doi: 10.17221/60/2015-RAE

Temperature effect on various biooils physical parameters

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Abstract

Božiková M., Hlaváč P., Híreš Ľ., Hlaváčová Z., Valach M., Vozárová V., Malínek M. (2017): Temperature effect on various biooils physical parameters. Res. Agr. Eng., 63: 145–151.

The article deals with thermal and rheological properties of two selected biooils (PL 64S – sample No. 1, and PL 04N – sample No. 2). For thermal parameters measurements, Hot wire method was used, for detection of rheological parameters rheometer Anton Paar MCR 102 was used and the density was measured by densimeter DM 40. For both biooil samples, two series of thermophysical parameters measurements were made. In the first series thermal conductivity and thermal diffusivity were measured at constant laboratory temperature. The second series was focused on identification of thermophysical parameters changes during temperature stabilisation. The parameters as dynamic viscosity, kinematic viscosity and density were measured in the temperature range (20–50°C). For samples with constant temperature basic statistical characteristics were calculated – standard deviation and probable error in %. For relations of thermal and rheological parameters to temperature nonlinear dependencies were obtained. The polynomial functions of the second degree were used for thermal parameters and exponential functions for rheological parameters.

Keywords: thermal parameters; rheological parameters; density; oil; measurement

The biooil is produced from bio-based raw materials using fast pyrolysis technology (Fortum 2015). The article deals with selected biooils physical properties as: thermal conductivity, thermal diffusivity, dynamic viscosity, kinematic viscosity, fluidity and density. The methods used and their theoretical principles are described below, as well as the results of measurements for two biooil samples – PL 64S – sample No. 1 and PL 04N – sample No. 2. Biooils have a very specific composition with variable chemical and physical properties according to the purpose of usage (Božiková, Hlaváč 2013a). Knowledge of physical properties of bio-based materials including biooils has a decisive importance for the realization of many technological processes, especially for monitoring of their quality (Božiková 2007; Hlaváč, 2009). According to some authors Božiková and Hlaváč, (2013b), Kertész et al. (2015), Kubík and Kažimírová (2015), the physical parameters (thermophysical, mechanical, electrical etc.) are significant characteristics that can be used for improving of the technological processes, mechanical and thermal processing of bio-based materials and their storage conditions. Dependencies between density, dynamic and kinematic viscosity and temperature were measured by Kumbár and Dostál (2014). Chemical and physical (thermogravimetric and mechanical) properties of bio-oils were examined by Lu et al. (2008) and Diebold (2002). The presented facts showed that the physical research applied on bio-based materials used in industry is very important because materials like biooils go through the thermal manipulation during processing to final products, storage and usage. The main aim of this contribution is to present the effect of temperature on various biooils physical parameters.

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MATERIAL AND METHODS

In the study, samples of biooils with innovated composition produced in Slovakia were examined. Sample No. 1 – PL 64S is a synthetic, rapidly biodegradable fluid based on sustainable raw materials. It is exceptionally suitable for applications in mobile and stationary hydraulic systems, for which a rapidly biodegradable hydraulic oil VDMA 24 568 HEES (standard for biodegradable hydraulic fluids) is recommended, especially if there is an environmental hazard to the ground, ground water or the surface waters due to leakage. Sample No. 2 – PL 04N is environmentally-friendly multigrade hydraulic oil based on rapeseed oil (HETG – mark for a group of hydraulic biooils according to ISO VG 46) for agricultural and construction machinery, meeting all requirements in accordance with VD MA 24568 HEES. With respect to its viscosity position, it belongs to engine oil SAE class 5W-20 and is recommended for hydraulic systems that require the use of SAE 5W, SAE 10W, SAE 15W, SAE 20W, SAE 20W-20 engine oils or hydraulic oils in accordance with ISO VG 32, VG 46, VG 68.

Thermal parameters measurement. Measuring of thermal parameters was performed by the simplified transient Hot wire (HW) method; it is a technique based on the measurement of 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 >> 200) heated at time $t > 0$ with a constant heat flux per length unit q and immersed in an infinite homogeneous medium, thermal conductivity λ and diffusivity a with uniform initial temperature, the temperature rise $\Delta T(t)$ of the wire is given by Eq. (1) (Carslaw, Jeager 1959):

$$\Delta T(t) = \frac{q}{4\pi\lambda}\ln\frac{4F_0}{C} \qquad (1)$$

with $C = e^{\gamma} = 1.781$

where: γ – Euler's constant (γ = 0.5772); F_0 – Fourier number defined by Eq. (2):

$$F_0 = \frac{a\,t}{r_0^2} \qquad (2)$$

Equation for is the analytical solution of an ideal thermal conductive model valid for $F_0 >> 1$ and r_0 – is a distance from the hot wire (Healy et al. 1976; Wakeham et al. 1991; Tavman 1996). From this ideal model and with known q values, the thermal conductivity can be calculated by Eq. (3):

$$\lambda = \frac{q}{4\pi}\left(\frac{dT}{d(\ln t)}\right)^{-1} \qquad (3)$$

where $dT/d(\ln t)$ is a numerical constant deduced from the experimental data for t values which satisfy the condition $F_0 >> 1$. Description and graphical model of dependency $dT/d(\ln t)$ is presented in publications of Healy et al. (1976); Wakeham et al. (1991); Tavman (1996). For practical applications of the HW method, wire and material sample dimensions, among other ideal model hypothesis, are finite and then the deviations from the ideal model have to be evaluated.

