# THE ROLE OF MOLECULARLY ORDERED STRUCTURES IN ENERGY TRANSPORT ENHANCEMENT DURING COMBUSTION PROCESS – A NEW CONCEPTION OF A REACTION MECHANISM OF FUEL COMPONENTS OXIDATION

**Tomasz Białecki, Wojciech Dzięgielewski, Bartosz Gawron**
**Urszula Kaźmierczak, Andrzej Kulczycki**

*Air Force Institute of Technology, Division for Fuels and Lubricants*
*Ksiecia Boleslawa Street 6, 01-494 Warsaw, Poland*
*tel.:+48 261 851 416, fax. +48 261 851 601*
*e-mail: tomasz.bialecki@itwl.pl, bartosz.gawron@itwl.pl*
*wojciech.dziegielewski@itwl.pl, urszula.kazmierczak@itwl.pl, andrzej.kulczycki@itwl.pl*

***Abstract***

*This article presents the results of investigations focused on the role of molecularly ordered structures (molecular clusters) on combustion process. The proposed new mechanism of the reactions initiation takes into account the role of molecular clusters in energy (heat and energy of electrons emitted by the surface of the walls of combustion chamber) conductivity regulation. Literature survey shows that molecular clusters created by aromatic hydrocarbons are responsible for particulate matter. The combustion process itself is not uniform in whole combustion chamber. Such diversity, caused mainly by heterogeneous thermal state of combustion chamber is recognized as significant reason to create various products of combustion including carbon oxides, carbon dioxides and nitrogen oxides. Jet fuel and its blends with n-butanol and biobutanol in concentration from 10 to 75 % (V/V) were subjected to laboratory tests. Such blends were also tested on the test rig with a miniature turbojet engine – MiniJETRig. Engine operating parameters and carbon oxide emission were measured. The relations between electrical conductivity and parameters of engine test (e.g. temperature in selected points in combustion chamber) were assessed. Engine tests were carried out according to specific profile of engine test, which models different engine operating modes. The results of experimental investigations, shown in the article, initially confirm the proposed mechanism of the oxidation reactions initiation during combustion process.*

*Keywords: molecular clusters, turbojet engine, butanol, combustion process, carbon oxide emission*

## 1. Introduction

Conventional fuels for gas turbines have been used in civil and military aviation for decades. The optimal chemical composition of these fuels was determined and was regulated by technologies for the production of components in oil refineries. Many years of experience have allowed these fuels to be considered appropriate for the construction of turbine engines and their operating conditions. The properties, which should characterise the fuel determined on the basis of experience from aircraft operation, reflect its impact on the processes occurring in the engine power supply systems and in the combustion chamber.

This article focuses on combustion process, which is complex and strongly dependent on the chemical composition of the fuel. The chemical composition of fuel together with conditions in combustion chamber both determine the skeleton of chemical reactions which lead to the final products of combustion, i.e. carbon dioxide ($CO_2$), water ($H_2O$), carbon oxide (CO), unburned hydrocarbons, soot and particulate matter (PM) as well as nitrogen oxides ($NO_x$) [12].

The chains of chemical reactions clearly show that the chemistry of hydrocarbons combustion is different from the chemistry of alcohols (butanol) combustion. In both cases, the conditions in the combustion chamber will affect the rate of individual reactions and, consequently, the concentration of individual combustion products in exhaust gases, i.e. $CO_2$, CO, unburned hydrocarbons, PM and

NO$_x$. The term "conditions in the combustion chamber" is not precise. It is known that in various areas of the combustion chamber the conditions are different. Energy heterogeneity is related to the whole combustion chamber, but also to microspheres, mainly drops of evaporating fuel, in which the process of oxidation of fuel components begins. In this situation, the transport of energy to the molecules of reagents – fuel components plays a decisive role in the course of the combustion process.

Butanol as a blending component for fossil fuels was discussed in papers [4, 9, 14, 15, 18]. Despite the difficulties in its direct application to power aircraft turbine engines, it can be used as an alternative fuel for stationary gas turbines.

