

## Selected physical properties of liquid biofuels

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### Abstract

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The goal of this study was the determination of basic physical properties such as density, calorific value and rheological properties of liquid biofuels. Biofuels on the base of bioethanol and rapeseed methyl ester were chosen. Following control samples were selected: diesel oil without admixture of methyl esters and commercially available diesel oils with small amount of methyl ester admixture (6.2 and 6.5%). Dynamic viscosities of individual samples were measured in the range from  $-10^{\circ}\text{C}$  to  $50^{\circ}\text{C}$ . Then dependence of shear rate on shear stress was measured at temperatures  $-10$ ,  $0$ ,  $20$  and  $40^{\circ}\text{C}$ . The most of samples showed the Newtonian behaviour. However, samples with high content of methyl esters or pure methyl esters showed thixotropy behaviour at the low temperature.

**Keywords:** rheology; thixotropy; density; methyl ester

Biofuels are referred to liquid, gas and solid fuels predominantly produced from the biomass. A variety of fuels such as ethanol, methanol, biodiesel, Fischer-Tropsch diesel, hydrogen and methane can be produced from biomass (DEMIRBAS 2008a).

Biofuels are very important because they can replace conventional petroleum fuels. In particular developing countries the biofuels are found as a key to reducing their reliance on import of foreign oil, lowering greenhouse gases (GHG) emissions and meeting rural development goals (FULTON et al. 2004; ARMBRUSTER, COYLE 2006; PICKETT et al. 2008). Between the year 1980 and 2005, worldwide production of biofuels increased by an order of magnitude from 4.4 to 50.1 billion litres (MURRAY et al. 2005; ARMBRUSTER, COYLE 2006).

REIJNDERS and HUIJBREGTS (2009) and DE VRIES et al. (2007) suggested that by 2050, up to  $300 \times 10^{18}$  J of liquid biofuels may be produced worldwide. An even higher estimate for liquid biofuel production by 2050 to  $455 \times 10^{18}$  J was predicted by MOREIRA (2006). Such amounts can in all probability cover demand for transport fuels in 2050, as the 2007 primary energy consumption for transport amounted to about  $100 \times 10^{18}$  J (DE LA RUE DU CAN, PRICE 2008). Use of transport fuels by means of transport was probably in the  $85\text{--}90 \times 10^{18}$  J range, with the remaining amount used for winning, refining and distribution (COLELLA et al. 2005; WINEBRAKE et al. 2007). The potential importance of biofuels in replacing fossil transport fuels is by now much stressed by the Brazilian government. In Brazil,

ethanol from sugar cane is currently a substantial transport biofuel. In 2004, its share in energy for road transport was near 14% and in 2007 about 20% (OECD 2008). In 2006, 70% of the new cars sold in Brazil were “flex cars”, able to run on either 100% ethanol or a fossil fuel-ethanol blend (QUADRELLI, PETERSON 2007).

Liquid biofuels are also an integral part of transport and agriculture in each member country of the European Union (EU). It is mainly a consequence of the European Parliament and Council Directive 2003/30/EC (2003). This directive orders to replace 20% of traditional fuel by alternative fuels in the transportation by 2020. From this reason EU member countries must ensure putting minimal percentage of biofuels and different renewable fuels on the market. For example in the Czech Republic the diesel is blended with biodiesel by 6% vol. and the petrol is blended with bioethanol by 4.1% vol. Similar situation is in all countries of the EU. Agriculture is one of the significant energy sources. That is why there is a tendency to start feeding engines with so-called renewable fuels (WAWRZOSEK, PIEKARSKI 2006). However, the influences of biofuels on food prices are being currently discussed. Nevertheless despite the debate about the meaningfulness of biofuels, a big influence of biofuels to transport and agricultural is expected in the entire world. Currently the various kinds of biofuels exist. For the proper functioning of combustion engines, pumping of these fuels or their storage, it is very important to know their basic physical properties. These are density, gross and net heat of combustion (calorific value) or rheological properties. The aim of the paper is to identify these basic physical properties of selected biofuels.

## MATERIAL AND METHODS

**Samples.** For the purpose of our experiment biofuels based on the bioethanol and on the rapeseed methyl ester from various Slovak refineries were used. Samples based on the rapeseed methyl ester were following: Biodiesel S and Biodiesel MB. These fuels are mixtures of rapeseed methyl ester and diesel oil. The next sample named MERO was pure rapeseed methyl ester. The sample E85 was the fuel based on bioethanol (the mixture of 85% of bioethanols and 15% of petrol). The last tested fuel was Sunflower Oil, which is sporadically used in agriculture and transport sector. The tested sam-

ples were the diesel blended with 6.5% of rapeseed methyl ester, named Diesel 6.5, the diesel blended with 6.2% of rapeseed methyl ester, named Diesel 6.2 and diesel without additives, used as control sample. The samples of traditional diesels was purchased at the petrol stations in Nitra, Slovak Republic.

