ACTA UNIVERSITATIS AGRICULTURAE ET SILVICULTURAE MENDELIANAE BRUNENSIS

Volume LVIII 8 Number 5, 2010

DIFFERENCES IN RHEOLOGICAL PROFILE OF DIESEL AND BIODIESEL FUEL

J. Čupera, P. Sedlák, P. Karafiát

Received: August 18, 2010

Abstract

ČUPERA, J., SEDLÁK, P., KARAFIÁT, P.: *Differences in rheological profile of regular diesel and bio-diesel fuel.* Acta univ. agric. et silvic. Mendel. Brun., 2010, LVIII, No. 5, pp. 67–74

Biodiesel represents a promising alternative to regular fossil diesel. Fuel viscosity markedly influences injection, spraying and combustion, viscosity is thus critical factor to be evaluated and monitored. This work is focused on quantifying the differences in temperature dependent kinematic viscosity regular diesel fuel and B30 biodiesel fuel. The samples were assumed to be Newtonian fluids. Viscosity was measured on a digital rotary viscometer in a range of 0 to 80 °C. More significant difference between minimum and maximum values was found in case of diesel fuel in comparison with biodiesel fuel. Temperature dependence of both fuels was modeled using several mathematical models – polynomial, power and Gaussian equation. The Gaussian fit offers the best match between experimental and computed data. Description of viscosity behavior of fuels is critically important, e.g. when considering or calculating running efficiency and performance of combustion engines. The models proposed in this work may be used as a tool for precise prediction of rheological behavior of diesel-type fuels.

diesel fuel, biodiesel, kinematic viscosity, modeling

Diesel fuel viscosity has a significant impact on how well fuel (either regular or biodiesel) burns. As viscosity increases, fuel molecules cluster together. The molecules on the outside of the cluster mix well with oxygen during combustion and burn well. The molecules on the inside of the cluster do not mix as well and do not burn completely. Knowledge of fuel viscosity is important for several reasons, as it determines the temperature for handling, the size of the centrifuges and the temperature at which the fuel is injected into the engine. It is well known that as the temperature of the fuel is increased, the viscosity is reduced, but differences between individual blends or e.g. regular and biodiesel can be expected. Some fuel suppliers publish temperature/viscosity charts which are based on the average data of a large number of samples. However, estimations from the charts cannot be regarded as precise since the exact relationship depends on the source and composition of the fuel. The viscosity usually quoted is the kinematic viscosity expressed in centiStokes (cSt) at some reference temperature. Although ISO 8217 has a reference temperature of 100 °C, it is anticipated that this will be changed to 50 °C at the next revision. This is a value widely used throughout the industry. A few extra degrees of preheating can often make a fuel suitable for injection equipment. Because of the viscosity/temperature relationship, a few degrees change could make a big difference to the injection viscosity. In practical terms, this means that if the actual fuel viscosity is greater than that ordered, it is likely that the fuel heater can accommodate this.

Biodiesel refers to a vegetable oil or animal fat-based diesel fuel consisting of long-chain alkyl (methyl, propyl or ethyl) esters. Biodiesel is typically made by chemically reacting lipids (e.g., vegetable oil, animal fat (tallow)) with an alcohol. Biodiesel is meant to be used in standard diesel engines and is thus distinct from the vegetable and waste oils used to fuel converted diesel engines. Biodiesel can be used alone, or blended with petrodiesel.

Historically, transesterification of a vegetable oil was conducted as early as 1853 by scientists E. Duffy and J. Patrick, many years before the first diesel engine became functional. Rudolf Diesel's prime model, a single 3 m iron cylinder with a flywheel at its base, ran on its own power for the first time in Augsburg, Germany, on August 10, 1893 running on nothing but peanut oil.

Despite the widespread use of fossil petroleum-derived diesel fuels, interest in vegetable oils as fuels for internal combustion engines was reported in several countries during the 1920s and 1930s and later during World War II. Belgium, France, Italy, the United Kingdom, Portugal, Germany, Brazil, Argentina, Japan and China were reported to have tested and used vegetable oils as diesel fuels during this time. Throughout the 1990s, plants were opened in many European countries, including the Czech Republic, Germany and Sweden. France launched local production of biodiesel fuel (referred to as *diester*) from rapeseed oil, which is mixed into regular diesel fuel at a level of 5%, and into the diesel fuel used by some captive fleets (e.g. public transportation) at a level of 30%. In 2009, ASTM published new Biodiesel Blend Specifications Standards (ASTM D6751).