## 2. The role of butanol in molecular ordered structures formation

Recent studies [1, 5, 13] indicate that molecularly ordered structures (molecular clusters) play an important role in the energy transport. Molecular clusters are created by hydrocarbons, the main component of liquid fuels. Manil et al. [13] studied fullerene clusters, whereas Gatchell and Zettergren [5] studied clusters created by polycyclic aromatic hydrocarbons and fullerenes. They stated, among others, that $C_{16}H_{10}$ pyrene forms clusters of 36 molecules $(C_{16}H_{10})_{36}$. Exemplary structures of molecular clusters are presented in [1].

Jet fuels do not contain polyaromatic hydrocarbons (PAH). Paraffin and aromatic hydrocarbons do not create molecular cluster, as durable as created by PAHs. Previous research described in [5, 13, 20] lead to suggestion that alcohols like butanol can create with hydrocarbons molecularly ordered structures. This can explain some of unexpected behaviour of blends containing various isomers of butanol.

Molecular clusters behave in a collision with other molecules, atoms or ions differently than single molecules of a given compound. The collision energy is transferred to the entire cluster. An important feature of molecular clusters is their ability to conduct electricity. However, it was found that clusters, even if they are insulators, have the ability to conduct current.

Table 1 shows that electrical conductivity of fuels containing butanol isomers does not depend on polarity of alcohols molecules. It was found that the influence of butanol isomers on fuels conductivity (Tab. 1) is different from blends of these isomers. All these data indicate that butanol molecules should create molecular structures responsible for energy transport inside the liquid phase. This conclusion can be supported by chromatographic methods of aromatic compounds detection in jet fuel (Fluorescent Indicator Adsorption): butanol moves along the column together with aromatic compounds despite that polarity of butanol and aromatic compounds are different.

*Tab. 1. The influence of various isomers of butanol on the blends electrical conductivity [19]*

| Butanol isomer | Dipole moment [μ/D] | Difference between electrical conductivity of butanol isomer blends with Jet A-1 and neat Jet A-1 | |
|---|---|---|---|
| | | 5%(V/V) butanol in Jet A-1 | 15%(V/V) butanol in Jet A-1 |
| Buthan-1-ol | 1.66 ± 0.03 | 61 | 1001 |
| Buthan-2-ol | 1.8* | -80 | 83 |
| 2-methylopropan-ol-1 | 1.64 ± 0.08 | -82 | 553 |

* Values obtained by liquid phase measurements, which sometimes have large errors because of association effects

These special features of clusters and the ability of various hydrocarbons to create them prompts to formulate the following hypothesis: fuel components, mainly aromatic hydrocarbons, form together with butanol molecular clusters that are responsible for energy transfer from its source to the inside of the liquid phase. This energy is then passed on to the molecules of the reactants modifying the combustion process. Proposed hypothesis was examined in engine tests carried out on MiniJETRig.

## 3. Experimental set-up

### 3.1. MiniJetRig test method

Bench tests presented in the article were carried out on MiniJETRig – Miniature Jet Engine Test Rig. This test rig consists of miniature turbojet engine, exhaust gas analyser and control system with data acquisition. These elements were described in [6], while the technical specification of used sensors was presented in [7, 9].

Engine test investigations were conducted according to the methodology and profile of the engine run described in paper [7]. Engine tests were conducted the same day, in order to minimise the influence of ambient conditions.

Experiments for each tested fuel were executed at least two times. The analysed parameters in every individual test were averaged in selected sets of measurement data, characterised by small values of standard deviations. Next, the results from three independent tests for a given fuel were averaged. The average value of each parameter was supplemented with a maximum and minimum value, which correspond the extreme values from single engine runs [8].

MiniJETRig is used not only for aviation alternative fuels research [8, 9]. One of its interesting application is toxicity evaluation of exhaust gasses on living cells [10, 11].

