SEDIMENTATION ANALYSIS IN LIQUID-LIQUID SYSTEM APPLIED TO BIODIESEL PRODUCTION RESEARCH.
INTRODUCING MATHEMATICAL MODELS

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This work is focused on description of gravitation separation process of the ester phase from the glycerol phase for biodiesel production. Four mathematical models describing separation were created. Two independent methods were used for monitoring of separation: the first method is based on the determination of the time dependence of the actual amount of the glycerol phase on the bottom of a sedimenting vessel by digital camera records. The second one measures light absorption changes caused by the lowering of the glycerol phase during the sedimentation. The obtained data was curve fitted by developed mathematical models, which are (i) based on Stokes equation and proposed distribution function, (ii) based on analogy to reaction kinetics. The distribution function has several simplified presumptions, e.g., interactions are neglected, the function has one peak. The obtained model parameters (from the curve fitting) can be

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consequently used for the quantification and the prediction of sedimentation behaviour such as the sedimentation conditions, the size of settling devices and the evaluation of dependences on raw material quality.

Introduction

Biodiesel is a renewable fuel for contemporary diesel engines originated from vegetable oil and animal fat [1,2]. The biodiesel production has several aspects in economy, politics and environmental. For example, in European countries it lowers the dependence on crude oil, helps farmers to sell their crops for non-food purposes since there is overproduction of food and also the technology prevents from liberating of additional carbon dioxide to the atmosphere [3], a highly discussed substance to be responsible for the greenhouse effect. In today's technological praxis, biodiesel is mostly produced by the alkaline catalysed methanolysis or ethanolysis of glycerides (vegetable oil and animal fats), which can be described in general by the following summary equation, where R', R'', R''' are alkyl groups of fatty acids

| Triglyceride (oil) | Methanol | Glycerol | Methyl ester (biodiesel) |
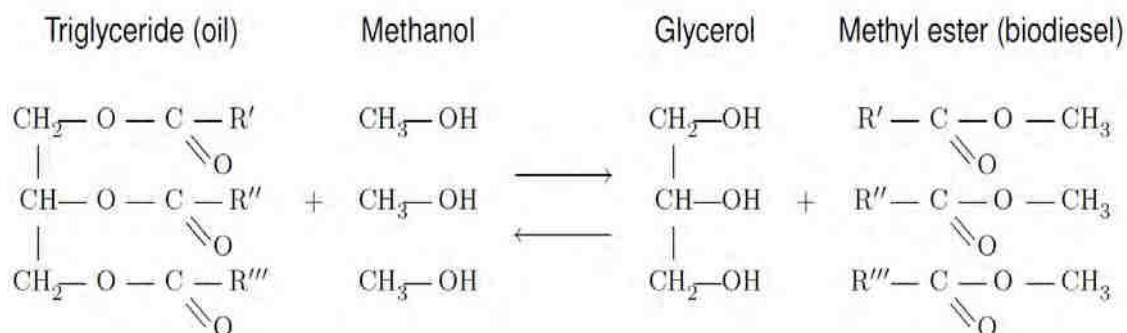
The alcoholysis of glycerides is a reversible reaction. To obtain a high quality product, the thermodynamical equilibrium of the chemical composition must be shifted towards products by excess of alcohol as a low-cost reactant. After the reaction time, the excess of alcohol is removed and recycled. The final products after purification steps are biodiesel (as a mixture of methyl or ethyl esters of fatty acids corresponding with composition of the oil or fat) and glycerol. A disadvantage of using of alkaline catalysis is the side saponification reaction of ester bond with hydroxide in the presence of water. The soap formed not only lowers the reaction yield, but it considerably affects the effectivity of the biodiesel separation.

In this work, the preparation of methyl esters differs from commonly used technologies in the industry [4] by a unique patented post-reaction treatment [5]. After the reaction period, the catalyst (KOH) is transformed to inactive form of

potassium hydrogen carbonate at first. Then, the surplus of methanol is removed directly from the whole reaction mixture by the low pressure distillation without preliminary separation of phases.

The raw reaction mixture (RRM) is always heterogeneous in the biodiesel production, because of different polarities of the present substances. The RRM is a coarse emulsion. That means, that it separates (spontaneously or by centrifugation) to lighter apolar ester phase (EP, biodiesel) and heavier polar glycerol phase (GP) with glycerol as the main component, the others being soap, water, methanol, salts. The ester phase (raw biodiesel) is the continuous phase with lower density, dispersed glycerol phase has higher density. The ratio between amounts of EP and GP is varying, dependent on the quality of raw materials, but typical value is approximately 8:1 [6]. Advantage of the patent mentioned above is simple. By removing of methanol, which is mostly present in the polar glycerol phase, the difference in densities of both phases grows and separation of phases becomes faster. Recovery of methanol, in comparison with distillation of separated phases, is also faster by this method. The reason is that the high interphase surface between EP and GP helps efficiently in extraction of methanol to ester phase, which then better releases methanol to vapour.

