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THE MOLECULAR CLUSTERS AS THE STRUCTURE THAT CAN DETERMINE THE RHEOLOGICAL AND TRIBOLOGICAL PROPERTIES OF DIESEL AND JET FUELS

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Abstract

The aim of this article is to show, that a deeper analysis of intermolecular interactions and resulting from them ordered structures could change views on the mechanisms of many processes involving fuels. The examples of unexpected behaviour of diesel and jet fuels blends, related to rheological and tribological properties were shown. The following conclusions were formulated: a) usually fuels are described as the mixture of molecules almost independent and the interaction between molecules is considered marginally; b) it was found that molecules of aromatic compounds create molecular clusters; c) the observed unexpected behaviour of fuels at low temperature and during lubrication can be explained by molecular clusters characteristics. The authors of this article opinion are that further research should be focused on the cluster formation by fuels components and the influence of clusters on fuels properties.

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Keywords: *molecular cluster, low temperature properties, fuels lubricity*

1. Introduction

The petroleum fuels, as the source of energy for road and air transport were used by decades. Two decades use of biocomponents as substitute for petroleum fuels is important part of energy policy, both all over the EU and in individual member countries. Increasing demand for fuels and energy connected with economy growth, due to decreasing sources of fossil fuels, means searching and supporting the use of biocomponents, liquid biofuels and other renewable fuels. Biocomponents contribution in total sum of consumed fuels, computed in relation to calorific value, shall increase successively up to 10% in 2020.

Currently available on the market diesel fuel contains ca 7 % (V/V) of FAME (fatty acids methyl ester). FAME is chemically quite different from petroleum diesel fuel. Fuels composition plays important role in their behaviour during all processes that occur in the system of engine supply and in combustion chamber, including low temperature operability [1] and fuel pumps lubrication. The introduction of non-conventional fuels such as FAME into diesel fuel blends has complicated fuel characterization. FAME changes distillation curve, density, viscosity at high and, what is more important, low temperature and reaction chains during fuels combustion. New generation biofuels consisting of hydrocarbons can contain high concentrations of specific n-paraffins. All of these components can have a significant impact on diesel and jet fuel characterization and low temperature properties. However, as write authors of [1], the basics for fuel characterization are the same as for conventional diesel fuel analysis.

Several analytical measurements can provide information for estimating a diesel and jet fuel's low temperature performance. Distillation, Cloud Point (CP), Pour Point (PP), viscosity, n-paraffin content and distribution as well as lubricity determined by HFRR and BOCLE tests are all very

useful fuel characteristics. Without analysis on molecular level of fuels chemical composition it is very difficult or impossible explain the unexpected behaviour of fuels during different processes.

Usually fuels are described as the mixture of molecules almost independent and the interaction between molecules is considered marginally. The aim of this article is to show, that a deeper analysis of intermolecular interactions and resulting from them ordered structures could change views on the mechanisms of many processes involving fuels.

2. Molecular clusters in fuels structure

The ordered structures, which were detected in fuels, are molecular clusters. The phrase cluster was coined by F. A. Cotton in the early 1960s to refer to compounds containing metal–metal bonds. Molecular clusters are aggregates of 5-10^5 molecules. They are classified according to the forces holding them together:

- Van der Waals clusters – attraction between induced electric dipoles and repulsion between electron cores of closed electronic configurations,
- Metallic clusters – long range valence electron sharing (over many successive adjacent atoms) and partially directional,
- Ionic clusters – valence electrons are almost entirely transferred among closest neighbours to yield 2 net, equal but opposite, electric charge distributions that mutually attract.

The role of cluster formation in the precipitation of liquid mixtures and in the condensation, adsorption to surface or solidification phase transitions has long been investigated from a theoretical standpoint.

Cluster system properties – stem from their both size and composition (which contributes to the binding force types) that determine:

- the number of dimensions of their phase space,
- the ranges of accessible positions and velocities of their atomic components.

