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The biofuel Bioxdiesel with ethyl components in feeding Diesel engines

This paper presents the physic-chemical properties and analysis and composition of biocomponents (ethyl esters and ethanol) and three components fuel named Bioxdiesel on utilitarian applications for CI engines. The assessment of efficiency of engines fed by fuel with significant participation of ethyl biocomponents in non stationary states showed, that the supply of energy is the same as for a standard fuel.
Positive test results of the fuel lubricity and its use in the low-temperature conditions show a positive impact of biocomponents compositions on durability and operating reliability.
Studies on Bioxdiesel with different content of biocomponents showed a significant reduction of CO, HC and the smokiness of the exhaust gases in the range of 40 - 80% compared to the feeding of the same engines by standard fuel, while NOx emissions remained at a similar level.
Research of biofuels ability to absorb water from the air show that in the case of a mixture of aliphatic hydrocarbons with alicil esters of higher fatty acids and anhydrous ethanol is much less hydrophilic than the same mixture of hydrocarbons with anhydrous ethanol (in similar proportions).
Key words: *Bioxdiesel, ethyl biocomponents, emission, toxic gases, non stationary states.*

Biopaliwo Bioxdiesel z komponentami etylowymi w zasilaniu silników o zapłonie samoczynnym

W artykule przedstawiono właściwości fizyko-chemiczne i analizę składu biokomponentów (estrów etylowych i etanolu), a także ocenę wpływu trójkomponentowego paliwa o nazwie Bioxdiesel na własności użytkowe silników o ZS. Ocena efektywności pracy silników w stanach nieustalonych, zasilanych paliwem ze znaczącym udziałem biokomponentów etylowych i standardowym paliwem wykazała, że podaż energii mechanicznej jest na zbliżonym poziomie.
Korzystne wyniki badań właściwości smarnych nowego biopaliwa i jego zastosowania w niskich temperaturach otoczenia wykazują pozytywny wpływ tych biokomponentów na trwałość i niezawodność działania silników.
Użycie paliwa Bioxdiesel z różną zawartością biokomponentów spowodowało istotne zmniejszenie emisji CO, HC i zadymienia spalin w zakresie 40 - 80% w porównaniu do zasilania tych samych silników standardowym paliwem, a emisja NOx utrzymywała się na zbliżonym poziomie.
Badania zdolności biopaliw do absorbowania wody z powietrza dowodzą, że mieszanina złożona z węglowodorów alifatycznych, estrów alkilowych wyższych kwasów tłuszczowych i bezwodnego etanolu jest znacznie mniej hydrofilowa niż mieszanina węglowodorów z bezwodnym etanolem (w podobnych proporcjach.
Słowa kluczowe: *Bioxdiesel, biokomponenty etylowe, emisja, gazy toksyczne, stany nieustalone.*

1. Introduction

Very intensive development of automotive industry as an element of civilization progress plays the significant part in causing negative changes in the environment.
It is estimated that the communication pollution make 21% of general pollutions and in large urban areas 75…80% of the total contamination.
Vehicles with Diesel engine, which are the main kind of transport, are the source of the fundamental emission of toxic and greenhouse gases to the atmosphere. Therefore, intensive works are carried out on the replacement of fossil fuels extracted from the interior of the earth and burnt on the surface with fuel plants raised on the surface of the earth, which absorb increasing inter alia. CO_2 - one of the main greenhouse gases [1, 2].
Current researches in the field of biofuels are mainly focused on the analysis of the possibility of feeding Diesel engines by raw vegetable oil [3], their esters or mixtures of diesel oil with esters or mixtures of diesel oil with alcohol [4,5].
The results of researches [6,7,8] and the researches carried out by the author, on plant and animal origin bio-fuels for Diesel engine, indicate that ethyl biocomponents can be applied to the Diesel engine beside the fatty acid methyl esters [9,10,11,12,13,14].

Very profitable proecological and energetistic properties of the ethyl esters of higher fatty acids, and especially the huge potential possibilities of their production exclusively from vegetable materials and / or the animal production wastes and also the huge possibilities of the logging of bioethanol, decided about the trial production of biofuel for Diesel engines involving the significant part of ethyl biocomponents i.e. ethyl esters and ethanol.

