



SELECTED THERMAL AND RHEOLOGIC PARAMETERS OF LIQUID FUELS

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Abstract

This article deals with thermal and rheologic properties of selected liquid fuels (diesel with different content of RME – Rapeseed Methyl Esters). Fuel samples had RME content 3 %, 7 %, 10 %, 15 %, 20 %. There were measured basic thermophysical parameters as: thermal conductivity, thermal diffusivity, volume specific heat and effusivity. Thermal conductivity and thermal diffusivity of samples were measured by two different transient method – Hot wire (HW) method and Dynamic plane source (DPS) method. The values of volume specific heat and effusivity were calculated from obtained experimental results. All results were statistically processed. Rheologic parameter – dynamic viscosity was measured during heating process in temperature range (20 - 80) °C. For dynamic viscosity detection was used digital rotational viscometer DV 2T. For every dependency were obtained decreasing exponential relations with high coefficients of determination. The results of physical properties measurement showed on significant influence of RME concentration in diesel.

Key words: thermophysical parameter, viscosity, diesel, method, component.

INTRODUCTION

The main advantages of biofuels are that these fuels are nontoxic, biodegradable and renewable with potential to reduce engine exhaust emissions. In Europe is one of the most important biofuel FAME – Fatty Acid Methyl Esters manufactured mainly as Rapeseed Methyl Esters – RME. RME is added to regular diesel fuels in amount of up to 7 % (MERKISZ ET AL., 2016). For biofuels quality determination is necessary to know basic chemical and physical parameters. From physical parameters are very important rheologic parameters and thermal parameters. These parameters could be supplemented with others physical parameters. Methods and results of direct thermal properties measurements of biofuels are presented by authors SNOWSTORM ET AL. (2011), MACHADO ET AL. (2012).

MATERIALS AND METHODS

In modern physical research are often used dynamic methods of measurements, which are quicker than static methods. By using dynamic methods we can get characteristics of material in the short time. This fact is very important for the practice. In this part are defined measured parameters and there are described theoretical basics from thermal and rheology measurement methods which were used for physical parameters detection.

Thermal conductivity λ is the property of a material which relates its ability to conduct heat. Thermal conductivity is defined as the quantity of heat transmitted

YAMANE ET AL. (2001), VOZÁROVÁ ET AL. (2015) presented general oil, biooil, fuel and biofuel characteristics and their influence on thermal and rheologic properties. Selected mechanical properties of biofuels were examined by KUBÍK AND KAŽIMÍROVÁ (2015) and rheologic properties as kinematic and dynamic viscosity were measured by TRÁVNÍČEK ET AL. (2013). Temperature dependences of density and kinematic viscosity for petrol, bioethanol and their blends were measured by KUMBÁR AND DOSTÁL (2014).

This article presents selected physical properties of diesel with RME component in relation to conventional diesel. The aim of the research was to determine changes of selected physical properties with increasing content of RME in diesel.

through a unit surface to a unit temperature gradient in unit time. This thermophysical parameter depends on many factors as: material structure, pressure, chemical content, temperature etc. Energy is transferred from the more energetic to the less energetic molecules when neighbouring molecules collide (SAHIN AND SUMNU, 2006). Thermal conductivity is mathematically defined by Fourier's law (1):

$$\vec{q} = -\lambda \left(\frac{\partial T}{\partial x} \vec{i} + \frac{\partial T}{\partial y} \vec{j} + \frac{\partial T}{\partial z} \vec{k} \right) \quad (1)$$



Where \vec{q} is the vector of heat flow and $\frac{\partial T}{\partial x}\vec{i} + \frac{\partial T}{\partial y}\vec{j} + \frac{\partial T}{\partial z}\vec{k}$ is temperature gradient. The unit of thermal conductivity is $\text{W}\cdot\text{m}^{-1}\cdot\text{K}^{-1}$.

Thermal diffusivity a characterizes the velocity of the temperature equalization in material during non-stationary processes. In numeric view it is equal to temperature change of unit volume caused by heat, which is transferred in unit time, by unit surface of coat with unit thickness, in unit temperature difference on her facing side. The unit of thermal diffusivity is $\text{m}^2\cdot\text{s}^{-1}$. Definition equation (2) for thermal diffusivity is:

$$a = \frac{\lambda}{c\rho} \quad (2)$$

Where λ is thermal conductivity and $c\rho$ is volume specific heat. The meaning of c is mass specific heat and ρ is density of material.

We could define effusivity of sample by equation (3).

$$e = \frac{\lambda}{\sqrt{a}} = \sqrt{\rho c \lambda} \quad (3)$$

The parameters in last equation were defined in the previous text.