A gradual transition occurs between the properties of the molecular species and those of the corresponding bulk mix. And yet the clusters exhibit physical and chemical properties specific only to their configuration space (in turn strongly atom-count-dependent) and not specific to their bulk counterparts.

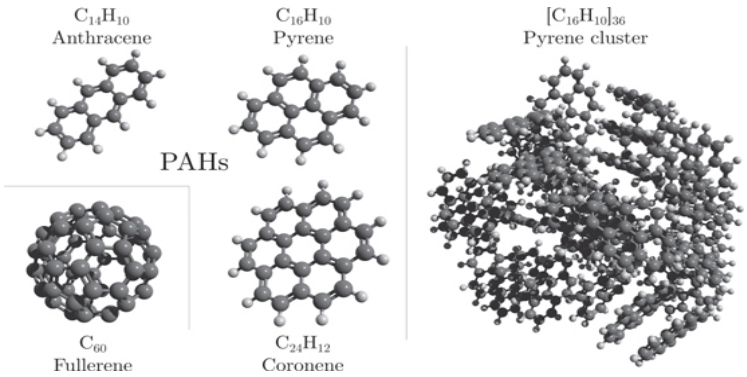

Fig. 1. Models of molecular clusters of PAH molecules [2]

Polycyclic aromatic hydrocarbon (PAH) molecules have been widely investigated as the building blocks of soot resulting from incomplete combustion of hydrocarbon fuels, and have been related to questions of the health hazards arising from the combustion products, the exploration of the interstellar space and applications of nanotechnology. An important open question regarding the role of PAHs in the formation and growth of soot is whether PAHs of a given size form stable clusters in a flame environment, and whether they exist as a solid or liquid-like phase [2]. In a previous study, homogenous clusters of pyrene and coronene have been investigated using

molecular dynamics simulations. It was shown that clusters of these small PAHs could not survive at flame temperatures, e.g. 1500 K. This suggests that soot particles may be composed of larger PAHs with higher thermal stabilities.

In this article, post the question whether molecular clusters formed by molecules in the fuel can influence on fuels behaviour at low temperature and during the fuel pumps lubrication.

3. The possibly influence of clusters on rheological properties of fuels

The rheological properties play important role in fuels behaviour in engines fuel supply systems, injectors and during fuels injection to combustion chamber. In warm part of this system, the main role plays viscosity at relatively high temperature and under high pressure. At temperature to about 100^{o}C diesel and jet, fuels can be treated as Newtonian liquids. This change when the temperature of fuel falls below 0^{o}C. It is difficult to explain this effect using Newtonian macroscopic description. The explanation can be done on molecular level, when viscosity will be treated as chemical reaction of disruption of intermolecular bonds. In this case, viscosity can be describe by Arrhenius equation (1) [3]:

$$\nu = A \exp (E_a/RT), \tag{1}$$

where:
ν – kinematic viscosity of fuel,
E_a – activation energy of disruption of intermolecular bonds,
T –temperature of fuels.

The value of activation energy is specific for each chemical reaction. When the nature of intermolecular bonds change the E_a should change as well. The Newtonian interpretation assumes that each of molecules creates intermolecular bonds with all neighbouring molecules and during fuels flow only bond between given molecule and the molecule, which belongs to the neighbouring layer, are disrupted. According to this theory, the increase in temperature will increase the average distance between molecules – between parallel layers of molecules, what is the reason of the energy of intermolecular bonds decrease. This is shown on Fig. 2, where calculated activation energy is significantly higher at low temperature than these calculated for low temperature.

These data are consistent with above interpretation of the temperature influence on the energy of intermolecular bonds. At higher temperature, the energy of intermolecular bonds is similar for such different fuels like mineral diesel fuel and rapeseed methyl ester (B100). The energy of intermolecular bonds become differs at lower temperature. Below 0^{o}C kinematic viscosity becomes rapidly increase. It is the similar effect as during pressure increase (see Fig. 3).