2. Methodology and results of studies of physicochemical properties

2.1. The qualification of the physic-chemical parameters of biocomponents

The qualifications of the physic-chemical properties of the fatty acids ethyl esters (FAEE) received while the ethanol transestryfication of the rapeseed oil with the use of the basic catalyst which was executed according to definite norms in the Tab.1.

The composition of ethyl esters was shown in Tab. 2. and the analysis of the dehydrated ethanol in Tab. 3.

Tab. 1. Physic-chemical parameters of FAEE (REE – rapeseed oil ethyl esters)

Tab. 1. Właściwości fizykochemiczne estrów etylowych wyższych kwasów tłuszczowych otrzymywanych z rzepaku

Properties	Value	Norm
Density in 288 K [kg/dm^3]	0,876	EN ISO 3678
Density in 293 K [kg/dm^3]	0,873	EN ISO 3678
Cetane index	50	EN ISO 4264
Kinematic viscosity at 313 K [mm^2/s]	4,53	EN ISO 3104
Ignition temperature [K]	398	EN 22719
Clouding temperature [K]	261	EN 116
Coagulation temperature [K]	249	EN 116
Cold Filter Plugging Point [K]	259	EN 116
Content of water [mg/kg]	50	ENISO 12937
Resistance of oxidation [K]	383	EN 14112
Acid number [mg KOH/g]	0,3	EN 14104
Number of iodine	105	EN 14111
Content of linolenic acid [%]	9	Analytical methods
Content of multiunsaturated esters [m/m %]	0,5	Analytical methods
Content of ethanol [m/m %]	0,17	Analytical methods
Total content of glicerin	0,22	Analytical methods
Content of potassium [mg/kg]	4	Analytical methods
Content of phosphor [mg/kg]	10	Analytical methods
Corrosivity test [3h at 323 k]	1 a	EN ISO 2160
Sulfur content	Does not contain	Analytical methods
Content of ethyl esters [%]	99,5	EN 14103

Tab. 2. Average contains of REE

Tab. 2. Przeciętny skład REE

Contains	Content by weight [%]
Ethyl oleate	87,30
Ethyl ester of hexadecanoin acid	7,90
Ester cyclopentanon of 2–hydrohydeconin acid	2,25
Ethyl ester of heptadekain acid	1,00
Ethyl ester of acetidecanoin acid	0,50
Ethyl ester of palimitic acid	0,35
Ethyl ester of stearin acid	0,48
Total content of odd acids higher fatty acids	0,22

Tab. 3. Average contains of ethanol

Tab. 3. Przeciętny skład etanolu

Alcohol proof in 20^{o}C in % vol.	99,8 ÷ 99,9
Carbonyl compound content in terms of acetaldehyde, g/l spirit 100%	0,09 ÷ 0,2
Fusels content in terms of amyl, propanol, butanol alcohol mixture g/l spirit 100%	2,0 ÷ 3,2
Methyl alcohol content in g/100 ml spirit 100%	0,01 ÷ 0,03
Acid content in terms of acetic acid, g/l spirit 100% (after gasification)	0,006 ÷ 0,01
Acid content in terms of acetic acid, g/l spirit 100% (before gasification)	0,2 ÷ 0,3
Water concentration , % mas.	0,057 ÷ 0,18
Residue of evaporation, g/l spirit 100%	0,003 ÷ 0,005

2.2. Exhaust gas toxic components analysis

The influence of the ethyl biocomponents contained in the fuel, on the emission of toxic compounds and gases that create a greenhouse effect, emerging as a result of combustion inside the cylinder engines, was calculated based on the research carried out on a specialized engine stand branch and research on urban transport traction engines.

The purpose of laboratory tests was to analyze the composition of exhaust from the engine fueled by fuel type Bioxdiesel, Diesel and REE. Composition of Bioxdiesel fuel is shown under Figure 1 and 2. The study has been carried out at test bench engine SB 3.1. For each point of the load characteristics the analysis of the toxic components content in outlet gases and grade smokiness of exhaust gases was made. The procedure contained the measurements of the concentration of carbon monoxide in the exhaust gases CO, nitrogen oxides NOx, and total unburnt hydrocarbons THC. In addition, smoke was measured using the apparatus and procedures of the Bosch company.

