(\frac{1 - \frac{T_0}{T_\infty}}{1 - \frac{T_b}{A^* \cdot T_\infty}}\right) \quad \dots (13)$$

$$\text{Where, } A^* = 1 - \frac{R \cdot T_b}{L} \ln\left(\frac{1 - \frac{T_0}{T_\infty}}{\left(1 - \frac{T(r_1)}{T_\infty}\right) \cdot \frac{\phi}{(1+\phi)}}\right)$$

It was established by calculations of *n*-octane droplet that A^* depended little on temperature and in the case of droplet ignition its value was close to one (Fig. 2).

Having evaluated this we can put the final expression of equation to calculate ignition delay as follows:

$$\tau_{ign} = \frac{\rho \cdot c_p^{liq} \cdot r_0^2}{3 \cdot \lambda^{gas}} \ln\left(\frac{T_\infty - T_0}{T_\infty - T_b}\right) \quad \dots (14)$$

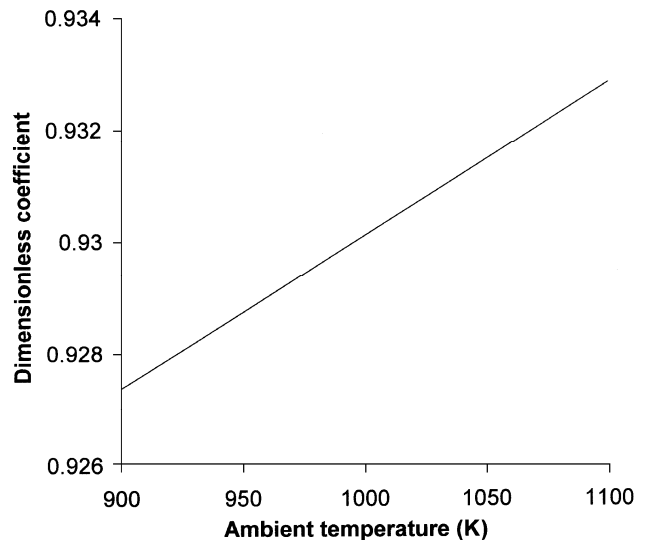


Fig. 2 – Dependence of the dimensionless coefficient A^* on ambient temperature T_∞ (*n*-octane drop radius $r_0 = 1$ mm)

It has been shown many times experimentally that under burning conditions the square of the droplet diameter is a function of the burning time^{1,17,19,20}. According to Eq. (14), ignition delay is directly proportional to r_0 . As illustrated in Fig. 3, drops of the bigger diameter related to higher values of ID. All numerical simulation data points are approximately on a straight line since their in-between data points are not many. Obtained results showed clear tendency, that when the ambient temperature becomes lower, the ignition delay becomes longer^{1,17,19,20,23-27} (Fig. 3).

In order to validate the simplified Q-S model, simulations into *n*-octane droplet ID were performed by using classical theory of combustion based complicated Eq. (11) and newly derived algebraic expression, better suited for modelling of the ignition characteristics of multi-component fuels because of the consisting of much less and simpler elements (Fig. 4).

As we can see, both curves describing the dependence of ID on ambient temperature are of the equable character. However, a newly deduced formula is in average 5-6% less precise compared with Eq. (11) but being much simpler and easy practised in the final solution. Hence, the developed simplified model is qualified for replacing the detailed expressions discussed above^{1,10-12,19,20}.