The used simple sedimentation is the first purification step in the biodiesel production and has its a time-dependent behaviour. The quality and speed of the separation can be influenced by previous technological steps, phases composition and conditions in reaction and separation. We looked for suitable and simple methods of the sedimentation measurements and data evaluation for describing and correlating with all possible influences. The conventional measurment methods, originally described by Odén [7], are more suitable for suspensions [8] and for high density differences of phases [9]. Therefore, we developed two original methods of data acquisition applicable for our liquid-liquid system. For the data evaluation, four models based on several acceptable simplification, comparable with other common published approaches were made. The main aim was to obtain very good correspondence of experimental data with the model fits. The evaluated model parameters, which have their physical meaning, can then be used for analysis and quantification of individual effects in further research.

Experimental

Preparation of Raw Reaction Mixture

For each sedimentation experiment, a new reaction mixture was prepared under the same reaction conditions to avoid the effect of the history of mixing and sedimenting [10].The transesterification was carried out according to the patented instructions [5] in the batch round-bottom glass reactor, equipped with a

mechanical stirrer Heidolph® and attachments for monitoring of temperature and pH. Approximately 450 grams of rapeseed oil (m_O) was supplied by the company RPN Slatiňany (the Czech Republic). To maintain a constant ratio between oil and the catalyst, the mass of catalyst (KOH) was calculated according to the formula

$$m_{KOH} = \frac{m_O}{\xi_{KOH}}\left(0.0065 + \frac{an}{1000}\right) \tag{1}$$

which comes from the patent [5] and where m_{KOH} is the mass in grams of potassium hydroxide (Lach:Ner, the Czech Republic), its purity is expressed as the mass fraction ξ_{KOH}, *an* stands for the acid number of used oil in conventional unit of milligrams of KOH per gram of oil (*an* was determined for the oil according to EN 14104).

The catalyst was dissolved in methanol (LachNer, the Czech Republic) whose amount was in the constant molar ratio methanol:oil equal to 6:1. The reaction took 90 minutes at vigorous mixing after addition of methanolic solution of KOH into the oil at 60 °C. Intensive stirring (400 rpm) is important, because the reaction mixture is heterogeneous all the time. The reaction was stopped by introducing gaseous carbon dioxide, which neutralized the rest of KOH to the catalytically inactive potassium hydrogen carbonate. The rest of unreacted methanol was removed from the whole RRM by low-pressure distillation at 2-3 kPa, 60 °C, for 45 minutes in which the level of methanol concentration in the EP was decreased to the standard desired level. After cooling to the room temperature, a small amount of water (2 wt. %) was added for even better separation of biodiesel and glycerol phases [6]. Typical composition and properties of the GP and the EP are in Table I.

Table I   Measurement of the evolution of sedimentation

	Glycerol phase	Ester phase
Volume fraction in the RRM, %	0.15	0.85
Methyl ester, wt.%	10	> 98.5
Glycerol, wt.%	60	0.2
Potassium salts, wt.%	15	0.007
Water, wt.%	13	0.05
Methanol, wt.%	2	0.1
Density, g cm^{-3}	1.12	0.88
Viscosity at 40 °C, mm^2 s^{-1}	200	4.5

Measurement of Time Course of Sedimentation

Two original methods were used for measurement of the sedimentation rate.

The camera method: The fresh RRM in the form of emulsion was placed into a glass cylinder equipped with a vertical longitudinal scale. The motion of the interface forming between the EP and the GP was measured by a digital camera. For right evaluation of interface position, the camera had to be placed on the same vertical position with the interface (movable holding).

Evaluation of the sediment level is complicated by diffuse interface (Fig. 1). Since both phases have different colour, we can analyse the colour intensity along the scale: A strip of picture near the scale was computationally decomposed to red, green and blue colour to digital form. Intensities of colours along the scale presented the profiles which in the position of interface rapidly changes their values. Exact position of the interface was evaluated as the inflection point in the green colour curve, because the green colour change was the most sensitive. The inflection point position in the scale was then recalculated to the volume of the sediment from an external calibration of scale-volume.
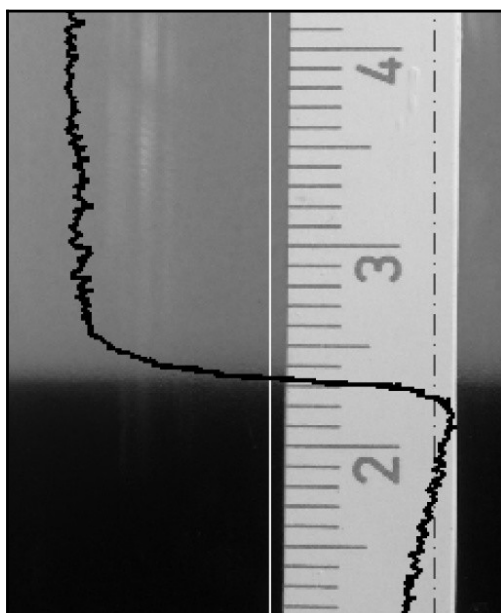