**Determination of the density.** The density of individual samples was carried out in accordance with CSN EN ISO 3838 (2004). Crude petroleum and liquid or solid petroleum products – Determination of density or relative density – Capillary-stoppered pycnometer and graduated bicapillary pycnometer methods. For this purpose pycnometers with stopper and with capillary with volume of 50 ml and analytical balance Radwag AS 220/X (Radwag, Radom, Poland) with an accuracy of 0.0001 g were used. For each sample of liquid fuel the density value was performed in three repetitions.

**Determination of the calorific value.** Gross calorific value of the individual samples of liquid fuels was carried out in accordance with CSN 65 6169 (1986). For the experimental measurements calorimeter Parr 6400 (Parr, Moline, USA) was used. The samples were weighed on an analytical balance Radwag AS 220/X with an accuracy of 0.0001 g. For each sample of liquid fuels gross calorific value was performed in three replications.

**Viscosity and rheological behaviour.** Rheological measurement of the samples was performed by the use of rheometer Anton Paar MCR 102 (Anton Paar, Graz, Austria) with measuring geometry cone-plate. The diameter of cone was 50 mm and angle 1°. Three curves were evaluated: dependence of a dynamic viscosity  $\eta$  (Pa·s) on a temperature and dependence of a shear stress  $\tau$  (Pa) on a shear rate  $\dot{\gamma}$  ( $s^{-1}$ ) (rheogram). Generally dynamic viscosity is given by fundamental equation:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad (\text{Pa}\cdot\text{s}) \quad (1)$$

where:

$\tau$  – shear stress (Pa)

$\dot{\gamma}$  – shear rate ( $s^{-1}$ )

The dynamic viscosity was measured in a temperature range from  $-10^{\circ}\text{C}$  to  $50^{\circ}\text{C}$  and with the constant shear rate  $50\text{ s}^{-1}$ . The measurement of shear stress dependence on shear rate was performed in the range from  $0\text{ s}^{-1}$  to  $100\text{ s}^{-1}$  and at the temperatures  $-10, 0, 20$  and  $40^{\circ}\text{C}$ .

