Development and study of ways to extend the multifuel capability of ICE

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Abstract. In the recent years, no considerable growth of use of alternative fuels by vehicle fleets has been observed, in spite of the availability of a vast volume of research data and recommendations. The identified reason is the reluctance of manufacturers to produce ICE modifications for operation with fuels different from DF. The problem could be solved by development and study of ways to extend the multifuel capability of ICE. Basic ways were identified to extend the limits of the usability of alternative fuels with different physical and chemical properties. Regressions were suggested allowing for determining the chemical nature of additives and their degree of influence on the decreasing of the kinematic viscosity of the fuel. A mathematical solution was obtained describing conditions of physical existence of a fuel emulsion. An analysis of a number of combustion inhibitors was carried out. A mechanism of inhibition of additives of new generation was analyzed. Subcaloric fuel combustion process (generator gas) was studied, ways to improve its efficiency were suggested. Based on the theoretical analysis and experimental data, generalized assessment criteria were formulated for the usability limits of non-conventional energy materials. The obtained results could help to essentially extend the fuel base of engines in real operation environments.

1. Introduction

In the recent years, no considerable growth of use of alternative fuels (AF) by vehicle fleets and in other branches of the national economy has been observed. Simultaneously, there is a vast volume of various research data in the sphere of alternative energy [1, 2, 3]. Published sources report on developed recommendations and experimental ICE designs, allowing for prompt introduction of a broad range of non-conventional energy materials in land-based vehicles.

The analysis of the causes of this juncture leads to the following main conclusion. It is known that the operational properties of non-conventional fuels are considerably different from those of the conventional DF (Table 1). Manufacturers are reluctant to manufacture different individual ICE series for specific alternative fuel types, which, in addition, differ in on-board storage facility designs, feed and (or) ignition methods, control packages and other operational limitations.

For problem solution it is highly advisable to develop and study the ways to extend the multifuel capability of ICE’s by extending the usability limits of alternative energy sources. These are, first of all, fuels with physical and chemical properties deviating from the requirements of the standards currently in effect.
Table 1. Distinctive properties of alternative fuels

| Alternative fuel | Differences of properties | Influence on engine performance |
|------------------|---------------------------|--------------------------------|
| 1. Vegetable oils| High kinematic viscosity, tendency to deposit | Increased loads on engine parts, increased deposits, appreciably reduced reliability and durability |
| 2. Lowest aliphatic alcohols | Low values:  - Cetane number  - Heat of combustion  - Physical stability of the mix | Reduced output power and fuel efficiency, increased cost of design manufacture |
| 3. Compressed natural gas | Molecular state | Increased cost of design and manufacture, appreciably reduced reliability and durability |
| 4. Industrially produced gases (biogas, generator gas) | Low lower heating value, molecular state | Reduced output power and fuel efficiency, increased cost of design manufacture |
| 5. Water | Poor lubrication properties, very high corrosion activity | Reduced output power and fuel efficiency, appreciably reduced reliability and durability |
| 6. Liquefied ammonia | Low lower heating value, appreciable corrosion activity | Reduced output power and fuel efficiency, appreciably reduced reliability and durability |

The range is rather broad – heavy fuels, fuel emulsions and compositions with low stability, fuels with low self-combustion ability, fuels with poor low-temperature properties, etc. [4].

2. Literature Review
In paper [5], based on the experimental results of paper [6] on the mechanical properties of mixtures of diesel fuel with rape seed and sunflower oils, empirical formulas for viscosity calculation of such mixtures were obtained. For approximation, two approaches were used, named by the authors algebraic and logarithmic. The divergence between the experimental and the calculated results reached up to 27% in case of rape seed oil.

The results of rather recent studies of fuel mixtures containing ethanol are reported in paper [7] and thesis [8]. The studies have demonstrated the efficiency of use as motor fuel of a mixture containing 96% of diesel fuel and 4% of absolute ethanol. Beside that, not solved problems are identified associated with increased emissions of carbon monoxide and unburnt hydrocarbons, as well as with the stability of the mixtures containing high ethanol percentage.