Kinematic viscosity of fuel at low temperature as well as under high pressure cannot be explain by Newtonian model of flowing liquid – the influence of temperature decrease and pressure increase on the distance between molecules. At temperature near melting point, the clusters of hydrocarbons, molecules, identified in PAH, should be taken into account. The Fig.4. shows the linear dependence between reduced melting point and 1/D, where D is the diameter of the clusters of PAH molecules [4].

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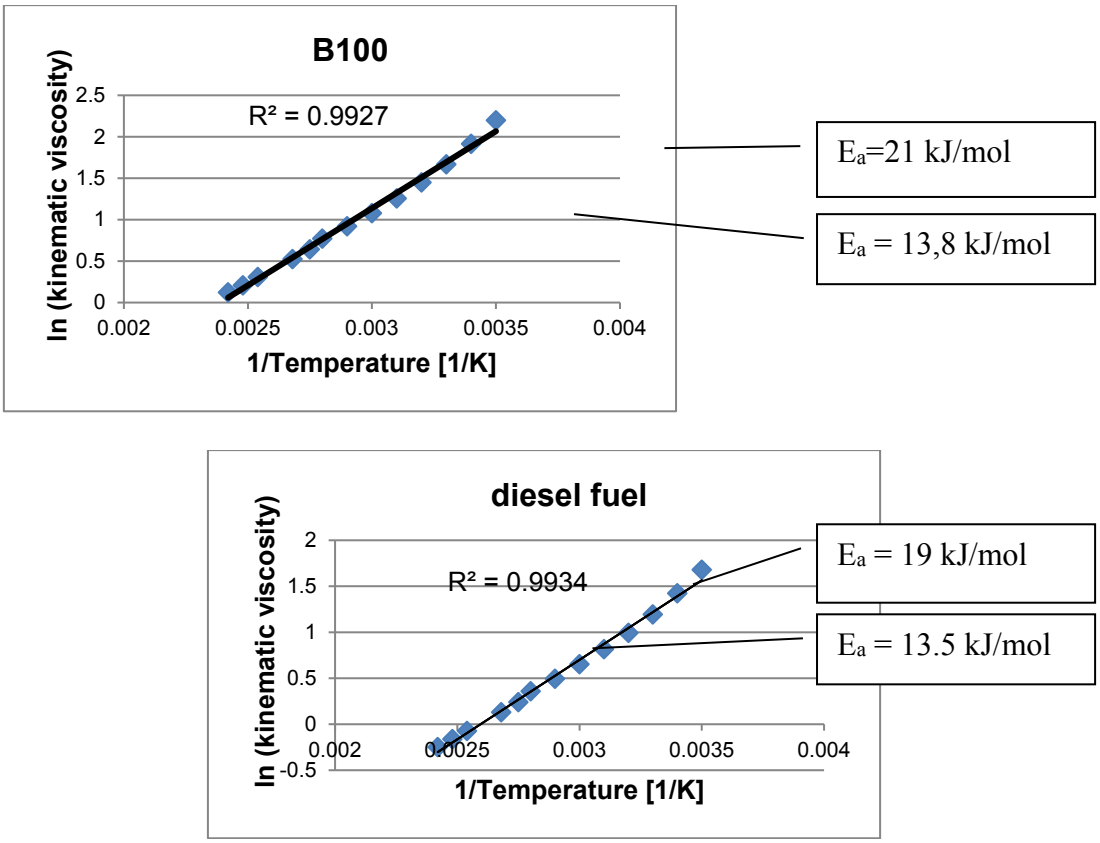


Fig. 2. Activation energy E_a of disruption reaction of intermolecular bonds, calculated for FAME (B100) and diesel fuel