Blends of biodiesel and conventional hydrocarbon-based diesel are products most commonly distributed for use in the retail diesel fuel marketplace. Much of the world uses a system known as the "B" factor to state the amount of biodiesel in any fuel mix: fuel containing (100% biodiesel is referred to as B100, while 30% biodiesel is labeled B30, 20% biodiesel is labeled B20, 5% biodiesel is labeled B5, 2% biodiesel is labeled B2).

Blends of 20 percent biodiesel with 80 percent petroleum diesel (B20) can generally be used in unmodified diesel engines. Biodiesel can also be used in its pure form (B100), but may require certain engine modifications to avoid maintenance and performance problems. New ways and strategies of blending are broadly discussed e.g. in Joshi *et al.* (2010). But the biodiesel's viscosity depends also on the other factors such as storing conditions (Tasyürek *et al.*, 2010)

Although fuel can be ordered to one of the grades in ISO 8217, frequently on delivery, only the viscosity grade is stated. For example IF 180 – this means that the viscosity is a maximum of 180 cSt at 50 °C. The majority of engine installations are fitted with fuel viscosity controllers so it is not normally necessary to estimate the injection temperature. Typically, a fuel with a viscosity up to 15–20% above that ordered can still be successfully used in the fuel treatment plant and engines. If the centrifuge is only marginally-sized, the slight increase in viscosity will reduce its performance. This may be overcome, if the piping configuration permits, by operating two purifiers in parallel with a clarifier in series.

There are several different methods for measuring fuel's viscosity. Except traditional methods (such us capillary, falling ball, rotary etc) – in detail described in Spearot (1989), Dawson (2000), or Troyer (2002), there are new approaches described eg. in Albertson *et al.* (2008). Biodiesel's kinematic viscosity and its influence on different operational characteristics are discussed and analyzed in Rahimi et al (2009) or Bhale *et al.* (2009). Fuel quality and its characteristics consequently affect the whole traction system and its performance (Chalupa, 2005; Chalupa *et al.* 2007).

This study is focused on analyzing the problem of temperature dependent kinematic viscosity of regular diesel fuel and biodiesel and quantification of differences in their behavior. This knowledge, as well as created mathematical models could improve understanding and description of processes running in the combustion engines.

MATERIAL AND METHODS

Fuel samples

Two different fuel samples were analyzed:

- regular diesel fuel (4,5% RME – requested by law)
- B30 biodiesel fuel (30% RME + 70% diesel fuel).

Prior to viscosity measurement, the samples were cooled to below zero temperatures. According to general assumption, the fuels were supposed to be Newtonian liquids (Li *et al.*, 2006), thus no pre–treatment or pre–shear was performed. All tested samples were new (fresh) fuels.

Viscosity measurement

A typical sampling procedure was applied for sample preparation. The adequate volume (200 ml) of fluid fuel was put into the apparatus cuvette without previous heavy mixing or any other kind of preparation.

There are several methods to measure kinematic viscosity of fluid or semi fluid materials and different geometries may be utilized: concentric cylinders, cone and plate, and parallel plates. Later discussed data were obtained from measurements performed on laboratory digital viscometer Anton Paar DV–3 P (Austria), which is designed to measure dynamic or kinematic viscosity (η, ν), shear stress (τ), and shear rate (). The DV–3 P is a rotational viscometer, based on measuring the torque of a spindle rotating in the sample at a given speed. Shear stress is expressed in [g/(cm.s^2)], shear rate in [1/s], kinematic viscosity in [mm^2/s], and speed of spindle in revolutions per minute [rpm]. The experiments have been performed with use of R3 spindle. Due to the parallel cylinder geometry shear stress, except other values, can be determined. Kinematic Viscosity is the ratio of absolute or dynamic viscosity to density – a quantity in which no force is involved. Kinematic viscosity can be obtained by dividing the absolute viscosity of a fluid with it's mass density

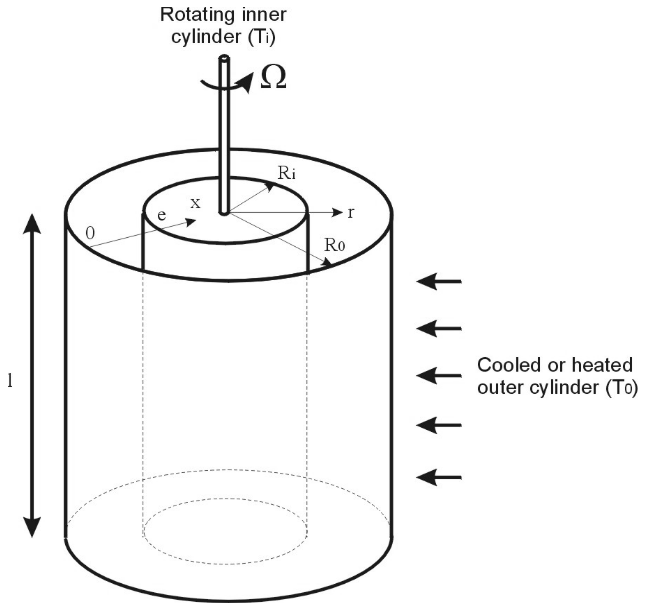
$$\nu = \frac{\eta}{\rho}, \qquad (1)$$

where

ν .... *kinematic viscosity (mm^2/s)*

η .... absolute or dynamic viscosity (mPa.s.)