### 3.2. Tested fuel

Fossil Jet A-1 fuel obtained from two different technological processes hydro treating and Merox and its blends with n-butanol, biobutanol and synthetic blending components obtained from hydro processed esters and fatty acids (HEFA) process were used to power the engine during bench tests. The tested fuels were marked as follow:
– Jet – blend of Jet A-1 from hydro treating/Merox process,
– Jet M – neat Jet A-1 from Merox process,
– Jet M/but X – blend of Jet A-1 from Merox process with n-butanol (where X indicates the percentage of n-butanol),
– Jet/biobut X – blend of Jet A-1 from hydro treating/Merox process with biobutanol (where X indicates the percentage of biobutanol),
– CAM – blend of Jet A-1 with HEFA component from camelina plant (52/48),
– UCO – blend of Jet A-1 with HEFA component from used cooking oil (50/50).

Selected properties of all tested blends carried out according ASTM D7566 [2] were presented in Tab. 2.

*Tab. 2. Selected properties of fuel blends*

| Property | Limits ASTM D7566 | Results | | | | | | | | | |
|---|---|---|---|---|---|---|---|---|---|---|---|
| | | Jet M | Jet M/but 10 | Jet M/but 20 | Jet M/but 40 | Jet | Jet/biobut 25 | Jet/biobut 50 | Jet/biobut 75 | CAM | UCO |
| Density at 15ºC, kg/m³ | 775.0-840.0 | 787.7 | 789.5 | 791.7 | 796.7 | 790.2 | 794.0 | 800.1 | 806.5 | 779.9 | 771.1 |
| Viscosity at -20ºC, mm²/s | max 8.000 | 2.997 | 3.177 | 3.631 | 5.229 | 3.117 | 4.070 | 6.320 | 8.902 | 5.004 | 3.514 |
| Specific energy, MJ/kg | min 42,8 | 43.99 | 42.68 | 41.72 | 40.23 | 43.31 | 40.73 | 38.18 | 35.63 | 43.70 | 43.74 |
| Smoke point, mm | min 19 | 26 | 26 | 32 | 38 | 25 | 27 | >40 | >40 | 31 | 26 |
| Aromatics, % | max 25.0 | 16.2 | 14.6 | 13.0 | 9.7 | 15.0 | 11.5 | 7.6 | 4.1 | 9.4 | 7.2 |
| Naphthalenes, % | max 3.00 | 0.40 | 0.36 | 0.32 | 0.24 | 0.47 | 0.32 | 0.21 | 0.11 | 0.56 | 0.24 |

Based on the laboratory tests it is concluded that adding of n-butanol/biobutanol increases the density and viscosity of the blend as well as reduces the specific energy. The change is proportional to the amount of the component concentration. Adding of synthetic blending components (from camelina and UCO) reduces density while increases viscosity. Changes in tested properties are reflected in combustion process.