Fig. 1   An example of sedimentation record with evaluation. Two vertical lines can be seen in this picture. The evaluation line (bright solid line, over the sample) is subjected to the colour intensity analysis and referential (dash-and-dot) line that should rectify non-equal light conditions of obtained picture. The layered dark curve is the result of the green colour intensity analysis

The absorbance method: A sample of fresh RRM was placed in a glass 30 ml cuvette with an optical path of 2 cm. The cuvette was placed in a spectrophotometer Specol 11 with an attachment for large cuvettes, equipped with

a stirrer (Fig. 2). After the stirrer was switched of the time dependence of absorbance on time was measured. The monochromatic optical beam passed through the sample in a known distance from the sample level. A wavelength of the beam of 550 nm was chosen, because this wavelength is absorbed only by the sedimenting particles of the GP, not by the EP.
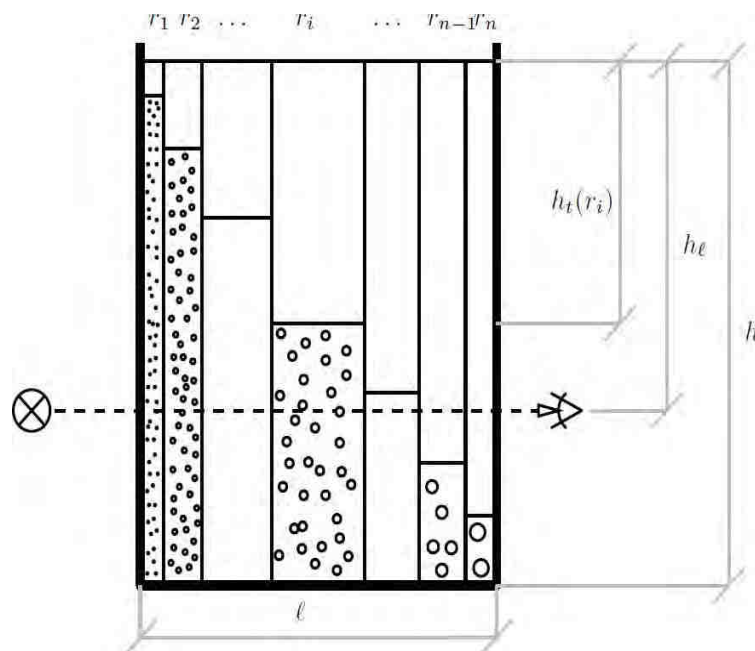

Fig. 2 Formal schema of sedimentation with spectrophotometry indication. Used symbols: l is the optical track, r_i are radiuses of fractions of dispersed particles, h is the total sedimentation height, h_l is the position of optical beam from sample level and $h_t(r_i)$ is the maximal distance, which can a single particle of radius r_i pass in given sedimentation time t

Results and Discussion

To evaluate our data, we have chosen the data fitting by mathematical (physical) models instead of statistical models evaluation. But we do not refuse the statistical evaluation at all. We have developed also one statistical model for fast and rough parameters estimation of dispersed particles distribution. The introduced models are based on physical laws and analogies to similar processes. An advantage of mathematical modelling of sedimentation processes consists in getting of model parameters which have their specific physical meaning. On the other hand, data fitting by physical model may be more complicated and the procedure may be computer time consuming. The aim was to create maximally simple models for our data measured in different ways for comparison of the results obtained.

General Assumptions in Modelling

The dispersed particles of liquid-liquid system do not have a uniform size, but their sizes are distributed in a large interval, detectable by a sedimentation analysis. Classical sedimentation analysis in the gravity field is based on analysis of the sedimentation curve (dependence of the amount of sediment on time) and by Eq. (2)

$$m_t = m_s + t\frac{\mathrm{d}m_t}{\mathrm{d}t} \tag{2}$$

where m_t is the amount of sediment in the time t, m_s is the amount of fractions of the GP particles, which are in the certain time t completely settled, and the term $\mathrm{d}m_t/\mathrm{d}t$ is the differentiation of the sedimentation curve in the time t. According to the work [4], the function m_s is related to the integral distribution function of dispersed particles $I(r)$ as

$$m_s = m_{\max}\left(1 - I(r)\right) = m_{\max}\left(1 - \int_0^r F(r)\mathrm{d}r\right) \tag{3}$$

where $m_{\max}$ is in our case the total amount of the GP, and $F(r)$ is the differential distribution function (DF) of the dispersed particles dependent on the particle radius r.

Direct use of this evaluation for our data is problematic, because of multiplying of the experimental error in the calculation of the differentiation $\mathrm{d}m_t/\mathrm{d}t$ from the experimental time dependence of m_t. Since our data measured can be quite noisy, it is better to fit experimental data by a curve, and then the cumulative distribution function $I(r)$ can easily be calculated using Eqs (2) and (3). In this work we tried not to use whatever statistical function to fit experimental data, but we developed the solution on the basis or analogy to natural laws.