Materials and Methods

Estimation of ignition delay values of the selected fuels

New simplified approximate mechanism for the numerical simulation into multi-component effects on

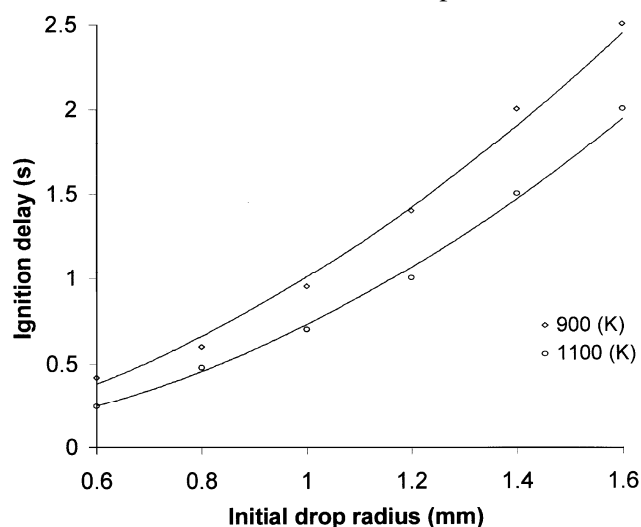


Fig. 3 – Dependence of the ignition delay of *n*-octane on initial droplet radius and ambient temperature

the ignition delay of oxygenated diesel fuel blends has been applied in a form of Eq. (14).

Reasoning of the selected parameters

Numerical simulation of ignition delay related to particular 4.2L T40M tractor diesel engine D-144 with mechanical power of 37 kW at 1600 min⁻¹ was performed. Specifications for the natural aspirated, direct injection, four-cylinder engine are as follows^{1,11,22}: compression ratio 16.5; piston bowl shape – dished piston; # fuel injector holes – 3; Ø fuel injector hole – 0.250 mm; initial fuel delivery starting – 25±1° before top dead center; needle valve lifting pressure for all injectors – 17.5 ± 0.5 MPa.

According to Gretchikhin²², an average radius of the diesel fuel droplets injected into combustion chamber of D-144 is approx. 2·10⁻⁴ m when engine speed is 2000 min⁻¹ and fuel consumption is 5 L/h. Concentration of the liquid fuel droplets in the fuel spray exceeds 1.09 × 10⁹ m⁻³. A particular size of diesel fuel droplets is characteristic at the typical ranges of combustion temperature (i.e. 770-870 K), velocity of injected fuel stream (285.2975-482.2420 m/s) as well as existing pressure difference between the measured within the combustion chamber and situated at the moment of squeezed fuel supply (35-100 MPa)²². Reasoning of the dominance of particular size droplets suits Nukiyama-Tanasava^{28,35} and Rosin-Rammler²⁹ size distribution functions against Gretchikhin²² performed experiments related to fuel spray visual monitoring very well.

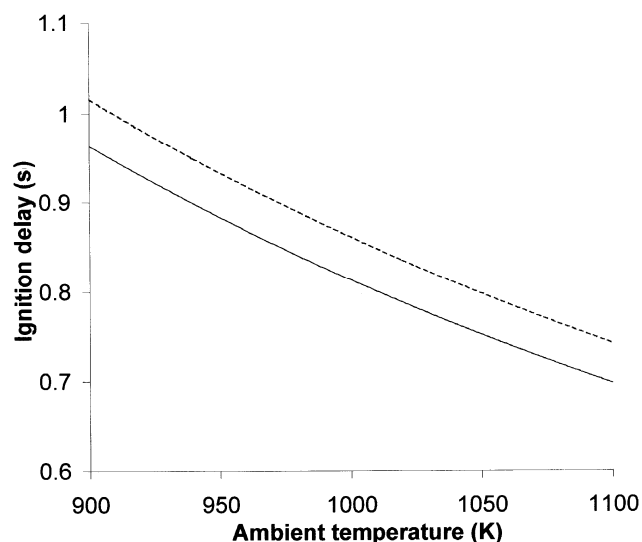


Fig. 4 – Dependence of the ignition delay of *n*-octane droplet ($r_0 = 1$ mm) on ambient temperature

Types of fuel subjected to the numerical simulation

Diesel fuel³⁰, rapeseed oil methyl ester³¹ and dehydrated ethyl alcohol³² compounded in various proportions (v/v) were a target of numerical simulation using a Q-S model.