## 4. The results of engine tests

The CO emission in exhaust gases was used as the indicator of combustion process similarity in case the various blends of fossil Jet A-1 fuel with different components. Measured CO emission was converted from ppm to g/kg of fuel. Fig. 1 a-c presents the course of CO emission as a function of component concentration. The data concerns three different rotational speeds, and thus different engine operating states.
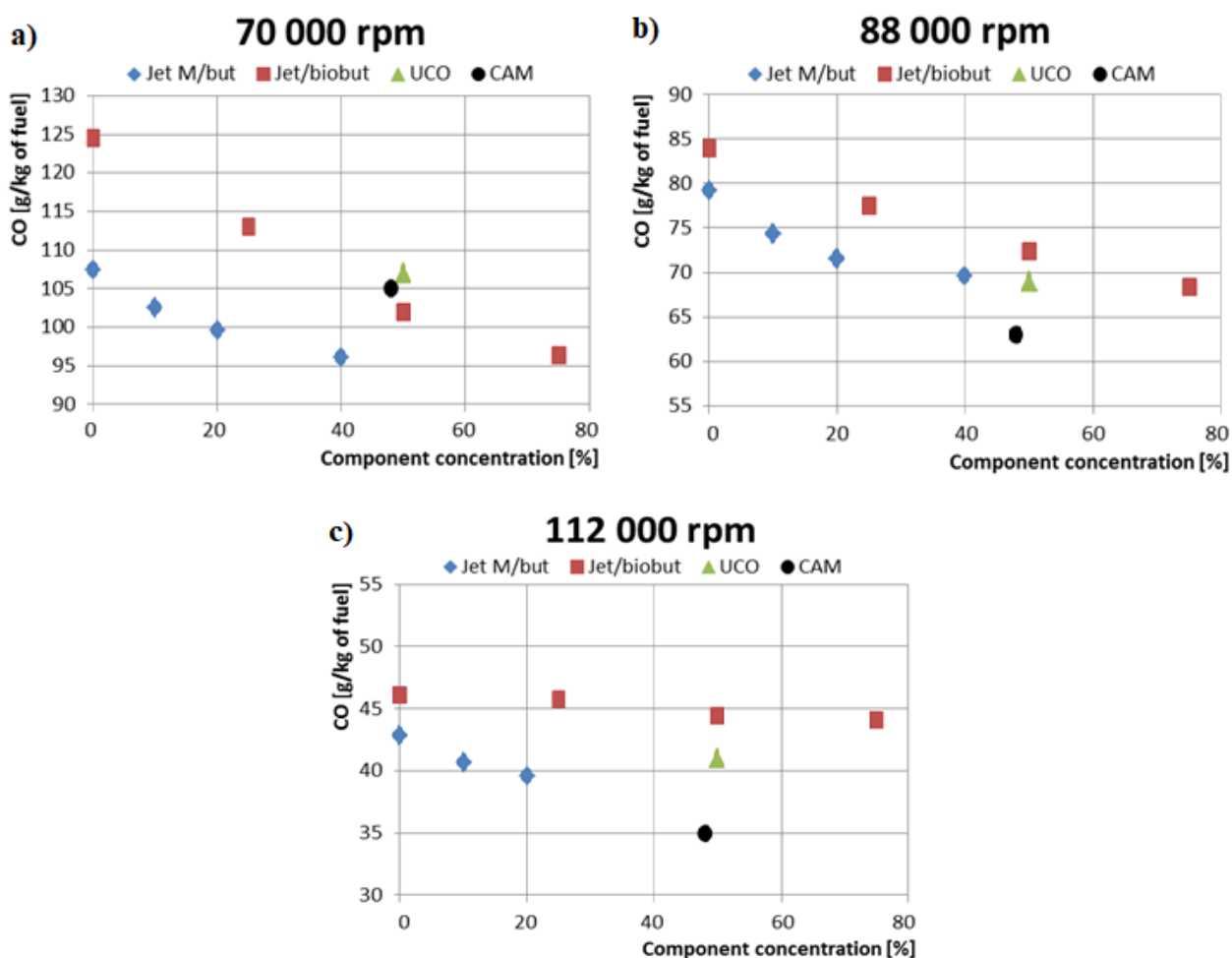






*Fig. 1. CO emission as a function of component concentration; a) 70 000 rpm, b) 88 000 rpm, c) 112 000 rpm*

Based on Fig. 1, the following conclusions can be drawn:
– depending on the chemical structure of conventional Jet A-1 fuel (from Merox or hydro treating), the effect of butanol on the CO emission in the exhaust gases is different,
– observed reduction of CO emission as the butanol concentration increases. This cannot be explained only by decreasing Jet A-1 concentration, affecting the formation of CO (the effect of diluting Jet A-1 with butanol). If the diluting effect predominated, the trend lines for JetM/but and Jet/biobut would run in parallel,
– to confirm the above conclusion, approximately 50% (V/V) of the HEFA component (UCO and

CAM) containing mainly paraffin hydrocarbons was introduced into the Jet A-1. The results obtained differ significantly from those obtained for butanol blends, which clearly indicates that reducing the CO emission in the exhaust gases as the butanol concentration increases does not result from the dilution effect.