ρ .... *density (kg/m^3).*



1: *Schematic of the measuring geometry (reworked version of the figure published in Severa and Los (2008)*

In the SI–system the theoretical unit is m^2.s or commonly used Stoke (St). Schematic of the measuring geometry is shown in Fig. 1.

The viscosity data were obtained for temperature ranging from 0 °C to 80 °C.

Density measurement

Fuel's density was determined using laboratory Mohr's balance (with calibrated accuracy 0.5 kg/m^3). The measurements were performed in the temperature ranging from 20 °C to 80 °C. The accuracy of selected measuring method is sufficient for given type of experiment.

Mathematical models

Software MATLAB® v. 7.1.0.246(R14) Service Pack 3, Curve fitting application (The MathWorks, Inc., USA) was used for creating of mathematical models. The suitability of the fitted models was evaluated by the determination coefficient (R^2) and the significance level ($p < 0.05$).

RESULTS AND DISCUSSION

High fuel viscosity can effect fuel atomisation upon injection into the cylinder and ultimately result in the formation of engine deposits. The viscosity of biodiesel is roughly one order of magnitude lower than the parent oil (Knothe *et al.*, 2004). Biodiesel has a higher viscosity than petroleum diesel as reflected in the relevant standards, which are 3.5–5.0 mm^2/s according to EN 14214 and 1.9–4.1 mm^2/s according to EN 590, respectively (Smith *et al.*, 2010).

Temperature dependent rheological behavior of two different fuels, diesel and biodiesel, was considered. Table I lists the values of diesel's kinematic viscosity at reference temperatures ranging from 0 °C to 80 °C, Table II the values of biodiesel's viscosity, Table III the values of fuel's density, and Table IV the values of biodiesel's density.

Increasing temperature influenced both, viscosity and density, as it was expected according to previously published works. E.g. Aksoy *et al.* (2010) comments this phenomenon with relation to different

I: *Kinematic viscosity of diesel fuel at selected temperatures*

Temperature (°C)	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**
ν (mm^2/s)	3.45	3.16	2.88	2.70	2.68	2.67	2.66	2.66	2.66

II: *Kinematic viscosity of biodiesel fuel at selected temperatures*

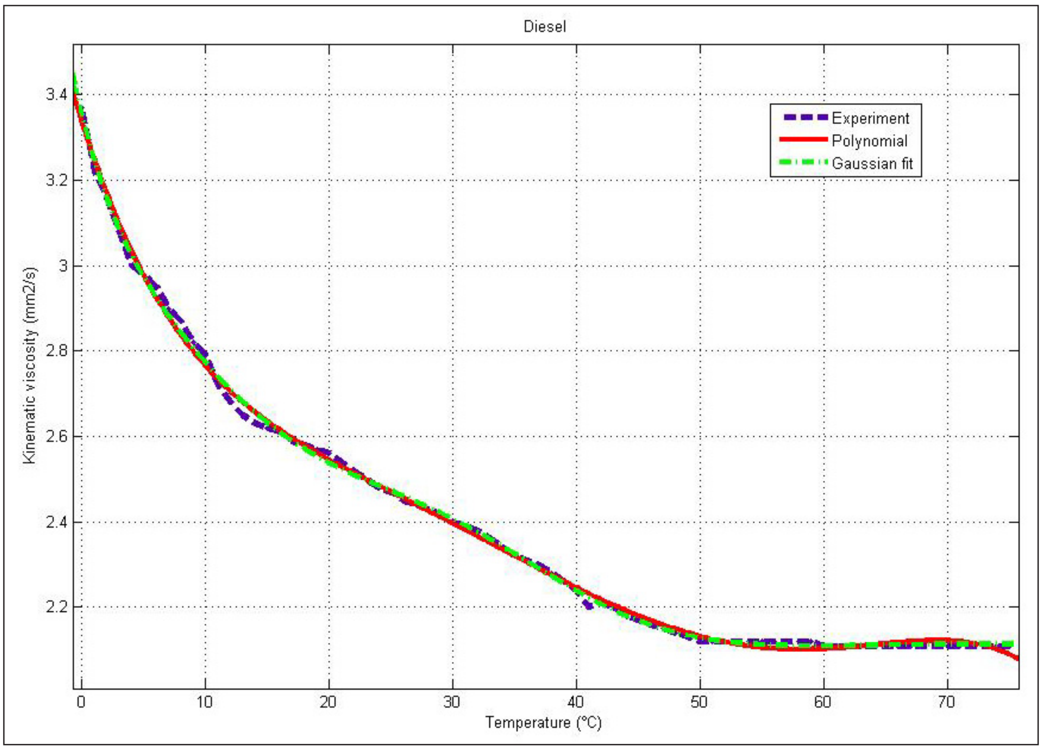
Temperature (°C)	**0**	**10**	**20**	**30**	**40**	**50**	**60**	**70**	**80**
ν (mm^2/s)	3.37	2.79	2.56	2.40	2.24	2.12	2.11	2.11	2.11