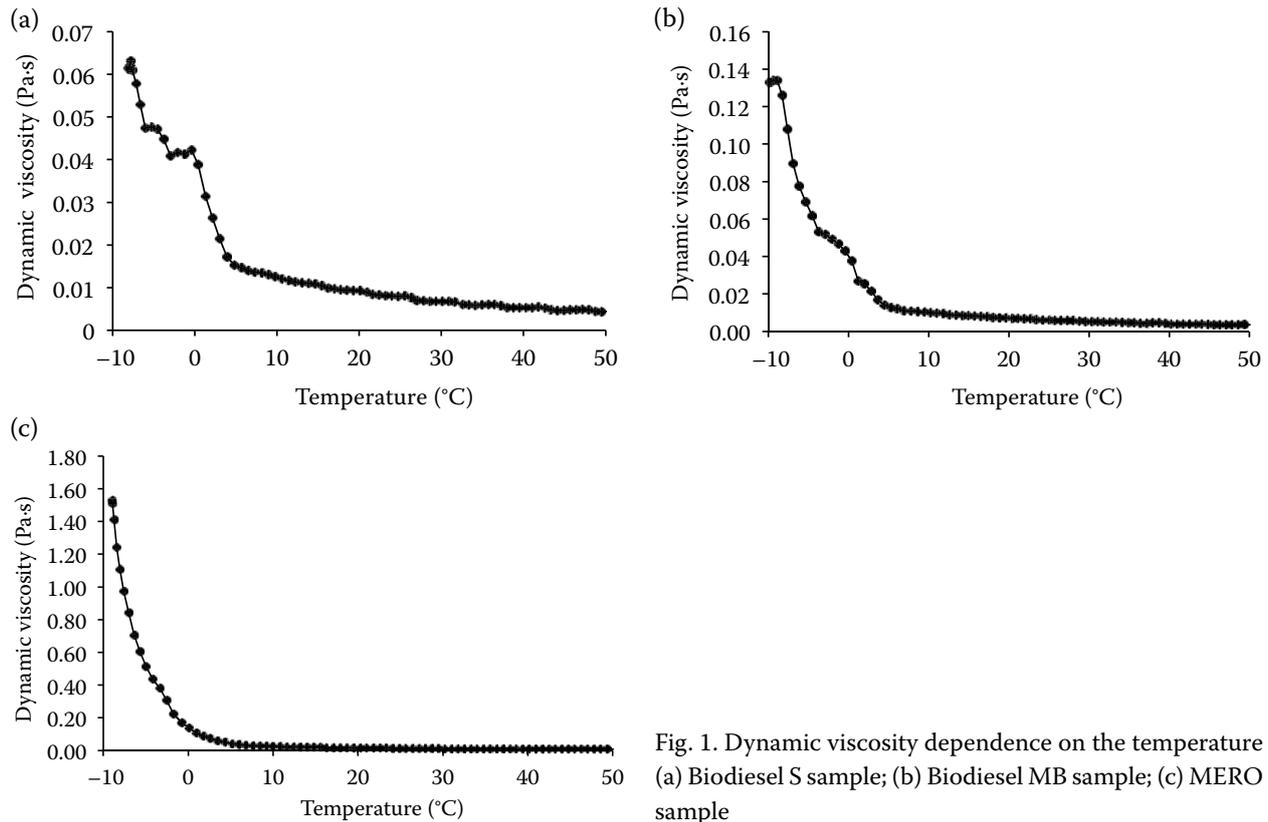


Fig. 1. Dynamic viscosity dependence on the temperature (a) Biodiesel S sample; (b) Biodiesel MB sample; (c) MERO sample

Various mathematical models are used for description of rheological properties of substances, where viscosity is the basic input parameter. These mathematical models include, e.g. Arrhenius model, Gaussian model, exponential model etc. (VÍTEŽ, SEVERA 2010). Arrhenius mathematical model is commonly used model, this model is given by equation:

$$\eta = \eta_0 \times e^{\frac{E_A}{RT}} \quad (\text{Pa}\cdot\text{s}) \quad (2)$$

where:

$\eta_0$  – constant, initial value of dynamic viscosity (Pa·s)

$E_A$  – activation energy (J)

$R$  – universal gas constant (J/K mol)

$T$  – thermodynamic temperature (K)

Arrhenius mathematical model was used for an evaluation of dependence of the dynamic viscosity  $\eta$  on the temperature and for an evaluation of the activation energy  $E_A$ . All measurements were performed in three repetitions. Subsequently arithmetic mean was evaluated from the measured data. The data were tested by the Grubb's test for remoteness values.

For evaluating of the Bingham fluid Bingham mathematical model was used, which is given by equation:

$$\tau = \tau_0 + \mu\dot{\gamma} \quad (\text{Pa}) \quad (3)$$

where:

$\tau$  – shear stress (Pa)

$\tau_0$  – yield stress (Pa)

$\dot{\gamma}$  – shear rate ( $\text{s}^{-1}$ )

$\mu$  – dynamic viscosity (Pa·s)

## RESULTS AND DISCUSSION

Values of calorific values and density at 20°C are shown in Table 1. In accordance with the expect-

Table 1. Calorific value and density of fuels

Samples	Calorific value (MJ/kg)	Density (20°C) (kg/m <sup>3</sup> )
Biodiesel S	39.88295	867.011
Biodiesel MB	39.4327	903.18
MERO	39.5732	904.555
E85	32.40785	771.325
Sunflower Oil	39.6085	941.179
Diesel 6.5	45.62265	855.784
Diesel 6.2	45.49	862.742
Diesel 0	45.81855	835.952

Table 2. Dynamic viscosity of fuels

Samples	Dynamic viscosity (Pa·s)			
	−10°C	10°C	30°C	50°C
Biodiesel S	0.0612	0.012	0.00682	0.00438
Biodiesel MB	0.124	0.0101	0.00528	0.00355
MERO	1.59	0.025	0.0117	0.00735
E85	0.00382	0.00236	0.00133	0.000707
Sunflower Oil	0.413	0.12	0.0483	0.024
Diesel 6.5	0.0107	0.00575	0.0029	0.00173
Diesel 6.2	0.00876	0.00477	0.00299	0.00178
Diesel 0	0.00635	0.00341	0.00232	0.00137

tations samples Diesel 6.5, Diesel 6.2 and Diesel 0 had the highest calorific values. These samples are fuels, which are commonly available at the petrol stations. On the contrary, the sample of E85 had the lowest calorific value. It is caused by the high content of bioethanol. Calorific value of bioethanol was in the range 26.8–29.6 MJ/kg (DODIC et al. 2009; STEPHENSON et al. 2010). Other measured data are also in accordance with authors of different papers (BLAŽEK, RÁBL 2006; DEMIRBAS 2008b; CENGİZ, SEHMUS 2009).