Based on literature survey, it was recognized that the group of hydrocarbons that can affect the formation of CO in the combustion process are aromatic hydrocarbons. Fig. 2 presents the values and course of aromatic hydrocarbons content as a function of n-butanol and biobutanol concentration.
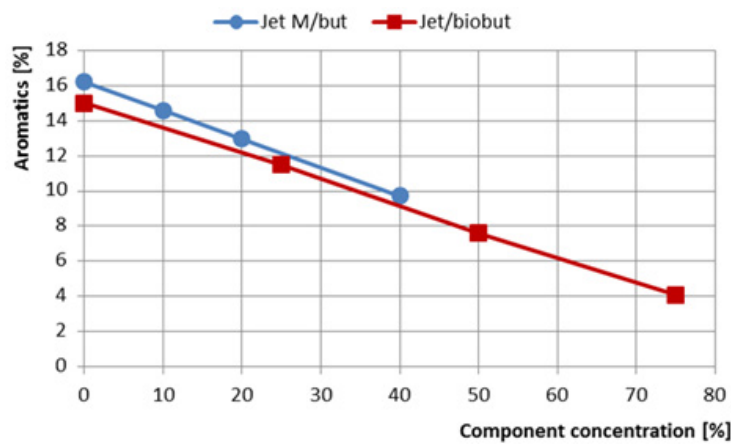


*Fig. 2. Aromatic hydrocarbons as a function of component concentration*

In Fig. 3 a-c was shown CO emission as a function of aromatic hydrocarbons content for a given blend for various engine-operating modes.
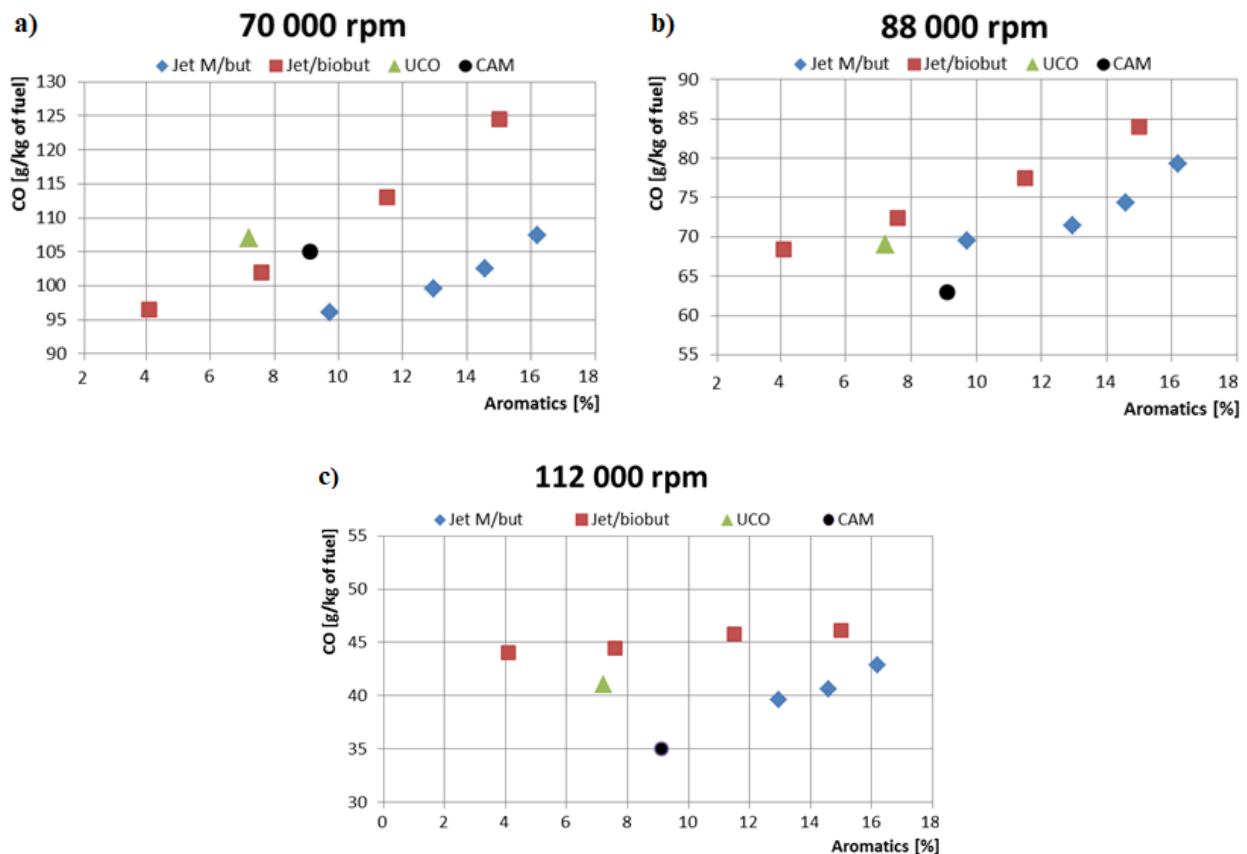