Thermal parameters were measured by two transient methods HW and DPS method because of methods comparison. In literature HW method is preferred but in convenient arrangement of experimental apparatus it can be used DPS method.

The HW (Hot wire) method is a transient dynamic technique based on the measurement of the temperature rise of a linear heat source (hot wire) embedded in the tested material (ASSAEL ET AL., 2008; KADJO ET AL., 2008). For an infinitely long metallic wire (length/radius ratio $\gg 200$) heated at time $t > 0$ with a constant heat flux per length unit q and immersed in an infinite homogeneous medium (thermal conductivity and diffusivity: λ and a with uniform initial temperature, the temperature rise $\Delta T(t)$ of the wire is given by (4) (CARSLAW AND JAEGER, 1959):

$$\Delta T(t) = \frac{q}{4\pi\lambda} \ln \frac{4F_0}{C} \quad (4)$$

$C = e^\gamma = 1.781$ where γ is Euler's constant ($\gamma = 0.5772$) and F_0 the Fourier number defined by:

$$F_0 = \frac{at}{r_0^2} \quad (5)$$

Equation (4) is the analytical solution of an ideal thermal conductive model valid for $F_0 \gg 1$ and without convective transfers (WAKEHAM AND NAGASHIMA, 1991; TAVMAN, 1996). From this ideal

model and with known q values, the thermal conductivity can be calculated by (6):

$$\lambda = \frac{q}{4\pi} \left(\frac{dT}{d(\ln t)} \right)^{-1} \quad (6)$$

Where $dT/d(\ln t)$ is a numerical constant deduced from experimental data for t values which satisfy the condition $F_0 \gg 1$. For practical applications of the HW method, wire and material sample dimensions, among other ideal model hypothesis, are finite and the deviations from the ideal model have then to be evaluated. In fact, the $e(t)$ answer to the wire heating $\Delta T(t)$ resultant of the Joule effect due to an electrical current i is (7):

$$R(t) = R_0(1 + \beta_0(T(t) - T_0)) \quad (7)$$

where $R(t)$ – is the instantaneous electrical resistance of the wire, R_0 – is the resistance of the wire at the T_0 reference temperature, and β_0 the temperature coefficient of the wire at 22 °C. Taking into account (6) and (7), the thermal conductivity λ may be calculated as follows:

$$\lambda = \frac{qR_0\beta_0 i}{4\pi} \left(\frac{de(t)}{d(\ln t)} \right)^{-1} \quad (8)$$

where $de(t)/d(\ln t)$ is a numerical constant deduced from the experimental data and from the linear part of the $e(t) = f(\ln(t))$ curve.

The DPS (Dynamic Plane Source) method is based on using an ideal plane sensor. The plane sensor acts both as heat source and temperature detector. The plane source method is arranged for a one dimensional heat flow into a finite sample. The theory considers ideal experimental conditions – ideal heater (negligible thickness and mass), perfect thermal contact between PS sensor and the sample, zero thermal resistance between the sample and the material surrounding sample, zero heat losses from the lateral surfaces of the sample (KARAWACKI ET AL., 1992). If q is the total output of power per unit area dissipated by the heater, then the temperature increase as function of time is given by (9):

$$\Delta T(x,t) = 2 \frac{q\sqrt{at}}{\lambda} \text{ierfc} \left(\frac{x}{2\sqrt{at}} \right) \quad (9)$$

Where a - is thermal diffusivity, λ - is thermal conductivity of the sample and ierfc is the error function (BECK AND ARNOLD, 2003). The principle of method resides in fitting of the theoretical temperature function given by theoretical equation over the experimental points. In case of the best fit, both parameters λ and a can be determined. The method of fitting based on least-squares procedure was described in detail (KARAWACKI ET AL., 1992; MALINARIČ, 2004).



We could define effusivity of sample by equation (10).

$$e = \frac{\lambda}{\sqrt{a}} = \sqrt{\rho c \lambda} \quad (10)$$

From rheologic parameters was measured dynamic viscosity η . Dynamic viscosity is very important rheologic parameter of liquids which can be defined as the resistance of a fluid to flow. The unit of dynamic viscosity in SI units is Pa.s. Viscosity of the liquids usually decreases with increasing temperature. The difference in the effect of temperature on viscosity of fluids is related to the difference in their molecular structure (BIRD ET AL., 1960). The temperature effect on dynamic viscosity can be described by an Arrhenius type equation (11):

$$\eta = \eta_0 e^{-\frac{E_A}{RT}} \quad (11)$$

where η_0 is reference value of dynamic viscosity, E_A is activation energy, R is gas constant and T is absolute temperature (FIGURA AND TEIXEIRA, 2007). Measuring of dynamic viscosity was performed by digital viscosimeter Anton Paar DV 2P. Principle of measuring by rotational viscosimeter is based on dependency of sample resistance against the probe rotation. Probe with signification ULA0 was used in our measurements. The frequency of probe rotation was 120 rpm.