III: *Density of diesel fuel at selected temperatures*

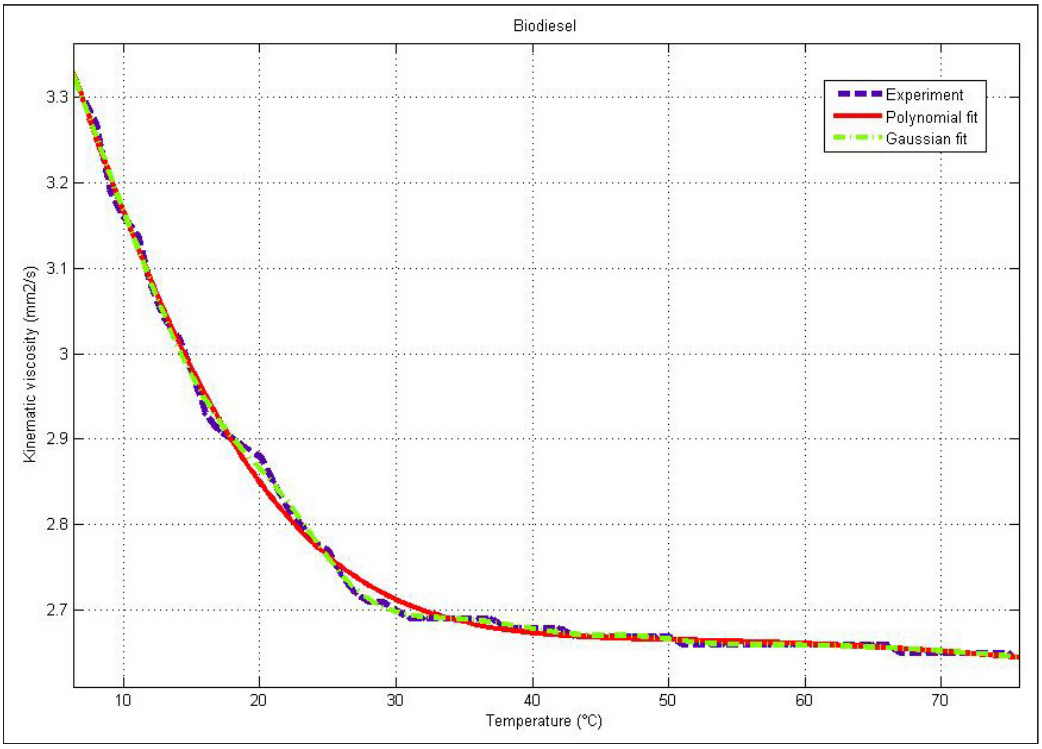
Temperature (°C)	**22.6**	**29.7**	**36**	**42.2**	**48.2**	**54.7**	**62.1**	**69.1**
Density (kg/m^3)	836	832	828	823	821	816	810	806