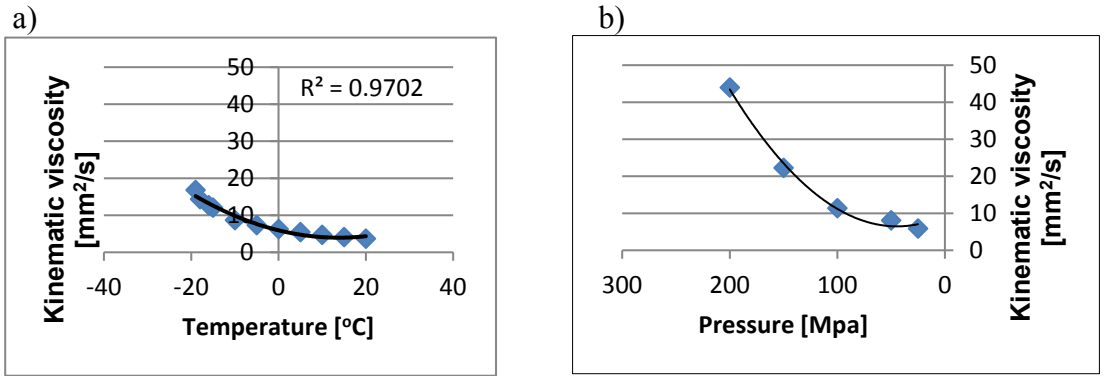


Fig. 3. The mineral diesel fuels viscosity change a) by cooling and b) by increase of the pressure

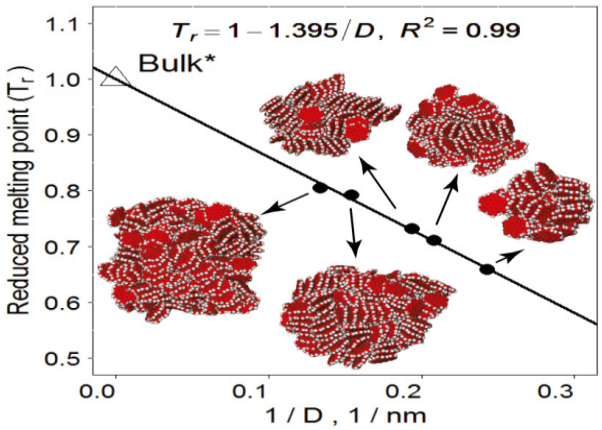


Fig. 4. Relation between reduced melting point and diameter of the clusters of PAH [4]

The unexpected effects arising from chemical composition of fuel cannot be explained by Newtonian model – example: the influence of the concentration of FAME in mineral jet fuel on the value of cloud point (CP) and freezing temperature, what was reported by authors of this article [5].

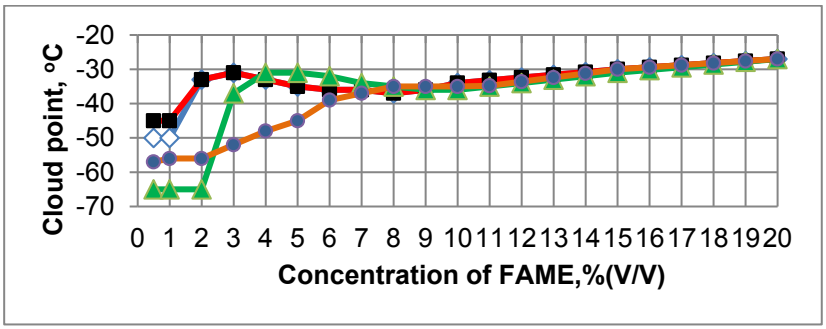


Fig. 5. Cloud point and freezing point change with the increase of FAME concentration in jet fuel; each line represents blend of jet fuel (two kinds of this fuel) and FAME (from two plants) [5]

The effects observed for FAME concentration between 0 and 10 % (V/V) can be explained by the clusters theory. According to these theory molecular clusters created by hydrocarbons, molecules are modified by FAME molecules. This modification depends on FAME concentration in mineral fuel, but this modification is not proportional to FAME concentration. The clusters size and structure, including geometric structure, can be the reason of unexpected changes of CP and freezing point.