Thermal diffusivity a could be calculated from the following Eq. (4):

$$a = \frac{\lambda}{c\,\rho} \qquad (4)$$

where: c – specific heat; ρ – the density of material

Thermophysical parameters were measured 10 times for every temperature.

Rheological parameters measurement. Dynamic viscosity η is one of the basic rheological parameters defined by Eq. (5). It is the constant between tangential tension τ and gradient of layer velocity grad v (Severa et al. 2009):

$$\tau = \eta \text{ grad } v \qquad (5)$$

From known density and dynamic viscosity at the same temperature kinematic viscosity v can be calculated Eq. (6), because kinematic viscosity is the ratio of the dynamic viscosity η to the fluid density ρ at the same temperature (Severa et al. 2009):

$$\upsilon = \frac{\eta}{\rho} \qquad (6)$$

Reciprocal value of dynamic viscosity η is called fluidity φ and it can be defined by Eq. (7):

$$\varphi = \frac{1}{\eta} \qquad (7)$$

For determination of dynamic viscosity rotational rheometer Anton Paar MCR 102 was used. The MCR rheometer could be used for basic rheological parameters measurements and also for combination of rheological tests in rotational and oscillatory mode. The modularity of this system allows the integration of a wide range of temperature

doi: 10.17221/60/2015-RAE

devices and application of specific accessories. The temperature measurement range is from –150°C to +1,000°C, the maximum torque is 200 mN·m, min. torque rotation is 5 nN·m, angular velocity is from 10^{-8} rad/s to 314 rad/s, angular frequency is from the range 10^{-7}– 628 rad/s and normal force range is 0.01–50 N. In our case temperature range 20–50°C was used, angular velocity was constant 20.944 rad/s. Initial conditions of measurements were chosen according to the sample characteristics – biooils can be classed among non-Newtonian fluids, for low temperature ranges their behaviour is, however, almost Newtonian. The measurements of rheological parameters were performed 5 times for every sample.

Density measurements. The density of homogeneous material is defined by Eq. (8).

$$\rho = \frac{m}{V} \tag{8}$$

where: ρ – density of material (kg/m^3); m – total mass of material (kg); V – total volume of material (m^3)

It is one of the most important parameters of biooils that strongly depends on temperature and chemical composition of the sample. For detection of biooil samples density, densimeter Mettler Toledo DM 40 (Mattler Toledo, Switzerland) was used. This instrument has the measurement accuracy 10^{-3} g/cm^3. Densimeter DM 40 measures density, concentrations and other related values. It has an internal Peltier thermostat for automatic temperature control and therefore does not require external thermostatic bath circulator. Results are automatically converted into user-defined units. It contains also error detection, single-point adjustment of the entire temperature range and viscosity correction. Density of biooil samples was measured 10 times for every temperature.

All measured values were statistically processed and standard deviation in all cases was in a range 0.2–0.5 %.

RESULTS AND DISCUSSION

The biooil physical and chemical parameters were examined by many authors e.g. Diebold (2002), Conceicao et al. (2005), Wan Nik et al. (2005), Zhang et al. (2009), Guo et al. (2011) and Ren et al. (2014). They detected that biooils differ in its composition, consistency and its physical properties, too. However, the present research was focused on identification of other parameters which are necessary at defining of material's state. The results obtained by the implementation of thermophysical, rheological and density measurement methods on biooil samples could be compared with parameters presented in the literature by Wan Nik et al. (2005) and Lu et al. (2008).

Thermophysical measurements

In the first series of measurements both thermophysical parameters were measured at the laboratory temperature 20°C and the samples were thermally stabilised 24 hours before the measurements. In the second series of measurements, relations of thermal conductivity and thermal diffusivity to the temperature were analysed in the temperature range of 20–50°C. Results are shown in Figs 1a and 1b. The statistical evaluations of thermal conductivity and diffusivity graphical dependencies are presented in Table 1. It is evident from the presented results that all measured dependencies are nonlinear. Polynomial functions of the second degree with polynomial coefficients and coefficients of determination were obtained for both thermophysical parameters and are summarised in Table 1. In all cases, the coefficients of determination of the second degree were relatively high, not less than the relevant value 0.95.