The measurement of gas (CO, THC, NOx) components was carried out by means of the AVL CEB II measuring equipment which inter alia included:

- The infrared absorption analyzer NDIR to measure the concentration of carbon monoxide CO,
- Heated CLD chemiluminescencic analyzer to measure the concentration of nitrogen oxides, NOx,
- Heated flame-ionization detector FID to measure the amount of unburnt hydrocarbons THC,
- Magnetooptic PMD analyzer to measure the concentration of oxygen O_2,
- The infrared absorption analyzer NDIR to measure the concentration of carbon dioxide CO_2,
- Heated path of exhaust gas sampling with heated pre-filter,
- Module for determining the efficiency of conversion NO_2/NO,
- Concentration divisor of calibration gases for the determination of the linearization functions of the used analyzers (16 linearization gases with concentrations from 0 to maximum were used- concentration of calibrating gas),
- Interference analyzers tester for CO and CO_2.

Figures 1 ... 4 present the results of the selected components of exhaust gas emissions.

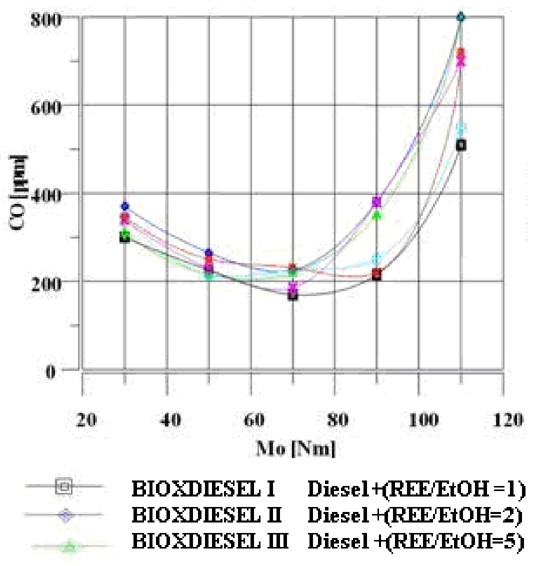

Fig. 1. Concentration carbon monoxide in exhaust at n=1600 rpm.

Rys. 1. Zawartość tlenków węgla w gazach spalinowych przy n=1600 obr./min.

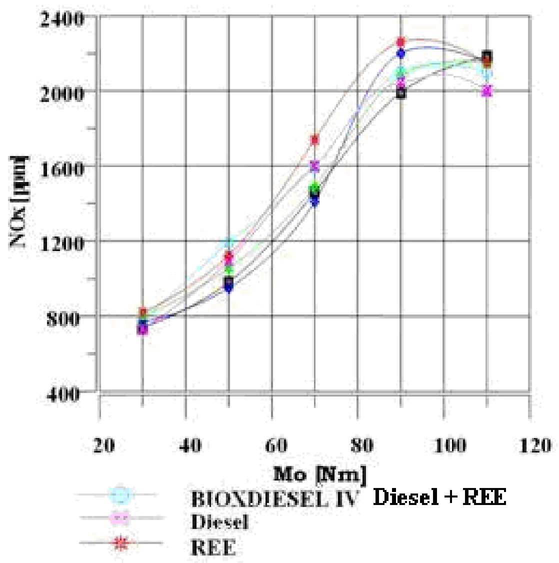

Fig. 2. Concentration nitric oxide in exhaust gases at n=1600 rpm.

Rys. 2. Zawartość tlenków azotu w gazach spalinowych przy n=1600 obr./min.

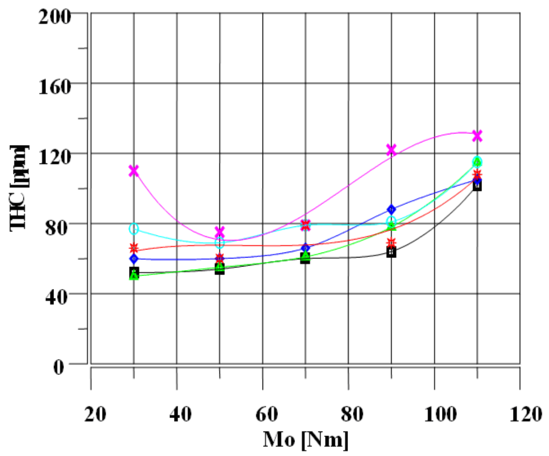

Fig. 3. Concentration hydrocarbon in exhaust gases at n=1600 rpm.