*Fig. 3. CO emission as a function of aromatics content; a) 70 000 rpm, b) 88 000 rpm, c) 112 000 rpm*

Based on Fig. 2 and 3, the following conclusions can be drawn:

– neat Jet A-1 contains the most aromatics. With the increase of n-butanol and biobutanol concentration in the fuel blend, the aromatics content decreases,

– the fewer aromatics in the blend, the lower CO emission.

The conclusions presented above suggest that butanol molecules form molecularly ordered structures with aromatic hydrocarbons of Jet A-1. These structures have an effect on CO emission generation in the combustion process in the engine. Papers [16, 17] indicate the dependence of the tendency to create CO from the local temperature in the combustion chamber (in the cooler zones of the combustion chamber more CO is produced). Considering the above, it is suggested that created molecularly ordered structures have an effect on the distribution of energy in the combustion chamber and through this effect affect on the amount of CO in the exhaust gases.

To verify this thesis, the results of temperature measurements in various areas of the combustion chamber (T3) were analysed. The results for two selected points (on the circumference of the combustion chamber) obtained at the engine rotational speed of 70 000, 88 000 and 112 000 rpm for fuels containing different biobutanol concentrations are shown in Fig. 4.

Presented results clearly show the temperature variety in different areas of the combustion chamber. This is a design feature of the turbine engine. However, a clear effect of the biobutanol concentration in the combusted fuel on the temperature at some of the measuring points was observed. This confirms the thesis about the influence of butanol on the distribution of energy inside the combustion chamber. The reason for this effect can be molecularly ordered structures formed by aromatic hydrocarbons of Jet A-1 and butanol molecules, which thanks to specific properties (different from the properties of individual molecules) modify the energy distribution inside the combustion chamber, favouring a more evenly distribution. In this way, these structures reduce the tendency to create cooler areas in the combustion chamber, which are the source of CO emission. As a result adding of butanol reduces the CO emission in the exhaust gases.
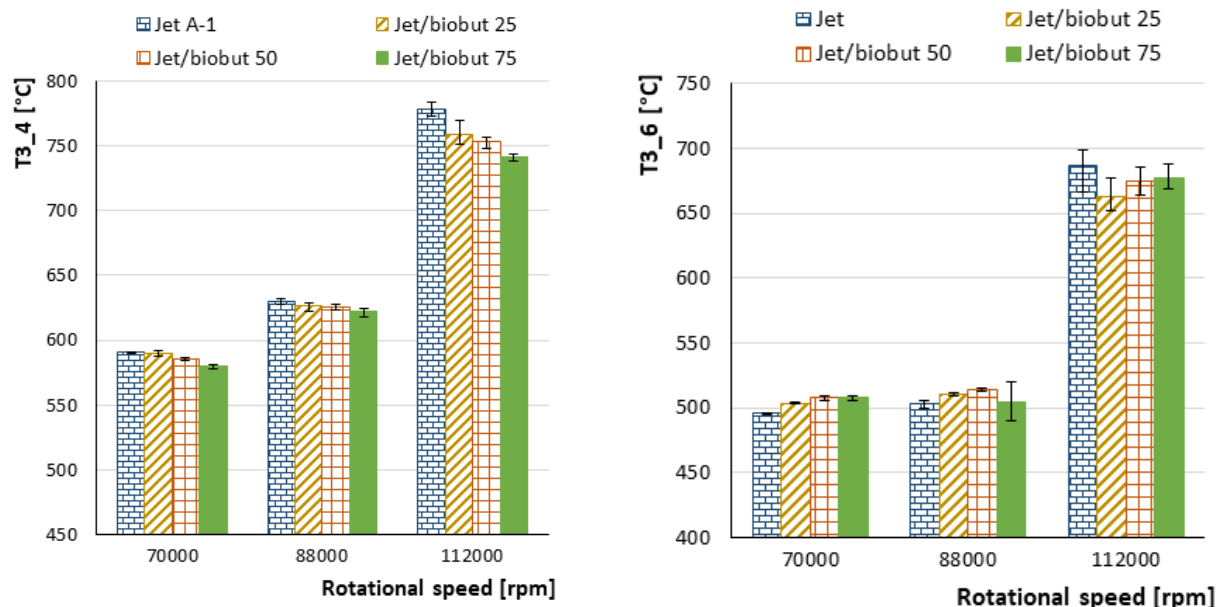