A pruned nomenclature of fuel blends B100 and B30 means what percentage of biodiesel (rapeseed oil methyl ester) is actually in the fuel, the rest is fossil diesel. Hereinafter applied abbreviations “+5DEA”, “+7.5DEA” and “+10DEA” given to describe dehydrated ethyl alcohol compounding volume to B30 blend, respectively 5%, 7.5% and 10%.

Establishment of physical-chemical characteristics of the selected fuels

Using a standard methodology and settled findings of different researchers, physical-chemical characteristics (density, specific heat capacity of liquid fuel, boiling temperature and thermal conductivity of fuel-vapour) of the fossil diesel^{1,9,19,23-26,30}, B100^{9,27,31,34}, DEA^{9,24,26,27,32,33} as well as their generic compounds^{9,24,26,27,30-33} (v/v) were obtained. The rest values in Eq. (14) as initial droplet radius and ambient temperature were freely selected.

Results and Discussion

Analysis of the multi-component effects on ignition delay

In the simplified Q-S model, phase change, gas phase transport, gas phase chemical reaction and regression of the liquid surface are all presented and coupled. Simulation results while applying the Q-S model showed that ignition delay for fossil diesel fuel is 28-30 % shorter as compared with B100 at the same ambient temperature ranges (770-870 K). The admix of 30% by volume of RME to pure diesel fuel causes the decrease in ignition delay, and DEA – on the contrary, helps to heighten duration of τ_{ign} for B30 blend (Fig. 5).

As figure 5 shows, rapeseed oil methyl ester (B100) displays lower values of ignition delay than fossil diesel, which is considered to be a significant advantage in terms of emissions^{1,10-12,20}.

We can see from Eq. (14), that the increase of τ_{ign} was determined by decreased boiling temperature due to DEA additive and increased specific heat capacity of the blend. These values determine increased vaporization rates and vapour-diffusion, therefore, the ignition delay of combustible mixtures (B30+5DEA, B30+7.5DEA and B30+10DEA) are increased compared to B30.

During numerical simulation it was established that the ignition delay closest to fossil diesel fuel was achieved by the blend B30+7.5DEA. For both types of fuel (DF and B30+7.5DEA), similarity into obtained values of ignition delay was in the range of the error margin (Fig. 6).

Further increase of the compounding volume of DEA (B30+10DEA) showed an effect of the significantly overtopped value of ignition delay. Gained research results are correct for temperature range noticeably exceeding a critical ignition temperature of investigated fuel compounds. Those conditions were necessitated by the fact that presented

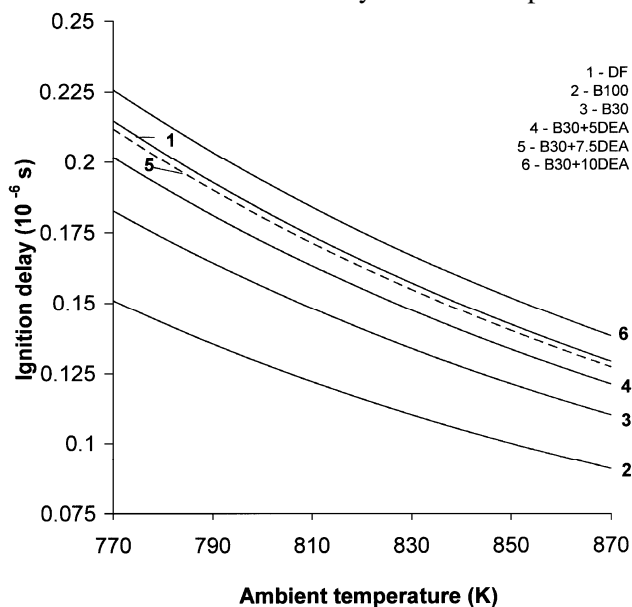


Fig. 5 – Ignition delay simulation using a Q-S model ($r_0 = 2 \cdot 10^{-4}$ m)