IV: *Density of biodiesel fuel at selected temperatures*

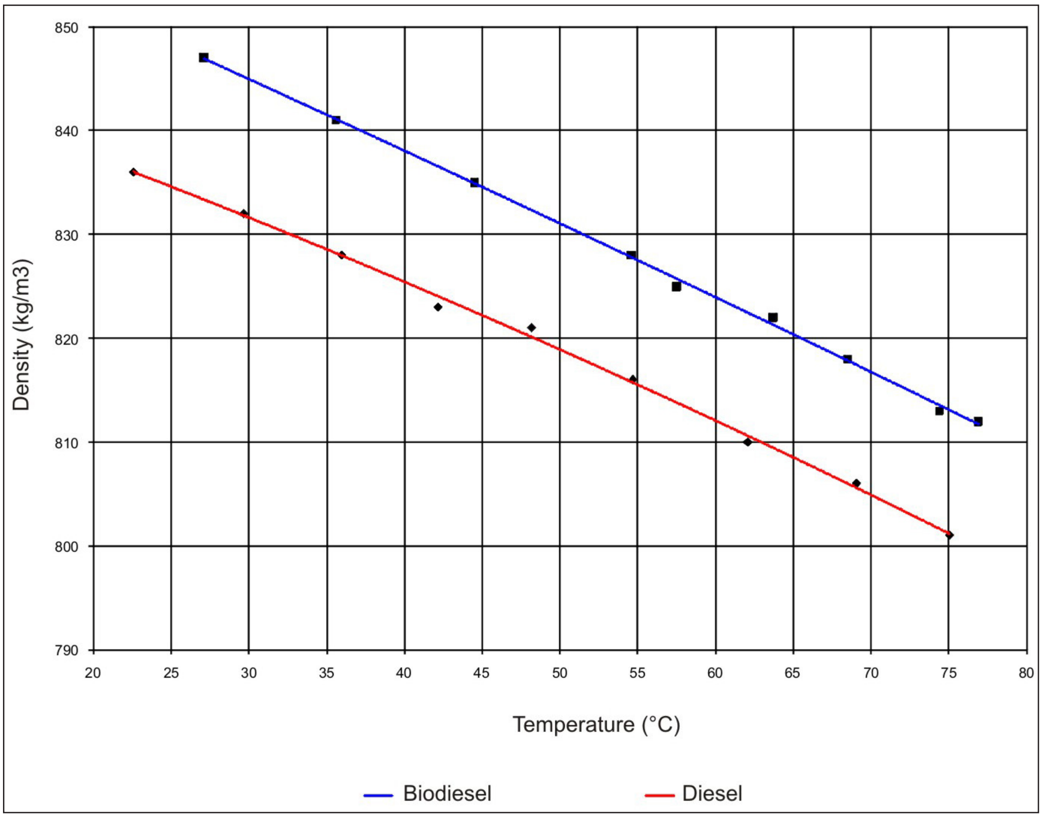
Temperature (°C)	**27.1**	**35.6**	**44.5**	**54.6**	**57.5**	**63.7**	**68.5**	**74.4**	**76.9**
Density (kg/m³)	847	841	835	828	825	822	818	813	812



2: *Temperature dependent kinematic viscosity of diesel fuel*



3: *Temperature dependent kinematic viscosity of biodiesel fuel*



4: *Temperature dependent density of tested fuels*

composition of biodiesel. The examples of viscosity-temperature dependences of diesel and biodiesel fuel are given in Fig. 2 and Fig. 3. The examples of density-temperature dependences are given in Fig. 4.

It can be seen in both cases, that the dependence is highly non-linear. This effect can be accounted to chemical processes proceeding in the fluid and consequential microstructure changes. For detailed explanation see e.g. Torres-Jimenes *et al.* (2010).

Unlike viscosity, the density temperature dependence is almost linear. This result is in accordance with findings reported by Baroutian et al (2010). Detailed description of microstructure phenomena and molecular thermodynamics can be found e.g. in Perdomo and Gil-Villegas (2010).

Fuel flow behavior and dependence of kinematic viscosity on temperature can be modeled with use of simple mathematical models. Modeling provides a means of representing a certain quantity of rheological data in terms of a simple mathematical expression. Many forms of the equations are possible and one master model, suitable for all situations, does not exist (Steffe, 1996).

One of the most popular equations used for description of temperature dependent viscosity of Newtonian fluids (including fuels) is an Arrhenius equation (Severa and Los, 2008). This equation involves the absolute temperature (T), the universal gas constant (R), and the energy of activation for viscosity (E_a):