RESULTS AND DISCUSSION

Measured samples of diesel were with different RME content. The first sample was pure diesel and next measured samples had concentration of RME 3 %, 7 %, 10 %, 15 % and 20 %.

Results for thermal parameters measurements – there were measured parameters as thermal conductivity and thermal diffusivity at laboratory temperature 22 °C. Samples were stabilised 24 hours before measurement. All measured samples were stored in special bottles. For data reliability protection were realized series of one hundred measurements for every sample of diesel with RME and every thermal parameter was measured by HW and DPS method. Results presented in Tab. 1 were obtained as valued averages. For every series of measurements were calculated probable error and relative probable average error in %.

Thermal parameters measurements showed that increasing concentration of bio-components in the fuel had significant influence of all investigated physical parameters. For sample of pure diesel were detected by Hot wire method the smallest values of thermal

parameters. Thermal conductivity of pure diesel was $\lambda = (0.1472 \pm 0.0002) \text{ W.m}^{-1}.\text{K}^{-1}$ and thermal diffusivity of pure diesel was $a = (0.7897 \pm 0.0011) 10^{-7} \text{ m}^2.\text{s}^{-1}$. From basic thermal parameters and density of samples was calculated value of volume specific heat $c\rho = (0.1864 \pm 0.0004) 10^7 \text{ J.m}^{-3}.\text{K}^{-1}$ and effusivity $e = (5.2381 \pm 0.0099) 10^{-5} \text{ W.m}^{-2}.\text{K}^{-1}.\text{s}^{-0.5}$. The highest values of thermal parameters had sample of diesel with the addition of 20 % RME – thermal conductivity was $\lambda = (0.1725 \pm 0.0009) \text{ W.m}^{-1}.\text{K}^{-1}$, thermal diffusivity of the sample was $a = (0.8297 \pm 0.0007) 10^{-7} \text{ m}^2.\text{s}^{-1}$. Presented results are in good agreement with values presented in literature (GUIMARÃES ET AL., 2012). Thermal effusivity of sample was $e = (5.9886 \pm 0.0510) 10^{-5} \text{ W.m}^{-2}.\text{K}^{-1}.\text{s}^{-0.5}$ and the volume specific heat was $c\rho = (0.2079 \pm 0.0006) 10^7 \text{ J.m}^{-3}.\text{K}^{-1}$. Values of volume specific heat and effusivity for diesel samples with different RME content were not compared with results in the literature, because they had not been published yet.



Tab. 1. – Results of thermal parameters measurements by HW method for samples of diesel with different RME content

Sample	Thermal conductivity $W.m^{-1}.K^{-1}$	Thermal diffusivity $. 10^{-7} m^2.s^{-1}$	Volume specific heat $. 10^7 J.m^{-3}.K^{-1}$	Effusivity $. 10^{-5} W.m^{-2}.K^{-1}.s^{0.5}$
	Probable error			
	$W.m^{-1}.K^{-1}$	$. 10^{-7} m^2.s^{-1}$	$. 10^7 J.m^{-3}.K^{-1}$	$. 10^{-5} W.m^{-2}.K^{-1}.s^{0.5}$
	Relative probable error %			
Diesel	0.1472	0.7897	0.1864	5.2381
	± 0.0002	± 0.0011	± 0.0004	± 0.0099
	± 0.1600	± 0.1400	± 0.2300	± 0.1900
Diesel with 3 % RME	0.1526	0.8034	0.1899	5.3832
	± 0.0004	± 0.0005	± 0.0005	± 0.0140
	± 0.2700	± 0.0600	± 0.2500	± 0.2600
Diesel with 7 % RME	0.1581	0.8153	0.1939	5.5367
	± 0.0004	± 0.0008	± 0.0004	± 0.0110
	± 0.2300	± 0.1000	± 0.1900	± 0.2000
Diesel with 10 % RME	0.1620	0.8199	0.1977	5.6593
	± 0.0003	± 0.0003	± 0.0004	± 0.0120
	± 0.2000	± 0.0300	± 0.2200	± 0.2100
Diesel with 15 % RME	0.1662	0.8217	0.2022	5.7970
	± 0.0004	± 0.0004	± 0.0005	± 0.0140
	± 0.2400	± 0.0400	± 0.2300	± 0.2400
Diesel with 20 % RME	0.1716	0.8278	0.2073	5.9643
	± 0.0004	± 0.0005	± 0.0005	± 0.0140
	± 0.2400	± 0.0600	± 0.2300	± 0.2300