4. The possibly influence of clusters on tribological properties of fuels

Lubricity of fuels for CI engines becomes one of very important parameter since the sulphur content was decreased to 50 and actually 10 ppm. In mineral distillates sulphides, polysulfide's and thiols are the main sulphur containing compounds. Sulphur removal from distillate practically eliminates these compounds. Organic sulphur compounds are well known as very effective lubricating additives, used for many years in lubricants. The sulphur containing additives are active in protective layers creation on the surface of lubricated elements of machines. Their activity depends on their chemical structure and operation conditions of machine. Thiols and sulphides are effective in Anti-war layer creation since polysulphides are effective EP additives.

Elimination of organic sulphur compounds from diesel fuel dramatically decreases the fuels ability to protective layer creation. As the result fuel pumps and unit injector's elements, they cannot be protect against intensive wear and seizure. To provide effective lubrication of fuel pumps and unit injectors elements in case fuel does not contain organic sulphur compounds, the oxygen containing organic compounds are added as lubrication additives. These additives are mainly organic acids with long hydrocarbon chains. The effectiveness of lubricating additives depends on the base fuel. As it is shown on Fig. 6, lauric acid improves effectively fuels lubricity, when is added to mineral diesel fuel. The same additive is not effective in n-hexadecane.

The adsorption theory of protective layer cannot explain this effect. The experience in the use of lubricating additives added to the fuels and lubricants points the important role of base fuel or base oil on effectiveness of lubricating additives. This is associated usually with the viscosity of base fuel or oil, but under conditions of fuels pumps as well as HFRR and BOCLE apparatuses during laboratory tests, the hydrodynamic lubrication cannot play important role. Authors of this article believe that molecular clusters created by hydrocarbons of fuel can play important role in protective layer formation by base fuels and by fuels containing lubricating additives.

One of characteristic of molecular clusters is their electrical conductivity, other than hydrocarbons, which do not create clusters. Fig. 7 shows the dependence between wear determined during BOCLE test and the conductivity measured for the number of Jet fuel blends with synthetic hydrocarbons and alcohols.

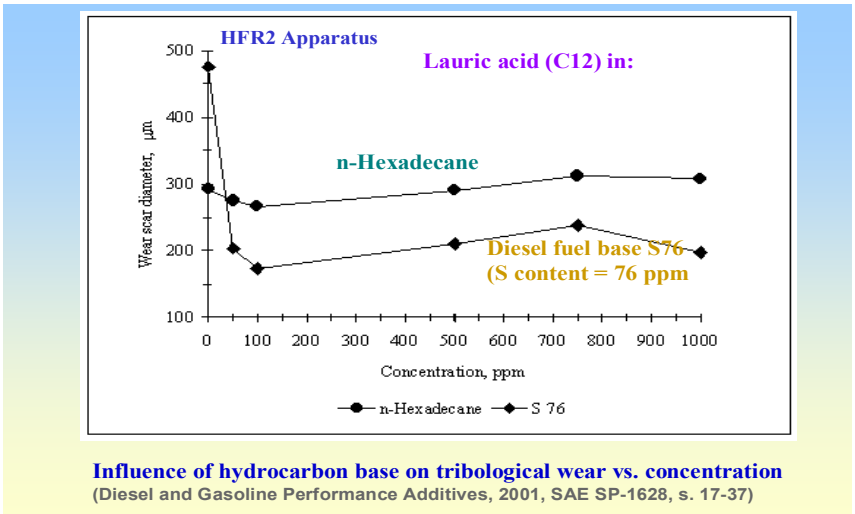


Fig. 6. The relationship between the result of HFRR test (balls wear) and additive (lauric acid) concentration [6]