Paper [9] reports on test results of a K6S310DR locomotive diesel engine operating with diesel fuel mixed with natural gas in several power output modes. It was found out that at 5% methane addition the smoke and carbon monoxide emissions, thereby, the most positive effect is reached in the rated mode of operation. A problem was identified, associated with the feeding of heterogeneous fuel mix into the cylinders of a diesel engine.

The problems associated with the stability and the viscosity of rape seed oil based fuel emulsions were considered in [10, 11]. Emulsions were studied with up to 40% methanol content, stabilized with alkenyl succinimide. It was found out that the methanol concentration growth is followed by decreasing mixture viscosity, thereby, the stability time of the emulsion also gets bad. Thus, in this situation, important operation factors contradict each other.
The maximum stability time of 51 min was achieved for an emulsion containing 10% wt. of methanol; thereby, the emulsifier concentration was extremely high – about 9%. The components ratio considered by the authors to be optimum – 29% of methanol and 5.4% of the emulsifier - has a very small time of emulsion stability of 14.5 min. Measurement data [11] demonstrate also insignificant viscosity of the fuel mixture along with the concentration growth of the emulsifier.

Papers [12, 13] suggest variants of the multifuel capability of diesel engines for areas with tropical climate using palm oil as alternative fuel. The authors note that the addition of palm oil to diesel fuel lead due to higher superficial tension coefficient and viscosity of the additive to the growth of the average droplet diameter of the pulverized fuel and to a narrower spray angle. These factors, in their turn, are followed by an increase of the ignition delay, combustion duration and, as a consequence, by a decrease of the engine efficiency. For compensation of the specified negative effects, it is recommended to additionally introduce hydrogen peroxide into the fuel mixture. In accordance with authors' statement, free radicals generated during the peroxide degradation will act as inchoative centers of chain reactions intensifying the oxidation of the fuel. Unfortunately, the theoretical calculations are not supported by any experimental data.

Paper [14] reports on studied of diesel engine operation with transesterified mustard oil with addition of vol.15 ppm titanium dioxide TiO₂ powdered to average particle size of 50 nm. It is stated that the titanium dioxide presence leads to delay time reduction of the ignition, accelerates the fuel vaporization grade, lowers the carbon activation temperature which stimulates its completer combustion, and accelerates the carburation. There is also a statement, that TiO₂ additive leads to reduced emission of carbon and nitrogen oxides and reduced smoke content in the exhaust.

### 3. Research objectives

The objective of the study was the extension of the multifuel capability of ICE by wider usability limits of liquid alternative fuels. The mission of the study was the development of adaptation ways of physical and chemical properties of alternative fuels to DF properties.

### 4. Methods and materials

The investigation methods were theoretical studies, laboratory tests, bench testing of diesel and spark-ignition ICE's.

#### Table 2. Devices and equipment as a part of experimental installation

| Type of test                              | Equipment                                  | Designation       | Note                     |
|-------------------------------------------|--------------------------------------------|-------------------|--------------------------|
| Kinematic viscosity                       | Viscosimeter                               | VPZh-2            | Divergence ± 1 %         |
| Stability                                 | Stop-watch                                 | SOP Pr-2a-2-010 "AGAT" | Accuracy ± 0.1 sec. |
| Limiting temperature of filtration capability | Temperature measurement instrument for filtration capability | ITF               | No regular error         |
| Bench tests                               | Internal combustion engine                 | D-245.S2, DDE UP168-1 | Power 70 kW             |
| Toxicity of exhaust gases                 | Gas analyzer                               | MGT-5             | Accuracy ± 3 %           |
General appearance and list of equipment and instruments, see figure 1 and Table 2.

The theoretical analysis and laboratory tests of physical and chemical properties of motor fuels were conducted by FGBOU VO Vyatka State University. The bench tests of the ICE's were carried out in UO Bielorussian State Agricultural Academy and FGBOU VO Vologda State Dairy Farming Academy named after N.V. Vereschagin.