Hence, three mathematical models were under following presumptions:

1. The dispersed GP particles have spherical shape and their sizes can be described by some frequency distribution function of volume fractions of the GP particles versus the radius.
2. All dispersed particles of the GP have the same density and chemical composition.
3. Interactions among sedimenting particles are neglected.
4. The sedimentation speed of a single GP-particle is constant, depending on balance of three forces: the Stokes' drag force, the buoyancy force and the gravity force. Using this equilibrium, a form of the well-known Stokes relation among particle radius (r), sedimentation time (t), sedimentation column height (h) and material constants was obtained. Final mathematical expression gives

in relation material constants, size of sedimenting particle and sedimenting time and track

$$r = \sqrt{\frac{9\gamma h}{2 \, tg\left(\frac{\rho_{GP}}{\rho_{EP}} - 1\right)}}$$

(4)

where γ is the kinematic viscosity ($m^2 \, s^{-1}$) of the EP, ρ_{EP} stands for the density of the EP, ρ_{GP} is the density of the GP, both in units kg m^{-3}, the standard gravity is denoted as g (= 9.81 m s^{-2}).

If the variable sedimenting track h is equal to total height of the sedimentation column (both in meters), the relation (4) becomes the dependence between the particle radius r (meters) and sedimentation time t (in seconds), necessary to pass the distance for this particle. All the constants in Eq. (4) can be summarised to one, the universal sedimentation constant κ

$$r = \frac{\kappa}{\sqrt{t}}$$

(5)

The formulas (4) and (5) simply say that larger drops fall faster.
5. We suppose only one peak distribution functions.

Let us note that the simplifying conditions 1-4 used in our models are the same as in the common evaluations.

Used Distribution Functions

The choice of a suitable differential distribution function (DF) is crucial. We have chosen several frequency distribution functions with one maximum and with the area under the curve $F(r)$ in interval r $\in$ (0; ∞) which is by definition equal to one.

The first DF is the transformed Gauss distribution function (6), where the mean value μ and the data scatter σ were substituted to have parameters of the curve peak position of the particles DF $[r_0; F(r_0)]$, and the particle radius r is independent variable.

$$F(r) = F(r_0) \exp\left\{-\pi F(r_0)^2 (r - r_0)^2\right\}$$

(6)

The integration of models which implement this distribution function is possible and leads to expressions with the erf-function. Moreover, this function

and other symmetrical function have domain of definition of R, which means that it contains also negative diameters. We define, that the integral of this function from 0 to infinity is equal to one and, our domain of definiton is R^+, which needs normalization of data.

For some data, it was better to choose a DF with a higher kurtosis. The symmetrical function, the Lorentz (also known as Cauchy–Lorentz or only Cauchy) distribution function was used, again transformed by the parameters of distribution apex r_0, $F(r_0)$ and one additional parameter r_s with a condition $r_0 < r_s$

$$F(r) = F(r_0) \frac{(r_s - r_0)r_0}{r^2 - 2r_0 r + r_0 r_s} \tag{7}$$

A good compromise of previous two distribution functions is the empirical Schultz–Zimm DF which is used in the polymer studies [11]. This distribution function has domain of definition of R^+ plus zero and contains two parameters, r_0 and b

$$F(r) = F(r_0) \left(\frac{r}{r_0}\right)^b \exp\left[b\left(1 - \frac{r}{r_0}\right)\right] \tag{8}$$

In the Schultz–Zimm DF, the maximum frequency parameter $F(r_0)$ is a function of other model parameters. Its value can be derived from the expression for the area under the curve equal to one

$$F(r_0) = \frac{\left(\dfrac{b}{e}\right)^2}{r_0 \Gamma(b)} \tag{9}$$

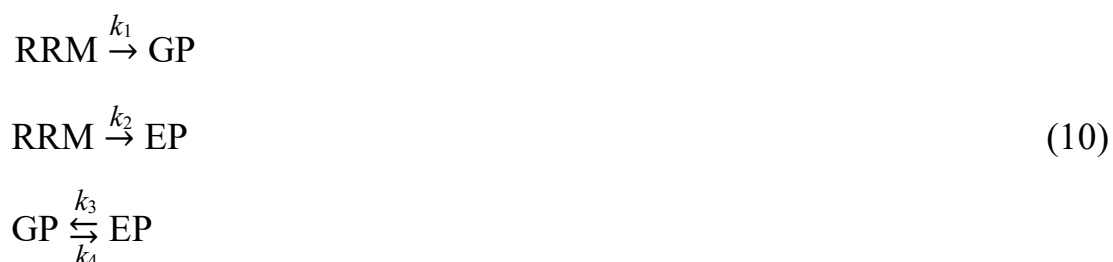where $\Gamma(b)$ is the gamma function of the argument b, $b \in \Re^+$.

The integration of the function (8) and its expressions in presented models cannot be performed in general. Results of integration can be obtained only by numerical methods.

Model I: Formal Kinetics Model

The first presented model is statistical, but based on analogy with a formal chemical kinetics — Scheme (10). The concentrations in the suggested Scheme (10) of the RRM separation are in fact amounts of separated phases. The assumptions (the first section of Results and Discussion) need not to be fulfilled

in this case, and the model is maximally simple. On the other hand, the simplicity of this model limits the usage of evaluated parameters. The data from the first method of measurement (the camera method) can be analysed by this model.