One of the main aims of the thermal parameters measurements was comparison of two different types of thermophysical parameters measurement methods. From results presented in Tab. 1 and 2 is evident, that relative probable error of thermal parameters measurement for Hot wire method was from ± 0.03 % to ± 0.27 % and the same relative probable errors for Dynamic plane source method were in range (± 0.06 % – ± 0.86 %). The results of two measurement methods comparison confirmed that for the liquid materials is more appropriate to use Hot wire method. This fact was presented in literature (RODER,

1981), but detected small differences between basic thermal parameters values showed that at appropriate arrangement of the measuring apparatus there can be used both thermophysical measurement methods. Results for rheologic parameter measurements - there was measured dynamic viscosity as one of the basic rheologic parameters. All samples were measured during heating process in the temperature range (20 – 80) °C. Every point in graphical dependencies on Fig. 1 was obtained as average from ten measured values for sample of diesel with different RME content.



Tab. 2. – Results of thermal parameters measurements by DPS method for samples of diesel with different RME content

Sample	Thermal conductivity $\text{W.m}^{-1}.\text{K}^{-1}$	Thermal diffusivity $. 10^{-7} \text{ m}^2.\text{s}^{-1}$	Volume specific heat $. 10^7 \text{ J.m}^{-3}.\text{K}^{-1}$	Effusivity $. 10^{-5} \text{ W.m}^{-2}.\text{K}^{-1}.\text{s}^{-0.5}$
	Probable error			
	$\text{W.m}^{-1}.\text{K}^{-1}$	$. 10^{-7} \text{ m}^2.\text{s}^{-1}$	$. 10^7 \text{ J.m}^{-3}.\text{K}^{-1}$	$. 10^{-5} \text{ W.m}^{-2}.\text{K}^{-1}.\text{s}^{-0.5}$
	Relative probable error %			
Diesel	0.1480	0.7902	0.1873	5.2650
	± 0.0005	± 0.0039	± 0.0011	± 0.0122
	± 0.3600	± 0.4900	± 0.5800	± 0.2300
Diesel with 3 % RME	0.1530	0.8045	0.1902	5.3945
	± 0.0007	± 0.0016	± 0.0009	± 0.0360
	± 0.4300	± 0.2000	± 0.4900	± 0.6700
Diesel with 7 % RME	0.1593	0.8170	0.1950	5.5735
	± 0.0006	± 0.0011	± 0.0010	± 0.0280
	± 0.3600	± 0.1300	± 0.5100	± 0.5020
Diesel with 10 % RME	0.1650	0.8208	0.201	5.7589
	± 0.0004	± 0.0005	± 0.0008	± 0.0340
	± 0.2500	± 0.0600	± 0.41	± 0.5900
Diesel with 15 % RME	0.1681	0.8226	0.2044	5.8617
	± 0.0007	± 0.0008	± 0.0008	± 0.0440
	± 0.4300	± 0.1000	± 0.37	± 0.7500
Diesel with 20 % RME	0.1725	0.8297	0.2079	5.9886
	± 0.0009	± 0.0007	± 0.0006	± 0.0510
	± 0.5100	± 0.0800	± 0.31	± 0.8600