The processing of the experimental data and the graph plotting were carried out in Microsoft Exel and Corel Draw applications [15].

5. Result and discussion.

1. One of the most critical properties restricting alternative fuel use is the kinematic viscosity. Appropriate accuracy is vitally important for determining of the chemical nature of the additives allowing for required decreasing of viscosity of the mixed fuel.

Absence of a reliable theoretical molecule interaction model of different high-molecular substances for calculation of the mixture viscosity makes it vital to construe particular empirical formulas. To describe the dependency of the viscosity of the mixture versus component concentration, exponential approximation is used sometimes [22]. Such approximation could be well consistent with experimental results in a certain range of concentrations, however, it is not backed by any objective physical reasons, being in this sense merely a formal expedient. Mixture viscosity calculations via the average balanced flowability of the components often misleads to results differing by several times from the experimental data.

The processing of the results of our measurements of the kinematic viscosity of mixtures of diesel fuel with rape seed oil containing 0 to 50% of the oil [16] demonstrated that the dependency of viscosity $\nu$ versus oil content $c$ is rather satisfactorily described by quadratic regression

$$\nu = \nu_0 + ac + bc^2,$$

where $\nu_0 = 4,524$, $a = 96,54 \cdot 10^{-3}$ and $b = 3,407 \cdot 10^{-3}$ ($\nu$ in cSt, $c$ in %).

If the mole fraction of the rape seed oil $\chi$ in the mixture is taken the argument, then, the measurement results fit well into a linear function

$$\nu = 4,17 + 69,24 \chi, \text{ cSt.}$$

The deviation of the experimental data from the results of the calculation results from the above-referred formulas do not exceed 3%.
In order to reveal the degree of influence of different physical factors on the mixture viscosity, we have undertaken for experimental evaluation of the viscous flow energy $E$. For that, viscosity versus temperature dependency was studied. In accordance with the generally acknowledged theory of activation, this dependency shall appear as follows:

$$
\nu = Ce^{E/kT},
$$

(3)

where $k$ is the Boltzmann constant; $T$ is the absolute temperature. The value $C$ has a weak dependence on $T$, and it can be assumed constant in a narrow temperature interval.

The obtained experimental evaluations of the activation energy, see Table 3.

The data of Table 3 make a certain trend to the growth of the activation energy along with the growth of the concentration of the admixtures in the solution visible, which could be associated with the presence of an additional dipole-dipole attraction of polar fragments of the oil and the additive molecules. However, the specified differences never reach beyond the experimental error, and cannot obviously be a reason for significant variations of the mixtures’ viscosity values observed in the reported measurements.

**Table 3.** Activation energy of viscous flow in mixtures of diesel fuel with rapeseed oil

| Mixture composition                               | Activation energy $E$, eV |
|--------------------------------------------------|---------------------------|
| 100% diesel fuel                                 | 0.120 ± 0.005             |
| 80% diesel fuel + 20% rape seed oil              | 0.101 ± 0.010             |
| 60% diesel fuel + 40% rape seed oil              | 0.135 ± 0.009             |
| 50% diesel fuel + 50% rape seed oil              | 0.128 ± 0.008             |
| 49% diesel fuel + 49% rape seed oil + 2% DIFRON H372 additive | 0.132 ± 0.009 |

We have also studied the influence of DIFRON H372 cetane number increasing additive on the fuel mixture viscosity, with 2-ethyl hexyl nitrate as effective substance. It was found out that adding of 2% (wt.) of the additive to the fuel mixture leads to a decrease of the kinematic viscosity by 10% and above.

The data of the theoretical analysis and the laboratory tests [16] confirm the indicated extension way of the usability limits of high-viscosity and weight-increased fuels.

2. The use of fuel emulsions and compositions goes hand in hand with the other not less important problem – the insufficient physical stability.