The concept of this model is easy. We formally substituted the concentrations in "reaction schema" (10) to separated volumes of phases. We can read the relations in this way: the ester and glycerol phase arise from reaction mixture with the rate constant k_1 and k_2. Furthermore, the equilibrium between the GP and the EP is supposed because of additional exclusion of the EP from the GP, which was experimentally proved (rate constants k_3 and k_4). This also means that we cannot look at the entities RRM, GP and EP as non-changeable units, but only as observable volumes.

$$\text{RRM} \xrightarrow{k_1} \text{GP}$$

$$\text{RRM} \xrightarrow{k_2} \text{EP} \tag{10}$$

$$\text{GP} \underset{k_4}{\overset{k_3}{\rightleftharpoons}} \text{EP}$$

The constants k_1-k_4 are rate constants of each "reaction" step with dimensions like kinetic rate constants of the first order reactions, i.e., the reciprocal time. According to laws of the formal reaction kinetics, the following set of differential equations (11) can be written

$$\frac{d[\text{RRM}]}{dt} = -(k_1 + k_2)[\text{RRM}]$$

$$\frac{d[\text{GP}]}{dt} = k_1[\text{RRM}] - k_3[\text{GP}] + k_4[\text{EP}] \tag{11}$$

$$\frac{d[\text{EP}]}{dt} = k_2[\text{RRM}] + k_3[\text{GP}] - k_4[\text{EP}]$$

Moreover, [RRM], [EP] and [GP] can be defined as ratios of the actual volumes of the RRM, and the separated EP and GP respectively, divided by the volume of the sample, and introduce the relative dimensionless volume of RRM, and the separated EP and GP respectively. It holds $[\text{RRM}] \in (0, 1\rangle$, $[\text{EP}] + [\text{GP}] \in \langle 0, 1)$. The result of integration of kinetic model is the dependence of dimensionless relative amount of each phase on time

$$[\text{RRM}] = \exp[-(k_1 + k_2)t] \tag{12}$$

$$[GP] = \frac{k_4}{k_3 + k_4} + \frac{k_4 - k_1}{(k_1 + k_2) - (k_3 + k_4)} \exp\left[-(k_1 + k_2)t\right] +$$

$$+ \frac{k_2 k_4 - k_1 k_3}{(k_3 + k_4)^2 - (k_1 + k_2)(k_3 + k_4)} \exp\left[-(k_3 + k_4)t\right] \quad (13)$$

$$[EP] = \frac{k_3}{k_3 + k_4} + \frac{k_3 - k_2}{(k_1 + k_2) - (k_3 + k_4)} \exp\left[-(k_1 + k_2)t\right] -$$

$$- \frac{k_2 k_4 - k_1 k_3}{(k_3 + k_4)^2 - (k_1 + k_2)(k_3 + k_4)} \exp\left[-(k_3 + k_4)t\right] \quad (14)$$

Equation (13), which describes the time dependence of [GP] (the sediment growth), was used as the most appropriate for evaluation of the rate constants k_1-k_4 from experimental sedimentation data using the non-linear regression. Moreover, in the set of Eqs (11), it is possible to deduct the equilibrium between the GP and the EP volume ratios in infinity time. For the equilibrium constant K of the reaction scheme one can write

$$K = \frac{[EP]_{t \to \infty}}{[GP]_{t \to \infty}} = \frac{k_3}{k_4} \quad (15)$$

Formula (15) allows us to fit data by model (13) only with 3 rate constants (parameters), because the value K can be found from the equilibrium values of $[EP]_{t \to \infty}$ and $[GP]_{t \to \infty}$ at the end of measurement. With known constant K, the value of the constant k_3 is dependent on k_4 and *vice versa,* and so the fourth parameter can be easily calculated after the nonlinear optimization routine.

Although the constants k_1-k_4 have a clear physical meaning in the chemical kinetics, as parameters in the sedimentation model they have only limited sense. For example, the constant k_1 has clear geometric sense: it is the value of the slope of the tangent line for $t = 0$ in the dependence of [GP] (t), see Eqs (13) and graphically in Fig. 3. The constant k_2 has the same meaning for the dependence (14), but volume of the EP cannot be experimentally measured, except of the equilibrium value. That is why, this way fitted model has only approximative usage. But, if we apply Eqs (2), (3) and (5), to the fitted curve, we can draw an approximative DF

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$$F(r) = \frac{2(K+1)\kappa^4}{r^5}\left[\frac{(k_1 k_3 - k_2 k_4)(k_3 + k_4)}{(k_3 + k_4) - (k_1 + k_2)}\exp\left\{-\frac{(k_3 + k_4)\kappa^2}{r_2}\right\} + \right.$$

$$\left. + \frac{(k_1 - k_4)(k_1 + k_2)^2}{(k_1 + k_2) - (k_3 + k_4)}\exp\left\{-\frac{(k_1 + k_2)\kappa^2}{r^2}\right\}\right]$$

(16)

The function (16) can be used only as the first step to get a mathematically correct distribution function, because this equation has not the properties required for a frequency distribution function.