The dependence of dynamic viscosity on the temperature is shown in Fig. 1. They display only the dependence of biofuels with high content of rapeseed methyl ester and undiluted rapeseed methyl ester by diesel oil (the sample MERO). The reason is that these samples showed the sudden change of the curve about of temperature 0–5°C. This was caused by formation of crystals in methyl esters. In according to BOSHUI (2010) the size and the

amount of crystals in methyl esters are changed with temperature, at decreasing temperature the size and the amount of crystals grow up (BOSHUI et al. 2010). In this paper soybean methyl ester was used but generally physical properties of vegetable oil methyl esters are very similar (BLAŽEK, RÁBL

Table 3. Activation energies of fuels

Samples	$R^2$	Activation energy (kJ/mol)
Biodiesel S	0.924	32.03
Biodiesel MB	0.869	40.00
MERO	0.82	56.83
E85	0.96	18.88
Sunflower Oil	0.996	33.79
Diesel 6.5	0.989	20.24
Diesel 6.2	0.988	18.67
Diesel 0	0.987	17.6

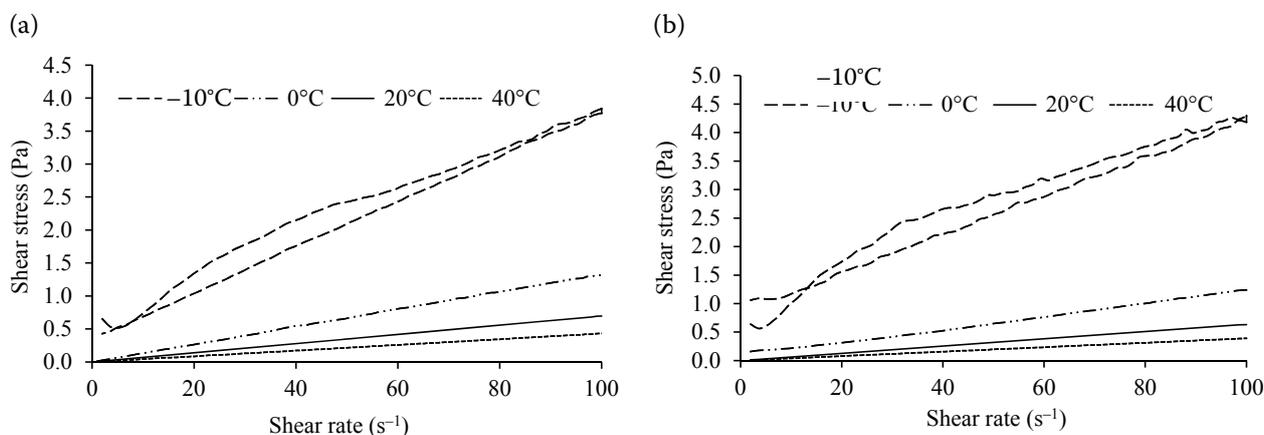


Fig. 2. Rheograms of (a) Biodiesel S and (b) Biodiesel MB sample at various temperatures

Table 4. Parameters of Bingham model at 0°C

Sample	$R^2$ (-)	Parameter $b$ (-)	Standard deviation* (-)	Yield stress (Pa)
MERO	0.9993	0.02594	0.02	0.57155

\*standard deviation is related to yield stress;  $b$  – infinite shear viscosity (Pa·s)

2006). For these reasons the change of rheological properties of biodiesels at low temperatures can be expected. As a consequence the loss of fluidity of biodiesels at low temperature may be observed.

Other researched fuels did not show sudden change of viscosity at low temperatures. It is due to the different structure of substances (samples E85 and Sunflower Oil) or very small or no content of methyl esters in fuels (samples Diesel 6.5, Diesel 6.2 and Diesel 0).

Dynamic viscosities of all the samples of fuels are shown in Table 2. The sample E85 showed the lowest values of viscosity. The sample MERO showed the highest values and the biggest change of viscosity at decreasing temperature.

The dependence of the viscosity on the temperature of all fuels was subjected to further mathematical analysis. Arrhenius mathematical model was used for this analysis. This model is shown in equation (2). The logarithm of this equation is:

$$\ln \eta = \ln \eta_0 + \frac{E_A}{RT} \quad (4)$$

The activation energy  $E_A$  was performed by using this equation with use of regression analysis. Values of activation energies are shown in the Table 3.