![Figure 2. Three emulsion states: a) homogeneous emulsion; b) partial stratification; c) full stratification](image)
Figure 2 shows in terms of time the three states of the emulsion of diesel fuel, distilled water + ethanol. Definition of the volumes: 1 – $V_1$ (emulsion volume), 2 - $V_{wc}$ (volume of the distilled water + ethanol solution), 3 – $V_{df}$ (volume of the diesel fuel (DF)), $V_0$ is the total volume of the entire emulsion composition.

Then, in any moment of time, the following equation is true:

$$V_{df} + V_{wc} + V_1 = V_0$$  \(4\)

We assume that the volume changes of the phases in the emulsion will develop in the course of time exponentially, since most of natural processes in the nature and in the engineering develop exponentially.

We set the change rate of the emulsion with the time:

$$(V_1)' = ce^{-k_3 t}$$  \(5\)

Similarly, we write now the change rates of the of the volumes of the diesel fuel and of the water-ethanol solution. Then, equation (1) can take the following appearance:

$$ae^{-k_1 t}dt + be^{-k_2 t}dt + ce^{-k_3 t}dt = 0.$$  \(6\)

Having integrated equation (3) we obtain the following solution:

$$\frac{a}{k_1} - \frac{ae^{-k_1 t}}{k_1} + \frac{b}{k_2} - \frac{be^{-k_2 t}}{k_2} + \frac{c}{k_3} - \frac{ce^{-k_3 t}}{k_3} = V_0.$$  \(7\)

The values $a, b, c$ correspond to the initial volume change rates of the respective phases, whereas the coefficients $k_1, k_2, k_3$ define the respective changes of the respective change rates of the respective volumes. Along with the dropping down of the water-ethanol drops, the density of the remaining emulsion will get back to the DF density on the top, и and the water-ethanol mix density on the bottom. Thus, it can be easily calculated, by which moment of time the emulsion volume will be zero, that is, the stability time can be obtained [17, 18].

3. Most of alternative fuels have the cetane number (CN) lower than that of the DF.

The analysis of references shows that the combustion process can be influenced by means of special additives.

It is known that the combustion process is distinguished by the radical mechanism. In the initial stage, free atoms, radicals and other instable compounds are generated which have high chemical activity. Subsequently, these compounds react with the initial substance, the chain furcates, and multiple active centers are built. Thereby, the reaction significantly accelerates. The interactions of the active centers between one another, with molecules of other compounds, with the combustion chamber (CC) walls, on the other hand, decelerate the reaction rate - a chain break occurs. With reference to the operation of a diesel ICE, it is vitally important to inhibit the chain furcation stage, which can affect the uniformity of the combustion process.

The main drawback of ethanol as alternative fuel is its low flammability. Quantitatively, this fact is illustrated by a significant decrease of the cetane number of the alcohol-DF mixture compared with pure DF. The cetane number of pure ethanol is 8, whereas the optimum cetane number for normal diesel engine operation must be 40…50. The reduced cetane number of the mixture is stipulated by the following circumstances. The specific heat of evaporation of ethanol is 3.5 times higher than that of DF, consequently, the temperature of the fuel-air mixture in the cylinder is reduces, and the delay time of its self-ignition grows, accordingly. On the other hand, due to the presence of an oxygen atom in the alcohol molecule, the combustion time of the fuel mixture is reduced followed by a rougher diesel engine operation with ethanol-fuel mixture.

An improvement of the properties of a fuel mixture can be achieved with additives which, as set forth above, either lower the self-ignition temperature or prolong the combustion time.