Rys. 3. Zawartość węglowodorów w gazach spalinowych przy n=1600 obr./min.

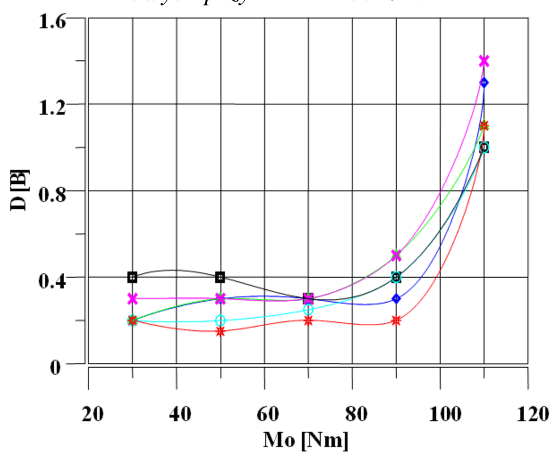

Fig. 4. Smokiness of exhaust gases at n = 1600 rpm.

Rys. 4. Zadymienie gazów spalinowych przy n=1600 obr./min.

Researches on Bioxdiesel fuels with different contents of biocomponents revealed: engine dynamometer tests showed a 40. .. 80% reduction of CO, HC, and 100% reduction of certain carcinogenic substances, compared to the same engines fed by traditional fuel, the NOx emissions remained at the same level and degree of smoke decreased by 50% in all engines and vehicles.

3. Efficiency of the engines fed by bioxdiesel and the bioxdiesel's ability to absorb water

Tests of Diesel engines, included a complete diagnostic evaluation of the engine torque, exhaust smoke measurement, expert vehicles operating examination and the measurement in the termoclimatical chamber.

3.1 The research engine efficiency

Bioxdiesel with proportions Diesel + (REE / Ethanol=5) and standard Diesel compatible with the ON EN 590 were used for the researches.

Ternary mixture (Bioxdiesel) obtained from the analyzed ethyl esters (Tab. 1. and 2.) and ethanol (dehydrated ethanol) (Tab. 3.) and diesel (diesel fuel) with physic-chemical parameters compatible with EN 590 is contained in the table of properties Tab. 4.

Tab. 4. Selected properties of Bioxdiesel
Tab. 4. Podstawowe właściwości paliwa Bioxdiesel

Parameter	Results	Requirements for Diesel according to EN 590
Density at 15°C	0.844 kg/dm^3	0,820 … 0, 845 kg/dm^3
Cetan index	50	min. 46
Kinematical viscosity	2,39 mm^2/s	2 … 4,50 mm^2/s
Ignition temperature	26 °C	>55 °C
Cloud point	-23 °C	<-10 °C
Freezing point	-37 °C	<-24 °C
Cold filter plugging point	-33 °C	<-20 °C
Lubricity	200 µm	max 460 µm
Content of water	97 mg/kg	max 200 mg/kg
Fraction analisys - to 250 °C - to 350 °C - to 370 °C	 42% 98% ---	 max 65% min 85%
Content of sulphur	<0,01%	<0,01%
Corosion	1a	1a

- Analysis of Bioxdiesel properties presented in Tab.4. shows that the fuel meets the requirements as Diesel, except for the flash point - what has only logistic importance;
- The fuel is characterized by better lubricity properties than Diesel, measured using both HFRR and SLBOCLE method, meeting lubrification standards provided for the U.S. and Europe, which contributes positively to the sustainability and reliability of engines;
- The fuel has also significantly better low temperature properties, what is important during winter operation**.**

The main difference of Bioxdiesel and Diesel are presented on boiling curves Fig. 5. The curves of boiling for ethyl ester and raw rapeseed oil were also shown in the figure.