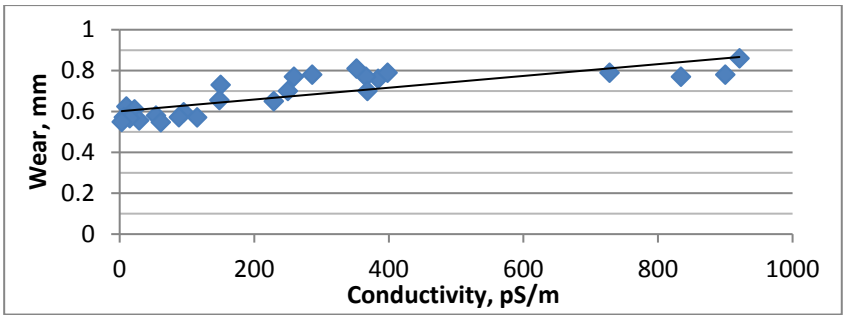
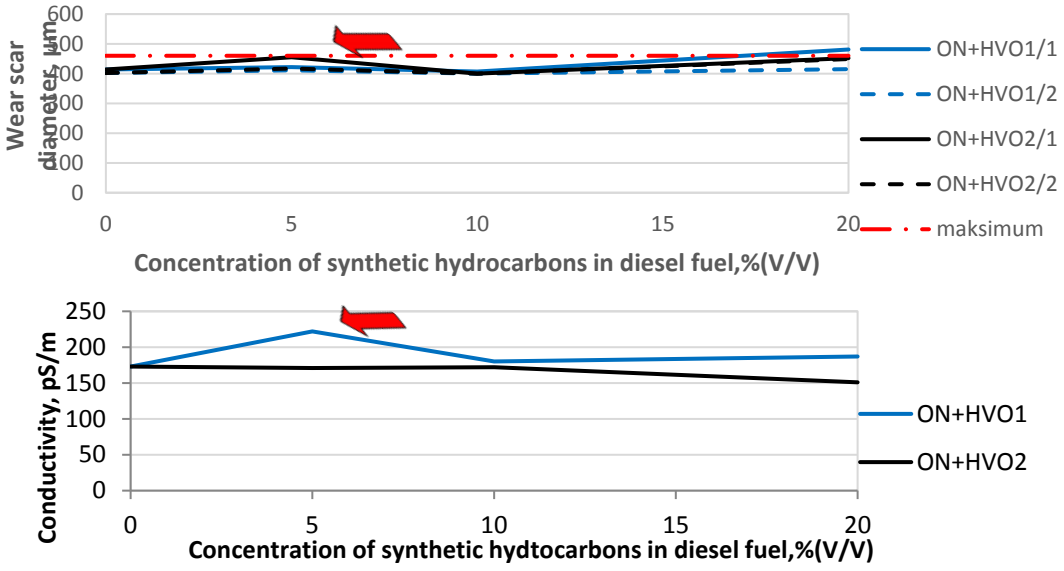


Fig. 7. Relationship between wear after BOCLE test obtained for the number of Jet fuel blends with synthetic hydrocarbons and alcohols and conductivity of these blends

Similar dependence was found for the blends of mineral diesel fuel (without FAME) and the blends of synthetic hydrocarbons, which play the role of the models of hydrotreated vegetable oils (HVO) (Fig. 8).



ON – diesel fuel; HVO – the model of hydrotreated vegetable oil

Fig. 7. The influence of synthetic hydrocarbons (n-paraffins) concentration in diesel fuel on lubricity (HFRR) and conductivity of the tested blends

The characteristic increase of wear and conductivity for the blend of 5 % (V/V) of synthetic hydrocarbons can be explained as the specific synthetic hydrocarbons influence on the structure of clusters built by the fuels molecules.

5. Conclusions

Presented in the article examples of unexpected effects in various blends of jet fuels and diesel fuels observed in relation to their behaviour at low temperature and during lubrication of fuel pumps leads to conclusion, that:

- usually fuels are described as the mixture of molecules almost independent and the interaction between molecules is considered marginally,
- it was found that molecules of aromatic compounds create molecular clusters,
- the observed unexpected behaviour of fuels at low temperature and during lubrication can be explained by molecular clusters characteristics.

The authors of this article opinion are that further research should be focused on the cluster formation by fuels components and the influence of clusters on fuels properties.

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