As combustion inhibitor increasing the cetane number, we suggest using molybdenum disulfide MoS$_2$ [19].
The assumed inhibition mechanism of the additive looks as follows: At interaction of the initial hydrocarbon with oxygen, free radicals are generated in the first oxidation stage:

\[ \text{RH} + \text{O}_2 \rightarrow \text{R}^\cdot + \text{HOO}^\cdot. \]  \hspace{1cm} (8)

Then, radical \( \text{R}^\cdot \) joins an oxygen molecule and becomes a peroxide radical \( \text{RO}_2^\cdot \):

\[ \text{R}^\cdot + \text{O}_2 \rightarrow \text{RO}_2^\cdot, \] \hspace{1cm} (9)

In its turn, the latter detaches a hydrogen atom from another hydrocarbon molecule:

\[ \text{RO}_2^\cdot + \text{RH} \rightarrow \text{ROOH} + \text{R}^\cdot, \] \hspace{1cm} (10)

building a hydroperoxide and a new free radical \( \text{R}^\cdot \) which continues the chain. In presence of MoS\(_2\), the kinetic chain can be broken. The catalyst activity of molybdenum disulfide is associated with the presence of anionic vacancies on the lateral crystallite faces. In MoS\(_2\) structure (Figure 3), there are three sulfur atom types with different co-ordination by molybdenum. A part of Mo ions is localized in partially unfinished trigonal prisms – on end faces and layer corners. It is supposed that the kinetic chains are broken by the reactions of peroxide radicals with molybdenum disulfide on the surface of its particles expressed by radicals' joining the "protruding" molybdenum atoms marked in Figure 3. As a result, the fuel oxidation process is slowed down. The combustion process is extended in time, the temperature and pressure growth gets smoother which is equivalent to a higher cetane number.

![Figure 3. Molybdenum disulfide structure](image)

One more, a bit less probable but generally possible influence mechanism of molybdenum disulfide on the combustion process of the fuel mixture could be as follows. At temperatures \( t \geq 650^\circ\text{C} \) characteristic for air-fuel mixture prior to self-ignition, dehydration of the hydrocarbons of the hydrocarbons could take place, e.g., by the following reaction:

\[ \text{C}_n\text{H}_{2n+2} \rightarrow \text{C}_n\text{H}_{2n+1}^\cdot + \text{H}^\cdot, \hspace{0.5cm} \text{H}^\cdot + \text{H}^\cdot \rightarrow \text{H}_2. \] \hspace{1cm} (11)

Along with that, in ethanol is present in the fuel mixture, it could also be dehydrated as follows:

\[ \text{CH}_3 \hspace{0.5cm} - \hspace{0.5cm} \text{CH}_2 \hspace{0.5cm} - \hspace{0.5cm} \text{OH} \rightarrow \text{CH}_3 \hspace{0.5cm} - \hspace{0.5cm} \text{CHO} \hspace{0.5cm} + \hspace{0.5cm} \text{H}_2, \] \hspace{1cm} (12)

since the characteristic energies of \( \text{C} - \text{H} \) and \( \text{O} - \text{H} \) links are close to each other (appr. 430 kJ/mole). The resulting hydrogen enters into a hydrocracking reaction with cyclic (naphtenic) hydrocarbons, which are mostly homologue to cyclohexane and cyclopentane. In these processes, molybdenum disulfide acts as a catalyst hydrocracking which can occur as follows:
C\textsubscript{n}H\textsubscript{2n} + H\textsubscript{2} → C\textsubscript{n}H\textsubscript{2n+2}; \quad (13)

for example, cyclopentane hydrocracking leads to the opening of the ring to n-pentane.

It is known that at equal C number, the cetane number of a cyclic hydrocarbon is, as average, by 20…40 less than that of the respective alkane, being a specific case of the general tendency of cetane number growth with the growth of the relative number of hydrogen atoms in a hydrocarbon molecule. Thus, the result of the hydrocracking process is the increased cetane number of the fuel, which, in its turn, leads to a shorter delay of the self-ignition and a smoother combustion process. Since the cyclic hydrocarbons content in the diesel fuel is rather big (20% to 60%) the influence of the assumed mechanism could be significant.

The results of the reported theoretical excerpts and the analysis data of the diesel engine performance parameters [19, 20] allow to consider the indicated extension way of the usability limits of low-cetane fuels vital and promising.

4. An essential problem of use of generator gas as a fuel are its low heat value and low combustion velocity.

The combustion processes of the generator gas, as well as those of the generator gas mixture with gasoline are for the time being poorly studied. That is why, a theoretical treatment of the operation conditions of an ICE fueled with a mixture of generator gas and gasoline is required.