An example of sedimentation measurements evaluated by Model I is depicted in Fig. 3.
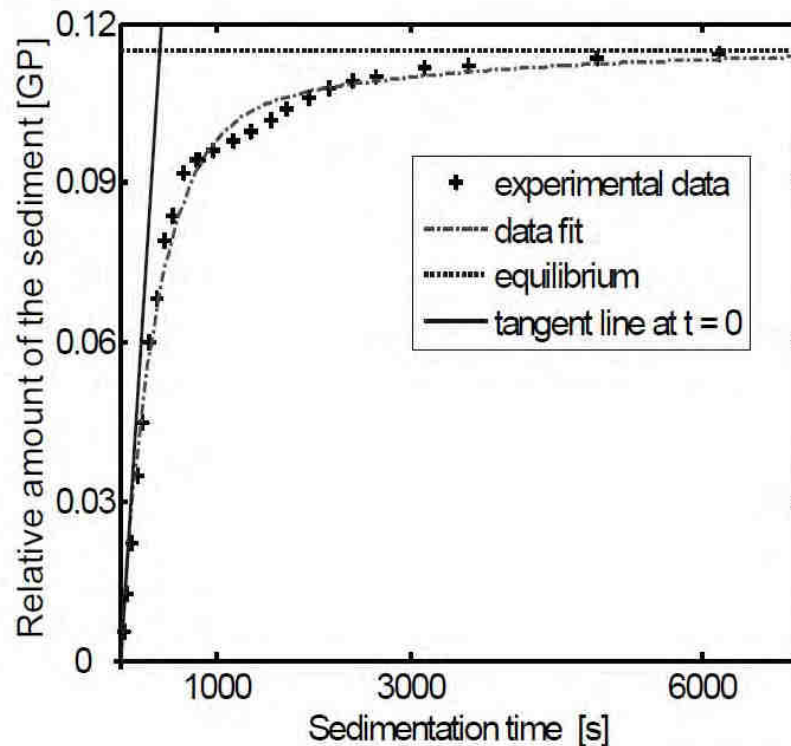

Fig. 3 Using of the Model I in praxis for experimental data. The regression yield is R^2 = 0.992

Model II: Basic Mechanistic Model

The assumptions (described at the beginning of section Result and Discussion) are valid for this and next models in following sections. Let us consider a general situation in the sedimentation process: During mixing the RRM, GP drops are

spread out evenly along the settling vessel, no matter how large they are. Sedimentation starts immediately the stirrer is stopped. In the sedimentation time t (with respect to the total height of the sedimentation column h_l), there is a fraction of particles with the radius r_t that have just sedimented completely, because even the last particle, which was situated near the surface in time $t = 0$, just reached the bottom. Particles with bigger size settled prior to this time, because their sedimentation speed was higher. The settled volume of the particles smaller than r_t is dependent (fraction $P \in (0, 1)$) on their exact size. For $r \leq r_t$, P is defined as the maximum vertical distance h, which could a single particle of radius r pass in time t, calculated from Eq. (4), divided by the total sedimentation height h_l

$$P(r,t) = \frac{h}{h_l} = \frac{2r^2 \operatorname{tg}\left(\frac{\rho_{GP}}{\rho_{EP}} - 1\right)}{9\gamma h_l} = \frac{r^2 t}{\kappa^2} \tag{17}$$

This dependence of r and P is depicted in Fig. 4 as multiplication of P with $F(r)$.
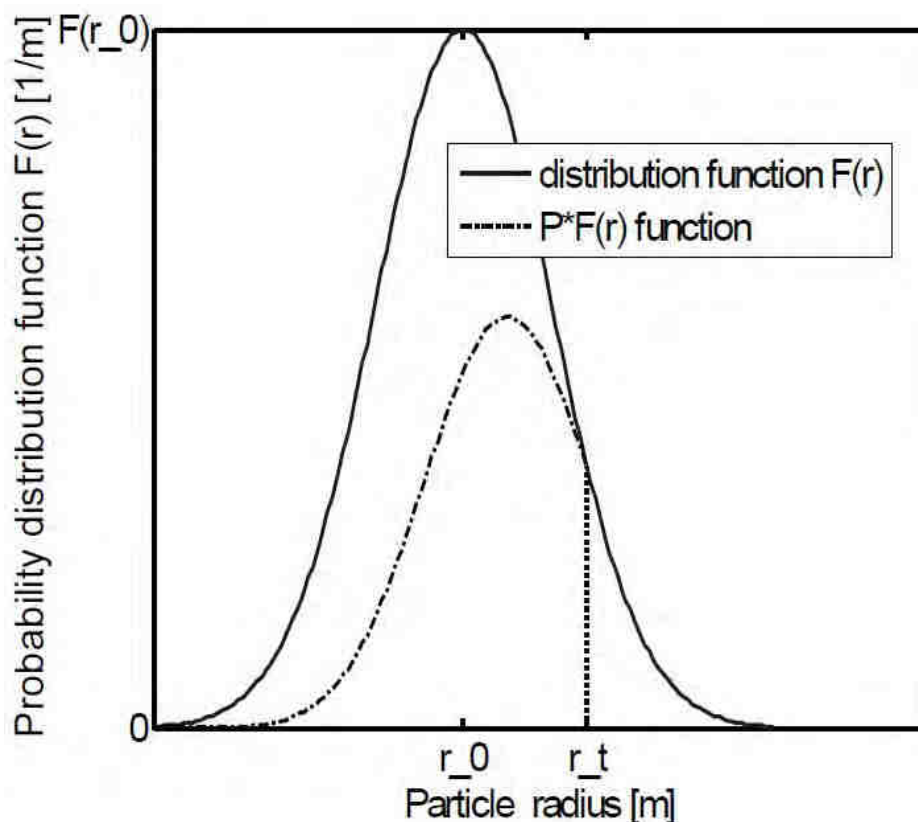