*Fig. 4. Temperature at selected points in combustion chamber as a function of rotational speed, a) point on the circumference No. 4, b) point on the circumference No. 6*

## 5. Summary and conclusions

The results obtained during MiniJETRig tests indicate that butanol change the chemical reactions of combustion process. The butanol influence on chemistry of fuels combustion depends on:

– butanol concentration in blends with Jet A-1 fuel,

– the chemical structure of Jet A-1 regulated by refinery technology – Merox and hydro treating,
– thermodynamic state of combustion chamber regulated by rotational speed.

The obtained dependence between CO emission in exhaust gases and aromatic hydrocarbons and butanol concentration in the fuel indicates that increase of aromatic hydrocarbons content, as well as decrease of butanol concentration in fuel results higher CO emission. This is general dependence, but different relationships were obtained for different conventional Jet A-1 fuels what indicates the interaction between butanol hydrocarbons and molecules.

To ensure that change of CO emission is not the result of aromatic hydrocarbons dilution by butanol, the relationship between CO emission and aromatic content obtained for different blends of Jet A-1 and butanol was compared with similar dependence obtained for blends of Jet A-1 and synthetic paraffinic hydrocarbons (HEFA). It was found that relationship obtained for HEFA blends is different from those obtained for butanol blends. The same general dependence obtained for blends containing butanol and blends containing HEFA suggests that the change in CO emission in exhaust gases is not the result of variation of burning chemistry, but is the result of molecular ordered structures influence on energy distribution in combustion chamber.

Concluding all results shown above indicate that CO emission in exhaust gases depends on chemical structure and concentration of molecularly ordered structures in burned fuel. In case blends of Jet A-1 and butanol these ordered, structures are created by butanol molecules and aromatic hydrocarbons of conventional jet fuel.

The conclusions presented in this article should be verified in further studies, which directly confirm the butanol participation in formation of molecular clusters and which confirm the role of molecularly ordered structures in energy distribution in combustion chamber.