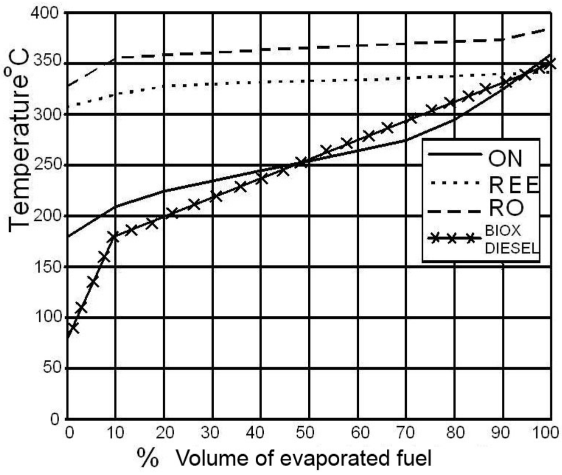

Fig. 5. The curves of boiling
Rys. 5. Krzywe wrzenia

The efficiency of engine operation was defined on the basis of measurements of its dynamic characteristics, which prestents the course of the torque produced by the engine when changing the speed of the crankshaft, due to the rapid delivery of fuel to the inside of cylinders, almost entirely devoted to overcome forces of inertia of engine (the power receiver disconnected)**.**
Changing of the torque induced in engine cylinders presents equation:

$$M_o = J \cdot \frac{d\omega}{dt} = J \cdot \varepsilon \qquad (1)$$

where :
ε - temporarily acceleration of engine parts focused on shaft axis;
J – polar moment of criteria of engine parts focused on shaft axis.

Research has been conducted on UTD-20 engine characterized by following parameters: cylinders structure V120/6; Engine capacity - 15.9 dm^3; fuel injection type - direct injection, the number of valves per cylinder - 4, the maximum power - 220 kW at 2,600 rpm., cooling system - liquid. The engine was powered by Diesel and BIOXDIESEL fuel. Phase portraits (dynamic characteristics of speed) which illustrating the fields of energy supply, as results of 24 trials of acceleration from minimum rpm to maximum rpm, are given on Fig.6.

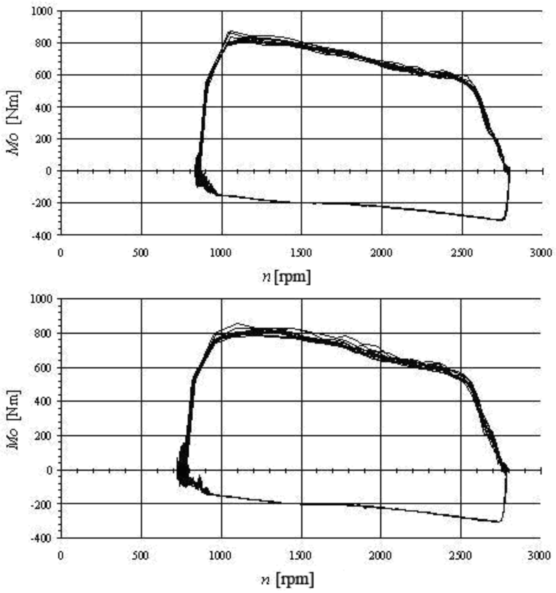

Fig. 6. The phase portrait of UTD-20 engine supplied by Diesel (a) and Bioxdiesel (b)

Rys. 6. Pola podaży energii silnika UTD-20 zasilanego ON (a) i Bioxdiesel(b).

Analysis of shape and surface fields obtained from dozens of researches shows that at the non stationary states of engine operation (during dynamic acceleration crankshaft), the value of the generated energy is almost identical at the feeding by Diesel fuel and Bioxdiesel.

The expert study included the observations of the real operating conditions of city-buses fed by Diesel and Bioxdiesel.

Basic construction data of city-buses engines presented in Tab. 5.

Tab. 5. Basic construction data of engines

Tab. 5. Podstawowe parametry silników

Properties	Engine	
	Volvo D7C275(290)	Man D0826LUH05
Cylinder structure	row, standing, 6	row, lying, 6
Capacity [dm^3]	7,284	6,871
Torque max [Nm] at rpm	1200/1200	850/1300-1500
Max power [kW] at rpm	213/2200	169/2400
Fuel injection	direct injection	direct injection
Type of combu-stion chamber	toroidal in the piston	toroidal in the piston
Compression ratio	19,5:1	17:1
Cooling system	liquid	liquid

Sample comparison of effective parameters is given in Fig.7. (a- comparison of power values, b- value comparison of torque and engine internal resistance).