Fig. 4 Explanatory sketch to derive the sedimentation model II

Let us use this figure for further model explanation. This curve $P \cdot F(r)$ divides the total area under the curve $F(r)$ (in other words, the total amount of the GP) into two parts: the first part represents sedimented volume of the GP and the second non-sedimented volume of the GP — area between $F(r)$ and $P \cdot F(r)$ in the interval $r \in (0, r_t)$. For the data fitting, we standardized the amount of the sediment by dividing it by the total amount of the GP, known from the end of experiment. The relative amount of the sediment $v(t)$ is then the area under the $P \cdot F(r)$ curve for $r \in (0, r_t)$, plus under the curve $F(r)$ for $r > r_t$. The time course of the sediment amount can be calculated as the difference between total amount of the sediment ($v(t \rightarrow \infty) = 1$, standard value) and the actual amount of the GP still dispersed in the EP calculated by Eq. (18).

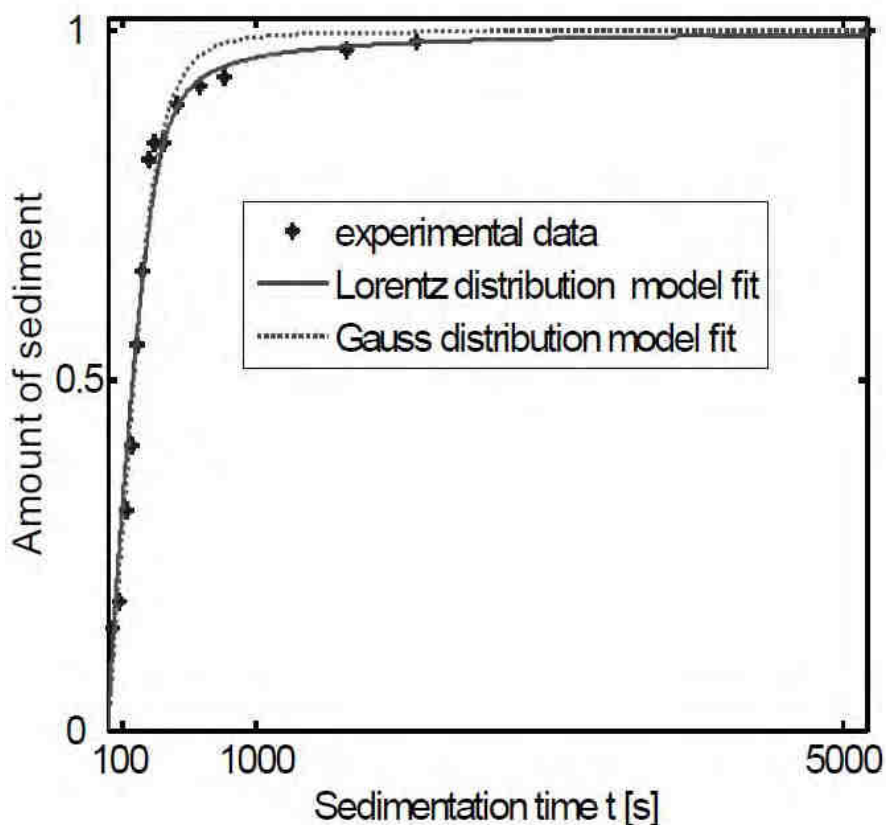$$v(t) = 1 - \int_0^{r_t} (1-P)F(r)\mathrm{d}r \tag{18}$$

Fig. 5 Experimental data and model fits by Model II using Gauss ($R^2 = 0.973$) and Lorenz ($R^2 = 0.982$) distribution functions

In Eq. (18), the upper integration limit r_t is a function of t. It is calculated from the formula (17), whereas $P = 1$, $r_t = r$. The integrability of Eq. (18) is strongly dependent on the distribution function in the model used. Using of most common distribution functions cause the equation to be non-integrable. This means that numerical integration must be performed in drawing the dependence (18) and also in non-linear curve fitting of experimental data. An example of experimental data fitted by models concerning two distribution functions (Gauss, Lorentz) each are in Fig. 5.