$$\nu = f(T) = A \exp\left(\frac{E_a}{RT}\right). \tag{2}$$

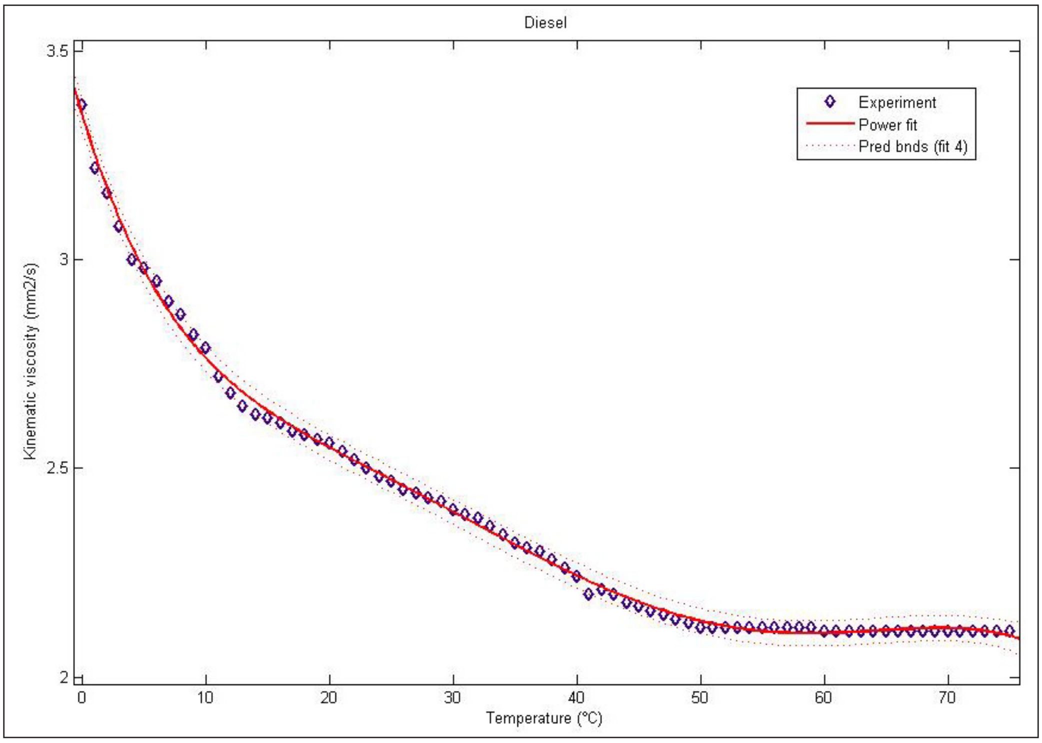
It is necessary to perform the experiments to get the values of E_a and A. More intensive changes of viscosity (as a function of temperature) are connected with higher E_a values (Friso and Bolcato, 2004).

Another approach is possible when considering an unknown viscosity (ν) at any temperature (T) and a reference viscosity (ν_r) at a reference temperature (T_r), the constant (A) may be eliminated and the resulting equation written in logarithmic form:

$$\ln\left(\frac{\nu}{\nu_r}\right) = \left(\frac{E_a}{R}\right) - \left(\frac{1}{T} - \frac{1}{T_r}\right). \tag{3}$$

This type of equation was successfully used for description of temperature dependent viscosity of different Newtonian fluids by many authors (Friso and Bolcato, 2004; Hlaváč, 2008; Hlaváč 2009). In case of presented research, use of this equation led to satisfying correlation between experimental and computed data $R^2 = 0.93$ and $R^2 = 0.94$ for diesel and biodiesel fuel, respectively.

Another effort was focused on fitting the experimental data with simple mathematical models, used and verified by other authors (Severa and Los, 2008; Severa et al, 2010b). Satisfying match between experimental and computed values was obtained using Gaussian, power or polynomial model. The examples of fits are displayed in Fig. 2 and Fig. 3,



5: *Experimental data and power model*

V: *Correlation coefficients between experimental and computed data received for different mathematical models*

		Diesel fuel		
Model	Arrhenius	Gaussian	Polynomial (5th degree)	Power
R²	0.93	0.99	0.97	0.97
		Biodiesel fuel		
Model	Arrhenius	Gaussian	Polynomial (5th degree)	Power
R²	0.94	0.98	0.97	0.98

and Fig 4. Figure 4 (with power model fit for diesel fuel) contains also prediction boundaries. The correlation coefficients for all tested models and equations are listed in Table V.

Above mentioned type of mathematical models is rather popular and it was successfully used for description of rheological behavior of different fluids, even those of biological nature (Severa *et al.*, 2008; Severa et al, 2010a; Severa *et al.*, 2010b, Vítěz and Severa, 2010).

Concerning both, diesel and biodiesel fuel, the best match and highest correlation coefficient was received for Gaussian model 0.99 and 0.98 respectively and the least satisfying result was achieved in case of Arrhenius model 0.93 and 0.94, respectively. In partial contradiction to this result, Baroutian *et al.* (2010) report the polynomial regression as the best-fit tool. But the differences in coefficient values are rather small indeed. It is worthy of noting that Arrhenius model is an equation with general use for different fluids while the other models (Gaussian, polynomial, power) and their coefficients are more specific to evaluated samples.

Knowledge of fuel's viscosity characteristics is of a great importance, especially when considering running efficiency and performance of combustion engines. Although there are rather complicated mathematical methods of modeling fuel viscosity behavior (described e.g. in Anand *et al.*, 2010), proposed simple mathematical models are accurate enough for precise description of diesel and biodiesel temperature-flow characteristics.