Measuring of dependence of shear stress on shear rate proved that samples E85, Sunflower Oil, Diesel 6.5, Diesel 6.2 and Diesel 0 are Newtonian fluid at all measured temperatures (-10 to 40°C). The dif-

ferent situation was with samples of Biodiesel S, Biodiesel MB and MERO. Rheograms of these samples are shown in Figs 2 and 3. These samples with high content of rapeseed methyl ester or undiluted rapeseed methyl ester had thixotropic behaviour at temperature -10°C. These samples had the thixotropic behaviour approximately until -5°C. Then these samples started to behave as Newtonian liquid. However, the sample MERO is an exception. This sample behaves as the Bingham fluid around temperature 0°C. The Table 4 shows parameters of Bingham model of sample MERO. If the temperature is higher than 0°C, rheological behaviour of sample MERO is Newtonian. Calculated hysteresis area (HA) of samples with thixotropic behaviour was at -10°C with following results:

Biodiesel S: HA = 20.16 Pa/s·ml

Biodiesel MB: HA = 19.13 Pa/s·ml

MERO: HA = 1,440 Pa/s·ml

The most significant thixotropy therefore had the sample MERO. Similarly, the mixture of fuels and animal fats can have thixotropic behaviour (GOODRUM et al. 2003), because formations of crystals are also created at low temperatures in fats (BUNJES, WESTESEN 2001).

Rheograms of MERO are shown in Fig. 3. Fig. 3a shows a step increase in shear stress at temperature -10°C. Shear stress is about 30 Pa at low shear rate. However in initial shear rate the shear stress reached up 1,200 Pa, if measuring was carried with

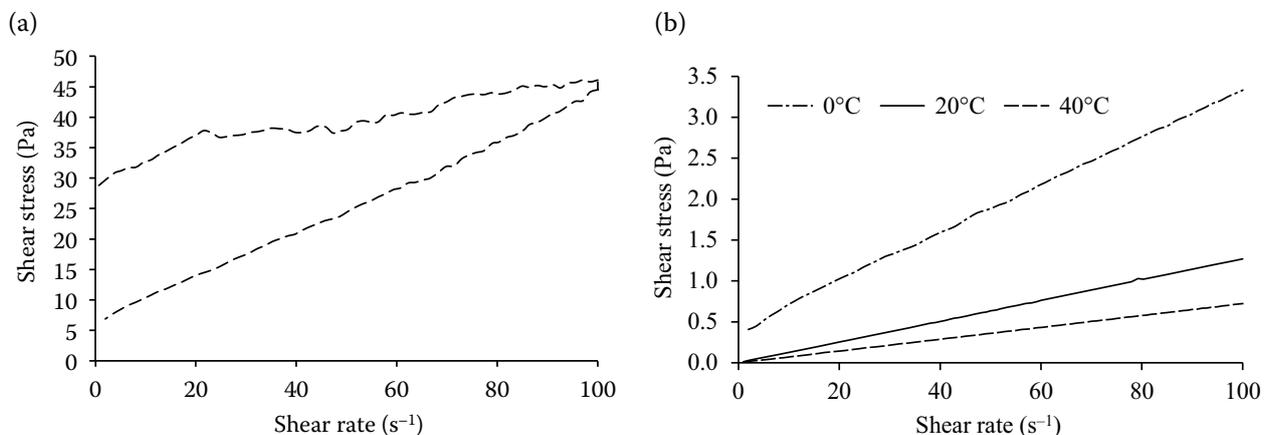


Fig. 3. Rheograms of MERO sample at (a) -10°C and (b) at various temperatures

10 min delay. Nevertheless during short time the strong structure of crystals is destroyed and curve of rheogram is very similar like in the previous case.

## CONCLUSIONS

Detailed information about physical properties of biofuels can improve efficiency of their utilization in the transportation. Above all, rheological properties of biofuels are branch, which is not explored very much. This is particularly case of rheological behaviour of biofuels with high content of rapeseed methyl ester or pure rapeseed methyl ester. The proof can be that a very small amount of papers deals with this theme. All tested fuels showed Newtonian behaviour. Only samples of Biodiesel B, Biodiesel MB and MERO had non-Newtonian behaviour at low temperature. This phenomenon is very distinct at sample MERO, which is pure rapeseed methyl ester. This behaviour is given by formation of crystal at low temperature, which changed rheological properties of the tested samples. Viscosity of the tested samples was lower during testing with constant shear rate. For these reasons the samples of Biodiesel B, Biodiesel MB and MERO were evaluated as thixotropy fluid at 10°C. However, crystals gradually melted at higher temperature and these fluids gradually started to behave as Newtonian fluid. The sample MERO is the exception. During increasing temperature this fluid behave as Bingham fluid approximately at 0°C and when the temperature is higher, the sample started behave as Newtonian fluid.

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