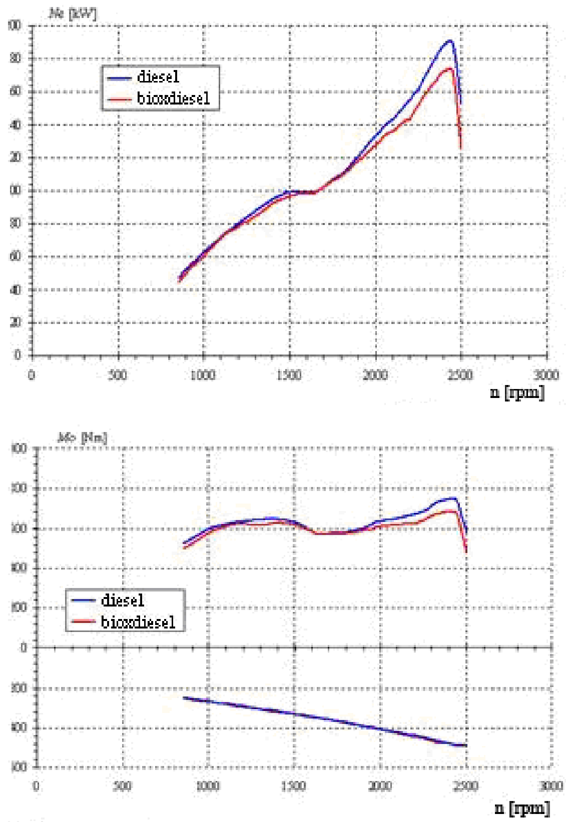

Fig. 7. The efficiency of Volvo engine

Rys. 7. Efektywność silnika Volvo

The same method (free acceleration) applied in the measurement of smokiness of exhaust gases - the size of the phenomenon by reducing transparency of gas mixture components as a result of the content in them of a certain amount of liquid and solid substances. Smokiness of exhaust gases is an indicator of soot in the exhaust gases, and its quantity depends on the quality of combustion of fuel.

The obtained values are less than the maximum permissible value of this coefficient, binding during the tests of the vehicles.

Tab. 6. The average value of smokiness (the coefficient k_{bd}) with engine fed by research fuel, compared to the average smokiness value (coefficient k_D) of the engine powered Diesel [%].

Tab. 6. Średnia wartość zadymienia spalin (współczynnika k_{bd}) przy zasilaniu silnika paliwem badawczym w porównaniu do wartości średniej zadymienia (współczynnika k_{on}) tego silnika zasilanego olejem napędowym [%].

No. Bus	8057	9023	8059
Engine	Volvo D7C275	Man D0826LUH05	Volvo D7C275
k_{bd}/k_D {%]	48,4	43,1	43,6

Researches showed that in case of engines fed by experimental fuel, smokiness is much smaller than in case of the same engine fed by Diesel. The obtained average value of smoke (the coefficient of extinction) is more than 50% less for all engines fed by research fuel than the average smokiness (extinction coefficient) obtained for Diesel.

3.2. Determination of Bioxdiesel sustainability and fuel use in low ambient temperatures

a) Determination of mutual affinity components of Bioxdiesel

The routine approach to biofuels including ethanol generally assumed that wherever we are dealing with absolute alkyl alcohol, regardless of the environment in which it is located, has to increase hydrophilic properties.

Determination of the hydrophobicity or hydophilocity degree of fuel Bioxdiesel made by spectroscopic and thermodynamic test to determine the interaction between the components of the mixture.

Studies have been made within the following configurations:

- a mixture of aliphatic hydrocarbons in the form of diesel fuel and ethyl ester of higher fatty acid fractions of a 0.7 weight: 0.3 (70% to 30%) of hydrocarbons to the ester;
- hydrocarbon mixture of 0.7 weight fraction, the ethyl ester and anhydrous ethyl alcohol fraction of a 0.3 weighting;
- a mixture of hydrocarbons above fraction 0.90 and below 0.10 weight fraction weighting. anhydrous ethanol.

The researches of these mixtures were carried out with the use of IR oscillating spectroscopy and raman spectroscopy method, testing thermogravimetric and NDES (nonlinear dielectric effect spectroscopy).

In the next step the nitrogen mixture of saturated steam was put through all the mixtures for a period of 30 minutes. Then the same tests and measurements were carried out as in the case of the original samples.

The results clearly demonstrate that the mixture comprising of a hydrocarbon fraction above 0.90 and below 0.10 weight fraction of anhydrous ethyl alcohol absorbed the largest amount of water vapor.