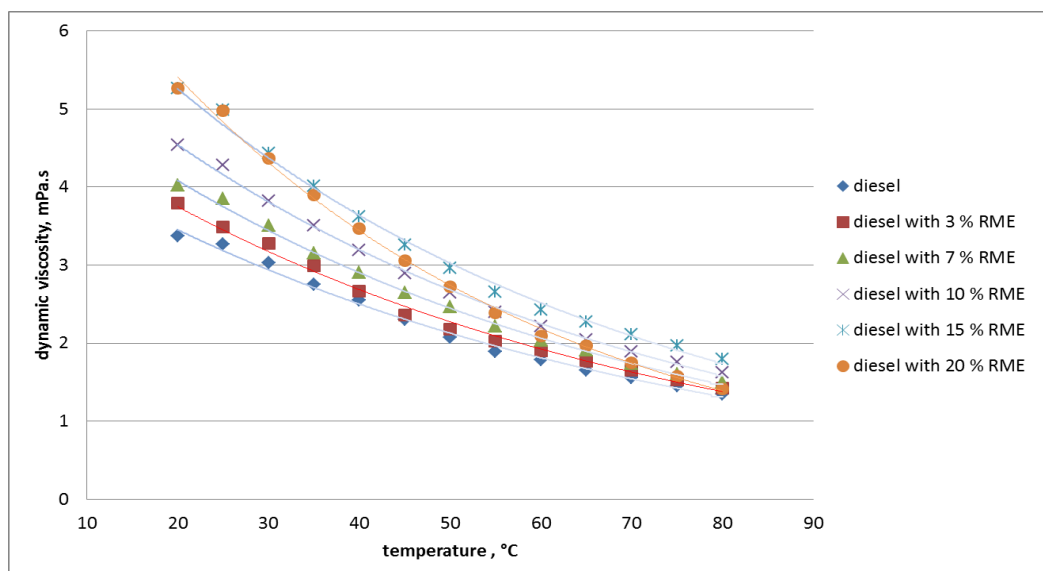


Fig. 1. – Temperature dependencies of dynamic viscosity for samples of diesel with different RME content

Measured values of dynamic viscosities for all measured samples are shown on Fig. 1. It is possible to observe from Fig. 1 that dynamic viscosity of diesel is

decreasing with increasing of temperature. The progress can be described by decreasing exponential function (12), which is in accordance with Arrhenius



equation (11) (MUNSON ET AL., 1994).

$$\eta = A e^{-B \left(\frac{t}{t_0}\right)} \quad (12)$$

Regression coefficients and coefficients of determination are shown in Tab. 3. On the base on presented

results is clear that coefficients of determination are in range (0.9932 – 0.9983).

Tab. 3. – Coefficients A, B of regression equation (12) and coefficients of determinations for relations of dynamic viscosity to the temperature

sample	Regression equation (12)		Coefficient of determination R^2 (-)
	Coefficients		
	A (mPa.s)	B (1)	
Diesel	4.7715	0.016	0.9944
Diesel with 3 % RME	5.2328	0.017	0.9932
Diesel with 7 % RME	5.7492	0.017	0.9983
Diesel with 10 % RME	6.4549	0.018	0.998
Diesel with 15 % RME	7.6053	0.018	0.9952
Diesel with 20 % RME	8.5145	0.023	0.9978

From Fig. 1 can be seen that dynamic viscosity of diesel with RME component is higher than pure diesel. This proportion should be caused by the RME content. In general, dynamic viscosity of diesel increasing with higher concentration of bio component

RME, which is evident from Fig. 1. There was detected difference only for diesel sample with 20 % RME content, but this change could be caused by too high proportion of bio-components.

CONCLUSIONS

Thermal parameters, such as temperature, thermal conductivity, thermal diffusivity, volume specific heat and effusivity characterize heat transfer ability of material, velocity of the temperature equalization and the intensity of the temperature changes in the material. Dynamic viscosity is very important rheologic parameter defined as the resistance of a fluid to flow. Accurate values of these properties are critical for practical design as well as theoretical studies and analysis, especially in the fields of heat transfer and thermal processing. The knowledge of thermophysical and rheologic properties of the materials are especially significant in the context of liquid bio-based materials or materials which obtained bio components. These materials are often thermally processed or they are exposed to natural changes of temperature conditions. The results obtained by the implementation of Hot wire method and Dynamic plane source method on the fuels samples (pure diesel and diesel with 3 %, 5 %, 7 %, 10 %, 15 % and 20 % content of RME) can be compared only with ranges of thermal parameters presented in the literature because of the fuels products variety. Usually are presented thermal parameters for diesel sample with 7 % content of bio-components,

because this concentration of bio-components is recommended by EU standards. Results of selected thermal parameters were presented by authors SADROLHOSSEINI ET AL. (2011) and GUIMARÃES ET AL. (2012), for thermal conductivity of fuels were determined values from range $\lambda = (0.143-0.175) \text{ W.m}^{-1}.\text{K}^{-1}$ and thermal diffusivity was in range $a = (0.784 - 0.835) 10^{-7} \text{ m}^2.\text{s}^{-1}$. Examined samples of fuels have thermal conductivity and thermal diffusivity from these ranges.

Rheological properties as dynamic viscosity, kinematic viscosity and fluidity were measured by many authors. Temperature dependencies of examined fuels dynamic viscosity had decreasing exponential shape for all measurements (Fig. 1). Coefficients of determination are very high (Tab. 3). Arrhenius equation (11) has decreasing exponential shape, so the dependency of dynamic viscosity on temperature can be described by it.

Nowadays we know many types of fuels and biofuels which differ in their composition and consistency and their chemical properties too, but for their quality evaluation is necessary to know their physical parameters.



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