Thermal parameters, such as thermal conductivity and thermal diffusivity, characterize heat transfer ability of material, velocity of the temperature equalization and the intensity of the temperature changes in the material. These facts known from the literature (Assael et al. 2008) are in accordance with the obtained results. For sample – biooil No. 1 higher values of thermal parameters were detected than for sample – biooil No. 2. Differences between thermal parameters are caused by different chemical composition which is in connection with the way of biooil usage. Biooil No. 1 is a synthetic oil with higher temperature range of usage – from –35°C to +90°C and with longer time of biological degradability – 90% after 21 days. On the other hand, biooil No. 2 has lower temperature range of usage – from –27°C to +70°C and with shorter time of biological degradability – 90% after 14 days. The degradability of biooils was examined by Ren et al. (2014).

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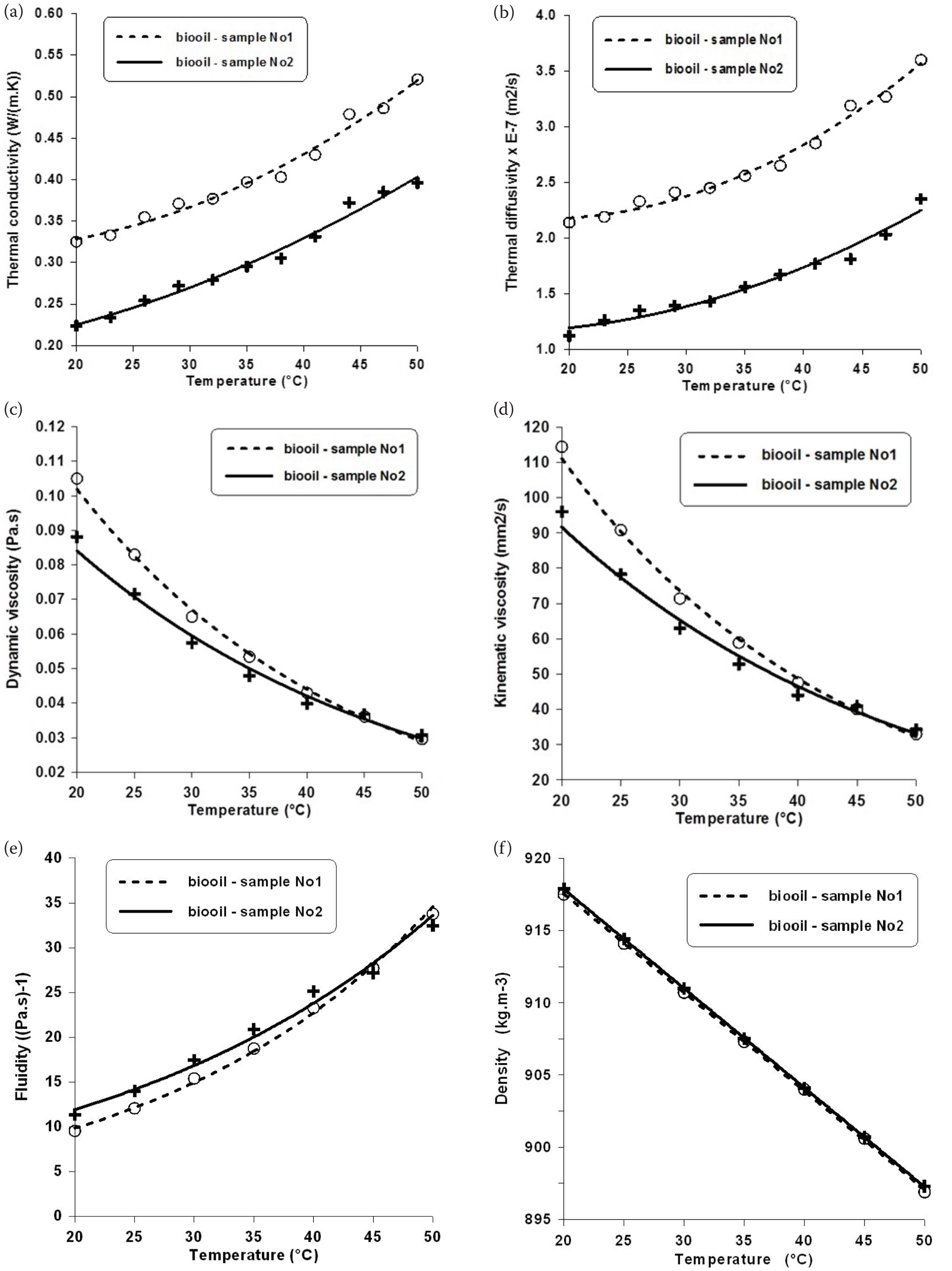