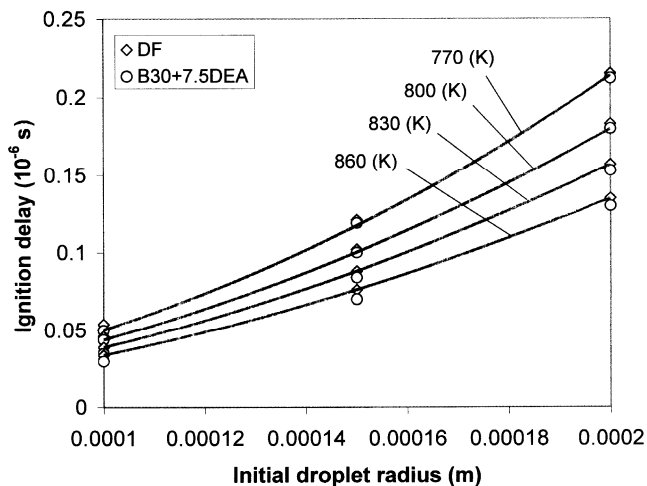


Fig. 6 – Dependence of the ignition delay on initial droplet radius ($T_\infty = 750$ K)

above quasis-stationary (Q-S) model cannot value a reaction between fuel vapor until the moment of ignition.

Comparison with other reported studies

A brief description of the numerical simulation method is given, and the derived data is analysed. To our knowledge there are no other studies that refer to the topic of combining of the first-generation biofuels as oxygenated compounds to blend fossil diesel by using Q-S combustion theory, caused by complexity of the method. Hence, obtained findings are in strong agreement to the practical works, describing the influence of bio-components on Cetane Number variations related to ignition delay^{20-22,33,34,36}.

Conclusions

The derived Q-S model may be used in solving numerous urgent problems associated with the improvement of the environmentally benign characteristics of diesel engines. Such problems include analysis and calculation of the process of combustion in engines involving the use of different fuels, by indirection of the processes of heat transfer, heat release and utilization of heat in the working cycle.

The suggested method may be employed to determine the ignition delay for almost any single-component as well as multi-component fuel used in diesel engines. Equation (14) may be recommended for use in simulating the working process and predicting the efficiency and environmentally fluent performance of a diesel engine.

Research into multi-component effects on ignition delay discovers following findings: rapeseed oil methyl ester distinguishes to reduce ID while been blended with fossil diesel fuel, and DEA is characterized as additive worsening blend's capability to ignite. With the help of derived Q-S model, precisely selected volumes of above mentioned bio-components led to obtain the ignition characteristics of the multi-component blend B30+7.5DEA alike to fossil diesel fuel and to utilize bigger volumes of biofuels normally be allowed by manufacturers, at the same time.

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Nomenclature

A^*	=	dimensionless coefficient
c_1	=	fuel-vapour molar concentration
c_2	=	oxidizer's molar concentration
c_{10}	=	fuel-vapour molar concentration of the drop surface (at the moment of ignition)
c_p^{liq}	=	specific heat capacity of liquid fuel
E	=	activation energy
k_0	=	temperature independent rate constant
L	=	latent heat of vaporization
Le	=	Lewis criterion;
Nu	=	Nusselt criterion;
p_1	=	partial pressure of the fuel-vapor
p_2	=	partial pressure of the oxidizer
r	=	radius
R	=	universal gas constant
r_0	=	initial drop radius
r_l	=	distance to the zone, where chemical reaction begins
t	=	time
T	=	temperature
T_0	=	droplet temperature at initial time moment
T_l	=	temperature of the drop surface at the moment of ignition
T_∞	=	ambient temperature
T_b	=	boiling temperature
W	=	rate of a chemical reaction
Y	=	dimensionless constant
<i>Greek symbols</i>		
θ_0	=	temperature tensions between droplet surface and environment
λ^{gas}	=	thermal conductivity of fuel-vapour
ρ	=	density
τ_{ign}	=	ignition delay time
φ	=	stoichiometric coefficient.

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