SUMMARY

The objective of this study was to measure and quantify, what are the differences in kinematic viscosity and generally in rheological profile of regular diesel fuel and biodiesel fuel. The study compares two commercially available samples: regular diesel fuel and B30 biodiesel fuel. The samples were assumed to act as Newtonian fluids, the flow curves were thus not constructed. The measurement was performed in the range of 0 to 80 °C. Kinematic viscosity (mm^2/s) was measured by the digital rotary viscometer with concentric cylinders geometry. As expected, kinematic viscosity of both materials was decreasing with increasing temperature. The bigger difference between minimum and maximum values (ranging from 2.2 to 3.4 mm^2/s) was found in case of diesel fuel in comparison with biodiesel fuel (ranging from 2.6 to 3.3 mm^2/s). Temperature dependence of both fuels was modeled using several mathematical models – Arrhenius, polynomial, power and Gaussian equation. The correlation coefficients ranged from 0.93 to 0.99 for Arrhenius equation and Gaussian fit of diesel fuel respectively. Generally, the Gaussian fit offers the best match between experimental and computed data. Temperature dependent density measurements were performed as an additional experiment for completing the information on fuel behavior. In accordance with literature data, this dependence can be characterized as linear. It can be said that precise description of viscosity behavior of fuels (especially in case of biodiesel since its short history of usage) as a function of temperature is critically important, e.g. when considering or calculating running efficiency and performance of combustion engines. The models proposed in this work can serve as a powerful tool for precise prediction of rheological behavior of diesel-type fuels.

SOUHRN

Rozdíly v reologickém profilu motorové nafty a bionafty B30

Práce je zaměřena na kvantifikaci a hodnocení rozdílů v reologickém chování a teplotní závislosti kinematické viskozity běžné motorové nafty a B30 bionafty. Nafta i bionafta byly považovány (na základě vlastních měření i údajů v literatuře) za newtonowskou kapalinu, tokové křivky tedy nebyly sestavovány. Kinematická viskozita byla sledována v rozmezí teplot 0–80 °C. Měření byla realizována na rotačním digitálním viskozimetru vybaveném adaptérem na měření kapalin s nízkou viskozitou. U obou testovaných kapalin došlo dle očekávání k poklesu viskozity s narůstající teplotou. Průběh poklesu byl výrazně nelineární. Větší rozdíl mezi maximálními a minimálními hodnotami viskozity byl zjištěn v případě nafty, kde se hodnoty pohybovaly v rozmezí 2,2 do 3,4 mm^2/s. U bionafty byl tento rozdíl nižší a viskozita klesla z původní hodnoty 3,3 mm^2/s na 2,6 mm^2/s. Teplotní závislost obou paliv byla modelována pomocí několika vztahů – Arrhéniovy rovnice, polynomu pátého stupně, mocninné a Gaussovy rovnice. Korelační koeficienty mezi experimentálními a vypočtenými daty se pohybovaly v rozmezí 0,93 (Arrhéniova rovnice) až 0,99 (Gaussova rovnice). Obecně platí, že nejlepších výsledků bylo dosaženo použitím Gaussovy rovnice. Jako doplňková informace byla zjišťována teplotně závislá měrná hmotnost obou paliv. V souladu s výsledky uváděnými v literatuře byla tato závislost shledána lineární. Přesný popis teplotně závislého tokového chování paliv (zvláště v případě bionafty) je kriticky důležitý, a to zvláště pro návrh a optimalizaci systému vstřikování. Modely navržené v této práci mohou být využity jako nástroje pro relativně přesné predikce tokového chování nafty a bionafty.

motorová nafta, bionafta, kinematická viskozita, modelování

Acknowledgement

This paper was prepared with the support of the COST 356 OC191 project “Transport in agriculture and its impact on the environment“, financed by the Ministry of Education, Youth, and Sports CR (MSMT) of the Czech Republic and with the support of IGA 2010 TP3/2010 project, financed by the Mendel University in Brno.

REFERENCES

ALBERTSON, W. C., STALEY, D. R., MC DONALD, M. M., PRYOR, B. K., 2008: Engine oil viscosity diagnostic system and methods, United States Patent 20080223114.

ASTM STANDARD, 2009: ASTM D6751 – 09a Standard Specification for Biodiesel Fuel Blend Stock (B100) for Middle Distillate Fuels, ASTM International, West Conshohocken, PA, www.astm.org, 2009.

BAROUTIAN, S., AROUA, M., RAMAN, A. A. A. and SULAIMAN, N. M. N., 2010: Viscosities and Densities of Binary and Ternary Blends of Palm Oil + Palm Biodiesel + Diesel Fuel at Different Temperatures. Journal of Chemical and Engineering data 55 (1), 504–507.

DOWSON, D., 2000: Thinning films and tribological interfaces. Published by Elsevier, ISBN–13: 978-0-444-50531-6.