## References

[1] Abeyrathne, C. D., Halgamuge, M. N., Farrell, P. M., Skafidasa, E., *Dielectric properties of liquid phase molecular clusters using external field method: molecular dynamics study*, Physical Chemistry Chemical Physics, Vol. 16, Is. 21, pp. 13943-13947, 2014.
[2] ASTM D7566, Standard specification for aviation turbine fuel containing synthesized hydrocarbons, 2018.
[3] Cuoci, A., Frassoldati, A., Faravelli, T., Williams, F. A., *Cool flames in microgravity droplet combustion*, 29th American Society for Gravitational and Space Research 5th International Symposium for Physical Sciences in Space, Orlando 2013.
[4] Dzięgielewski, W., Gawron, B., Kaźmierczak, U., Kulczycki, A., *Butanol/biobutanol as a component of an aviation and diesel fuel*, Journal of KONES, Vol. 21, No 2, pp. 69-75, 2014.
[5] Gatchell, M., Zettergren, H., *Knockout driven reactions in complex molecules and their clusters*, Journal of Physics B: Atomic, Molecular and Optical Physics, Vol. 49, No 16, pp. 1-36, 2016.
[6] Gawron, B., Białecki, T., *The laboratory test rig with miniature jet engine to research aviation fuels combustion process*, Journal of Konbin, Vol. 36, pp. 79-90, 2015.
[7] Gawron, B., Białecki, T., *Measurement of exhaust gas emissions from miniature turbojet engine*, Combustion Engines, Vol. 167, pp. 58-63, 2016.
[8] Gawron, B., Białecki, T., *Impact of a Jet A-1/HEFA blend on the performance and emission characteristics of a miniature turbojet engine*, International Journal of Environmental Science and Technology, Vol. 15, Is. 7, pp. 1501-1508, 2018.
[9] Gawron, B., Białecki, T., Dzięgielewski, W., Kaźmierczak, U., *Performance and emission characteristic of miniature turbojet engine fed Jet A–1/alcohol blend*, Journal of Kones, Vol. 23, pp. 123-129, 2016.
[10] Gawron, B., Białecki, T., Górniak, A., Janicka, A., Zawiślak, M., *An innovative method for exhaust gases toxicity evaluation in the miniature turbojet engine*, Aircraft Engineering and Aerospace Technology, Vol. 89, No. 6, pp. 757-763, 2017.

[11] Janicka, A., Zawiślak, M,. Zaczyńska, E., Czarny, A., Górniak, A., Gawron, B., Białecki T., *Exhausts toxicity investigation of turbojet engine, fed with conventional and biofuel, performed with aid of BAT-CELL method*, Toxicology, Letters, Vol. 280, pp. 202, 2017.

[12] Kulczycki, A., *Modelowanie procesów w eksploatacji silników spalania wewnętrznego. Konwencjonalne i alternatywne paliwa płynne w eksploatacji silników*, Wydawnictwo Instytut Technologii Eksploatacji – Państwowy Instytut Badawczy, Radom 2018.

[13] Manil, B., Maunoury, L., Huber, B. A., Jensen, J., Schmidt, H. T., Zettergren, H., Cederquist, H., Tomita, S., Hvelplund, P., *Highly charged clusters of fullerenes: charge mobility and appearance sizes*, Vol. 91, No. 21, 2003.

[14] Methling, T., Richter, S., Kathrotia, T., Braun-Unkhoff, M., Naumann, C., Riedel U., *An Investigation of Combustion Properties of Butanol and its Potential for Power Generation*, Journal of Engineering for Gas Turbines and Power, Vol. 140, No. 9, 2018.

[15] Mendez, C. J., Parthasarathy R. N., Gollahalli S. R., *Performance and emission characteristics of butanol/Jet A blends in a gas turbine engine*, Applied Energy, Vol. 118, pp. 135-140, 2014.

[16] Merkisz, J., *Ekologiczne problemy silników spalinowych*, Tom I, Wydawnictwo Politechniki Poznańskiej, Poznan 1998.

[17] Merkisz, J., *Emisja dwutlenku węgla z pojazdów z różnymi układami napędowymi w rzeczywistych warunkach eksploatacji*; Transport Samochodowy, Vol. 2, pp. 115-127, 2010.

[18] Muelas, Á., Remacha, P., Martínez, A., Ballester, J., *Combustion behavior of Jet A droplets and its blends with butanol*, ASME Turbo Expo 2017: Turbomachinery Technical Conference and Exposition, Vol. 4A, Combustion, Fuels and Emissions, Charlotte 2017.

[19] Rosamonte's physical chemistry website, *Dipole moment*, https://physicalchemistryrosamonte. wordpress.com/material-balances/material-balances-on-a-crystallizer/physical-properties-of-pure-methanol/ dipole-moment/.