Fig. 1. Relations of thermal conductivity (a), thermal diffusivity (b), dynamic viscosity (c), kinematic viscosity (d), fluidity (e) and density (f) to the temperature

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Table 1. Measurement results for thermophysical parameters

Statistical evaluation of the measured values at 20°C					
Thermal conductivity			Thermal diffusivity		
Sample	No. 1	No. 2	Sample	No. 1	No. 2
Arithmetic average (W/(m.K)	0.325	0.224	tarithmetic average × 10^{-7} (m^2/s)	2.140	1.120
Standard deviation (W/(m.K)	± 0.056	± 0.054	standard deviation × 10^{-7} (m^2/s)	± 0.391	± 0.281
Probable error (W/(m.K)	± 0.012	± 0.005	probable error × 10^{-7} (m^2/s)	± 0.057	± 0.027
Relative probable error (%)	± 3.69	± 2.23	relative probable error (%)	± 2.66	± 2.41
Statistical evaluation of graphical dependencies for temperature range 20–50°C					
Thermal conductivity relations			Thermal diffusivity relations		
Type of function – Polynomial function of the 2nd degree					
Min. value (W/(m.K)	0.325	0.182	min. value; × 10^{-7} (m^2/s)	2.140	1.140
Max. value (W/(m.K)	0.486	0.224	max. value; × 10^{-7} (m^2/s)	3.270	2.040
Polynomial coefficients					
Degree 0	0.599	0.295	degree 0	5.869	1.044
Degree 1	0.035	0.224	degree 1	–0.399	0.053
Degree 2	0.599	0.385	degree 2	0.011	0.003
Coefficient of determination (R^2)					
Degree 0	0	0	degree 0	0	0
Degree 1	0.954	0.953	degree 1	0.935	0.976
Degree 2	0.976	0.988	degree 2	0.979	0.983

Rheological and density measurements

Rheological parameters and density were measured in the same temperature range as thermal parameters. For dynamic and kinematic viscosity exponential decreasing relations were obtained (Figs 1c and 1d) in the measured temperature range 20–50°C. On the basis of definition, the temperature dependence of fluidity can be described by exponential increasing function (Fig. 1e). It was found out that with increasing temperature the density of samples decreased linearly (Fig. 1f). Graphical relations shown in Figs 1c–1f can be characterized by regression Eqs (9–12):

$$\eta = A\,e^{-B\left(\frac{t}{t_0}\right)},\quad \nu = C\,e^{-D\left(\frac{t}{t_0}\right)},\quad \varphi = E\,e^{F\left(\frac{t}{t_0}\right)},\quad \rho = G - H\left(\frac{t}{t_0}\right) \qquad (9, 10, 11, 12)$$

where: *A, B, C, D, E, F, G, H* – constants dependent on material, its composition and ways of processing;

Table 2. Measurement results for rheological parameters and density – coefficients *A*, *B*, *C*, *D*, *E*, *F*, *G*, *H*, of regression Eqs (9–12) and R^2

	Sample	No. 1	No. 2		Sample	No. 1	No. 2
Dynamic viscosity	*A* (Pa·s)	0.23593	0.16814	Fluidity	*E* (1/(Pa·s))	4.23861	5.94744
	B (1)	0.04198	0.03465		*F* (1)	0.04198	0.03465
	R^2	0.99734	0.98676		R^2	0.99734	0.98676
Kinematic viscosity	*C* (mm^2/s)	253.228	180.483	Density	*G* (kg/m^3)	931.175	931.582
	D (1)	0.04121	0.03396		*H* (kg/m^3)	0.68214	0.68643
	R^2	0.99730	0.98607		R^2	0.99983	0.99998

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t – temperature (°C); t_0 = 1°C

The measured and calculated values of biooils rheological parameters confirmed differences between both samples. The biooil No.1 had higher values of dynamic and kinematic viscosity than the second sample, but the differences were higher at lower temperatures (20–35°C) and almost the same for higher temperature (43–50°C), which is in accordance with hydraulic biooil technical and operational requirements. Third analysed parameter – fluidity was higher for the second sample, which was explained in the theoretical part. For biooils density values in the whole temperature range no significant differences were observed. The coefficients of regression equations and coefficients of determination are presented in Table 2.

CONCLUSION

In general, the presented results show that the biooil quality cannot be described by one type of physical parameter because important changes could be observed in other types of physical parameters. In our case, the most significant changes were determined for thermophysical parameters. During processing, storage and usage of biooils go through the temperature manipulation, so another very important parameter is temperature. The physical parameters of oils are usually examined only at one temperature, but in practice, oils are used in different temperature ranges according to the way of usage. It is the main reason why it is important to identify complexes of physical parameters that can exactly determine the biooil quality.

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doi: 10.17221/60/2015-RAE

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Received for publication August 21, 2015
Accepted after corrections June 17, 2016