From literature references, it is known that the basic combustible components of the generator gas are hydrogen Н\textsubscript{2} and carbon monoxide СО, with respective volume fractions of 12…20% vol. and 17…32 % vol. The reaction of their oxidation, as per Arrhenius equation, is determined as follows:

\[
\frac{dC}{dt} = C\textsubscript{i}C\textsubscript{o}\textsubscript{2}k = C\textsubscript{i}C\textsubscript{o}\textsubscript{2}Ae^{\frac{-E}{RT}}, \quad (14)
\]

where \( k \) is the oxidation reaction constant; \( E \) is the activation energy; \( T \) is the absolute temperature; \( R \) is the universal gas constant; \( A \) is a pre-exponential factor characterizing the efficiency of the collision of the molecules of the reacting substances; \( C\textsubscript{i} \) is the fuel (hydrogen of carbon monoxide) concentration; \( C\textsubscript{o}\textsubscript{2} \) is the oxygen concentration.

The activation energy for Н\textsubscript{2} and CO molecules, in accordance with literature reference, is 242 and 201 kJ/mole, respectively. The known activation energy value of gasoline vapors is 78.5…80 kJ/mole, that is, 2.5 times less than the activation energy of carbon monoxide. As to the pre-exponential factor \( A \) in (14), determined by the effective sections of the interacting molecules, for combustion reactions of hydrogen, carbon monoxide and gasoline vapors, it must be of the same numerical order. However, no significant growth of the gasoline combustion rate relative to the generator gas combustion is observed, which for good reasons could be anticipated due to the exponential dependency on the activation energy. The absence of such growth is obviously stipulated by the limitation of the gasoline combustion rate by the evaporation rate of its droplets, being quite a slow process. On the average, the decrease rate of the square of the gasoline droplet diameter for gasoline combustion temperatures will be, in accordance with the available reference data, as follows:

\[
K = \left| \frac{d(d^2)}{dt} \right| = 4,3 \cdot 10^{-6} \text{ m}^2/\text{s}. \quad (15)
\]

Then, the preliminary calculation of the combustion time could be made based on the following formula:

\[
\tau = \pi d_0^2/K, \quad (16)
\]

where \( d_0 \) is the initial gasoline droplet diameter being, on average, 0.065 mm. The calculation shows that the combustion time will be, for gasoline, the combustion time \( \tau = 0.0031 \text{ s} \).
Calculation example of combustion time in an ICE with spark ignition operating with pure gasoline, pure generator gas and with a mixture of 30% gasoline and 70% GG (Table 4).

**Table 4. Combustion time calculation data**

| Frequency of rotation, min⁻¹ | Structure of a mix                          | Time of combustion, sec |
|-----------------------------|---------------------------------------------|------------------------|
| 3,000                       | Gasoline – 100%                             | 0.0031                 |
| 3,000                       | Gasoline – 30% + Generating gas - 70%       | 0.0036                 |
| 3,000                       | Generating gas - 100%                       | 0.0039                 |

Based on the data of Table 4, the time required for combustion of generator gas under given conditions is longer than that of gasoline by approximately 0.001 seconds. In case of the mixture containing 30% of gasoline and 70% of generator gas, the time growth will be 0.0005 seconds.

Comparative data of bench tests of an ICE with spark plugs at operation with pure gasoline, pure generator gas and their mixture completely confirm the results of the theoretical studies [21].

Thus, the problem of use of low-calorie alternative fuels can also be partially coped with.

**Conclusions**

1. Based on the data of the studies, generalized criteria of the assessment of the usability limits of alternative fuels were identified.
2. Sufficient proof was provided of real possibilities of operation of serial ICE’s with alternative fuels with certain distinctive engine properties.
3. The extension of the usability limits of alternative fuels by adaptation of their motor properties improves the multifuel capability and extends the fuel base of internal combustion engines.

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