The smallest change in the IR spectrum and raman spectrum and NDES is observed in a mixture consisting of 0.7 mol fraction of hydrocarbons, 0.24 weight percentage of ester and 0.06 weight fraction of anhydrous ethanol.

Justification:

Alkyl esters of higher fatty acids include, inter alia, of a highly basic proton-acceptor functional group C = O bound protons from alkil alcohol form strong hydrogen bonding to the free electron pair of oxygen from carbonyl group.

Water molecules in the carried out experiment compete with a more alkaline carbonyl group than hermaphrodited hydroxyl group, thus the competitiveness of the ester carbonyl group with OH group of alcohol is greater in this case, which was clearly showed in a spectroscopic test. In the case of a mixture of hydrocarbons with alkyl alcohol water molecules do not have any competition, because the aliphatic hydrocarbons do not have acidic or alkalic centers through which the centers of free electron pairs, or „acids" protons of OH group could be affected .

Thus, this combination is particularly susceptible to hydration. The system is de facto hydrophilic and requires special protection from moisture.

The study shows that the mixture of aliphatic hydrocarbons with higher fatty acids alkyl esters and anhydrous ethanol is much less hydrophilic than the same mixture of hydrocarbons with anhydrous ethanol (in similar proportions). This result has significant logistic and operational meaning.

b) Low temperature researches

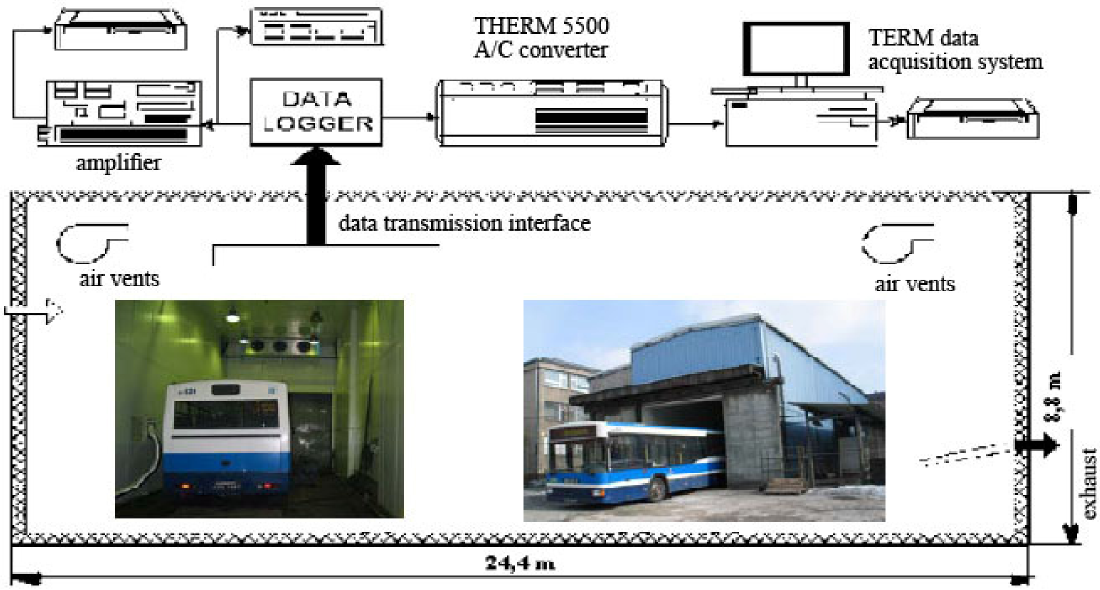

Fig. 8. The purpose of research in the low temperature chamber

Rys. 8. Stanowisko badawcze w komorze niskich temperatur

The purpose of research in the low temperature chamber (Figure 8) was to examine the possibility of start-up of the compression ignition engine fed by that fuel in the extremely low (-30 C) temperatures. Giant termoclimatic chamber is characterized by the following parameters:

- Range of stabilized temperature limit: 236...333K
- The accuracy of temperature stabilization on the selected level: ± 1 deg
- The range of humidity: semi-automatic control
- Range of air movement speed in the chamber: 0÷3 m/s

A scheduled urban bus powered by Man engine, characterized by parameters presented in Tab.4, was used for researches. Base Diesel fuel was replaced by Bioxdiesel, and the engine was equipped with sensors recording temperature. The cooling of engines in the termoclimatic chamber was carried out in accordance with the graphs shown in Figure 9.