FRISO, D. and BOLCATO, F., 2004: Rheological properties of some newtonian food liquids. Rivista di Ingegneria Agraria 2, 75–80.

HLAVÁČ, P., 2008: Temperature and time of storing dependencies of dark beer rheological properties. Journal of Processing and energy in Agriculture 12 (3), 114–117.

HLAVÁČ, P., 2009: Temperature and time of storing dependencies of some brew rheological properties. Proceedings of Physics 2009, October 2009, Nitra, Slovakia, pp. 1–8. ISBN 978-80-552-0264-8.

CHALUPA, M., 2005: Combined method of driving system dynamic properties analysis. Machinebuilding & Electrotechnics 3, 14–15.

CHALUPA, M., KRATOCHVÍL, C., KOTEK, V., HERIBAN, P., 2007: Computer Method of Analysis of Driving System Dynamic Propereties. AT & P Journal Plus 1, 277–279.

ISO 8217: 2005, Petroleum products – Fuels (class F).

JOSHI, H., MOSER, B. R., TOLER, J., SMITH, W. F. and WALKER, T., 2010: Effects of blending alcohols with poultry fat methyl esters on cold flow properties. Renewable Energy 35, 2207–2210.

KNOTHE, G., KRAHL, J. and VAN GREPEN, J., 2004: The biodiesel handbook. Champaign, IL: AOCS Press.

LI, H., SHEN, B. X. and YU, H., 2006: The Cold Temperature Fluidities of Biodiesel Prepared from Vegetable Oil. Energy sources 13, 1195–1200.

PERDOMO, F. A. and GIL-VILLEGAS, A., 2010: Molecular thermodynamics of biodiesel fuel compounds. Fluid Phase Equilibria 293 (2), 182–189.

RAHIMI, H., GHOBADIAN, B., YUSAF, T., NAJAFI, G. and KHATAMIFAR, M., 2009: Diesterol: an environmental-friendly IC engine fuel. Renewable Energy 34, 335–342.

SEVERA, L. and LOS, J., 2008: On the influence of temperature on dynamic viscosity of dark beer. Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis 2, 303–307.

SEVERA, L., MÁCHAL, L., KŘIVÁNEK, I., MACHATKOVÁ, M. and MAMICA, O., 2008: Selected rheological parameters of stallion ejaculate. Archiv fur Tierzucht 51 (1), 16–22.

SEVERA, L., NEDOMOVÁ, Š. and BUCHAR, J., 2010a: Influence of storing time and temperature on the viscosity of an egg yolk. Journal of Food engineering, 96 (2), 266–269.

SEVERA, L., BUCHAR, J., NEDOMOVÁ, Š. and ŠUSTOVÁ, K., 2010 b: Rheological profile of raw whey. Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis 1, 167–174.

SMITH, P. C., NGOTHAI, Y., NGUYEN, Q. D. and O'NEIL, B. K, 2010: Improving the low-temperature properties of biodiesel: Methods and consequences. Renewable Energy 35, 1145–1151.

SPEAROT, J. A, 1989: High–Temperature, High–Sheer (HTHS) Oil Viscosity Measurement and Relationship to Engine Operation, ASTM Publication, Philadelphia, ISBN 0-8031-1280-7.

TASYÜREK, M., ACAROGLU, M. and KAHRAMAN, A, 2010: The effects of etorage conditions on viscosity of biodiesel. Energy Sources, Part A 32 (7), 645–656.

TORRES-JIMENEZ, E., JERMAN, M., GREGORC, A., LISEC, I., DORADO, M. P. and KEGL, B., 2010: Physical and Chemical Properties of Ethanol–Biodiesel Blends for Diesel Engines. Energy Fuels 24 (3), 2002–2009.

TROYER, D. 2002: Understanding Absolute and Kinematic Viscosity. Practicing Oil Analysis Magazine 1, 15–19.

VÍTĚZ, T. and SEVERA, L., 2010: On the rheological characteristics of sewage sludge. Acta Universitatis Agriculturae et Silviculturae Mendelianae Brunensis 2, 287–294.

WIKIPEDIA CONTRIBUTORS, 2010: "Biodiesel" Wikipedia, The Free Encylcopedia – English Version (accessed June 28, 2010).

Address

Ing. Jiří Čupera, Ph.D., doc. Ing. Pavel Sedlák, CSc., Ing. Petr Karafiát, Ústav techniky a automobilové dopravy, Mendelova univerzita v Brně, Zemědělská 1, 613 00 Brno, Česká republika, e-mail: xcupera@node.mendelu.cz, pavel.sedlak@mendelu.cz, petr.karafiat@mendelu.cz