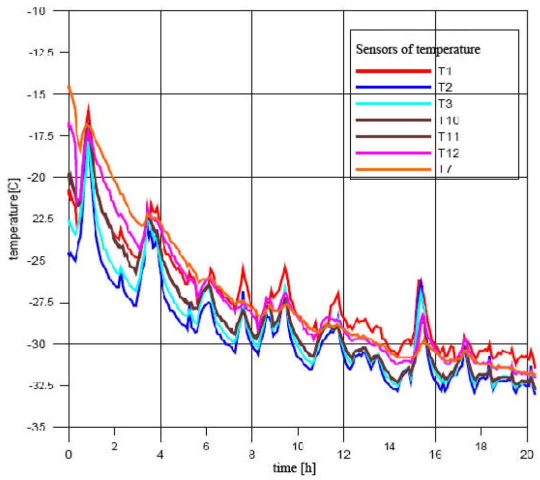

Fig. 9. The cooling in the termoclimatic chamber

Rys. 9. Schładzanie w komorze termoklimatycznej

After 24 hours of cooling of the bus, engine and the fuel, the starting process of the engine started. Fig.10 presents the increase of the temperature inside the engine due to the ignition in the first cylinders.

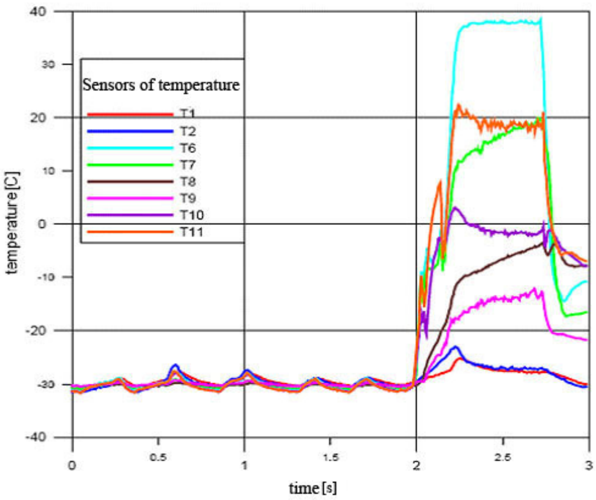

Fig. 10. Temperature during starting the engine
Rys. 10. Przebiegi temperatury podczas uruchomienia silnika

The obtained results prove very favorable low temperature properties of the fuel.

The experts researches included the observation of buses fed by fuel with biocomponents in the real world operating conditions.

The obtained results confirmed the research hypothesis that a comparable operating characteristics of vehicles powered by experimental fuel and standard fuel in terms of acceleration of vehicles, fuel consumption and reliability of operation**.**

4. Conclusions

Researches of Bioxdiesel with different contents of biocomponents revealed:
- Reduction of CO, HC in the range of 40 ... 80%, compared to the same engines fed by Diesiel;
- NOx emissions remained at approximately the same level (much lower values at low engine loads, and comparable values for the emission of high engine load);
- The value of smokiness of exhaust gases decreased by 50% compared to fueled by Diesel;
- The fuel is characterized by better liquid properties than Diesel, meeting the liquid standards set out in the directives of the U.S. and Europe, which contributes positively to the sustainability and reliability of engines;
- The fuel has also significantly better low temperature properties than Diesel and pure plant biofuels, what is important during winter operation;
- Mixture of aliphatic hydrocarbons with higher fatty acids alkyl esters and anhydrous ethanol is much less hydrophilic than the same mixture of hydrocarbons with anhydrous ethanol (in similar proportions), which has significant operational and logistic importance;
- Ethyl biocomponents stand out as a renewable (manufacture possible only with the agricultural products), biodegradable (98% biodegradability in soil and water within 21 days) and significantly less toxic than traditional Diesel.

Nomenclature/*Skróty i oznaczenia*

FAEE Fatty acids ethyl esters/*estry etylowe kwasów tłuszczowych*
REE Rapeseed oil ethyl esters /*estry etylowe kwasów tłuszczowych oleju rzepakowego*
EtOH Dehydrated ethanol/*odwodniony etanol*
Diesel, ON Diesel/*olej napędowy*
RO Raw oil/*surowy olej*
Bioxdiesel Bioxdiesel/*paliwo trójskładnikowe*

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