Model III: Advanced Mechanistic Model

This model was constructed for experiments with a non-monotonic sedimentation curve, where the previous mechanistic model could not be used because real sedimentation in the liquid-liquid system may be more complicated than sedimentation in the solid-liquid system. The reason of such behaviour lies in the non-ideal sediment layer formation caused by the slow coagulation of the sedimented GP. During sedimentation, variable amount of the EP stays trapped in the sedimented part of the GP and it is then continually displaced back to the continuous phase. But in the meantime, it increases the volume of the sediment measured and its amount cannot be neglect. We are mainly interested in obtaining of parameters of dispersed particles and such behaviour complicates the evaluation.

Determined actual amounts of the GP were divided by the final amount of the GP to get the relative scale of the sediment s. In this case, the value of s can be higher than 1 — for example, see Fig. 6.

The basis of this model is in the model II, Eq. (19). Redefined variable of relative amount of the sediment (s) consists of pure glycerol phase (v), calculated from Eq. (18) and newly added the transition layer (o) representing the amount of the trapped EP in the sediment in this way

$$s = v(t) + o\,(o, v, t, r_t) \qquad (19)$$

Measured data and mainly the sedimentation function v is then free of false signals caused by non-ideal sediment layer formation. Function o, which was suggested from several experimental data fittings, is described by differential equation with two terms

$$\frac{\mathrm{d}o}{\mathrm{d}t} = c_1 f(r) \left(\frac{\mathrm{d}v}{\mathrm{d}t} \right)^2 - c_2 \frac{o}{v+o} \qquad (20)$$
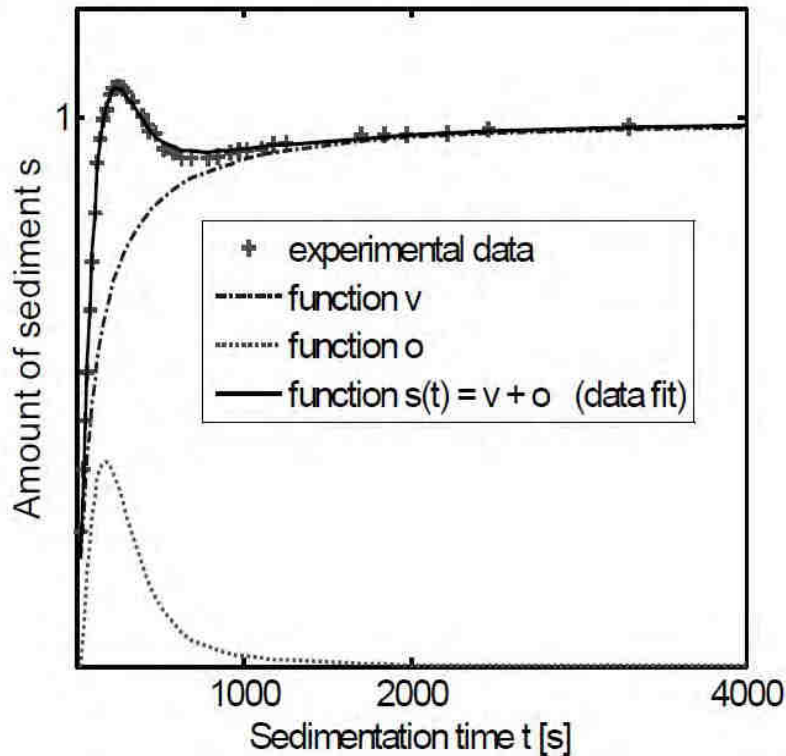
Fig. 6 Using of Model III for non-ideal data, hardly fitted by other models, the regression yield $R^2 = 0.996$

The first term is positive and expresses growing of the amount of the layer o and consists of the product of the constant c_1, approximative function of the effect of just-sedimenting-particles $f(r)$ and the square value of the sedimentation rate dv/dt. The second term lowers the speed of the transition layer o formation and even causes this layer to decay. Its value proportional to a constant c_2 and the relative abundance of o the sediment layer: $o / (v + o)$.

The advantage of such definition of the function o is clear. It is a mechanistic definition and, moreover, it gives very large shape variability of the function s. The model gives the information about the distribution function and the information about the sediment layer formation. On the other hand, the model is defined as a set of differential, integral and algebraic equations, and the data fitting can be successful only with the help of skilled computer fitting programmable software such as Matlab, Scilab, Maple and others.

According to our experiments, the function $f(r)$ for just-sedimenting-particles is necessary, but it has not been completely understood until now. It seems that the $f(r)$ function would be a monotonic function, decreasing with decreasing radius of the GP particles. For simplification, we assumed the greatest influence of the r_t particles. The most successful approximations were in using of the power function and exponential function of r_t with one adjustable parameter as exponent or multiplier of the argument. For example

$$f(r) \approx e^{c_3 r_t} \qquad (21)$$

Model IV: Sedimentation Indicated by Spectrophotometry

This model differs from the previous ones by the method of measurement, but in general, it is derived on the same basis. By the light absorption of the GP particles, we can measure the absorption changes during experiments. Mathematically, this is a mechanical model easier to derive and evaluate than the model II and even than the model III.

On the other hand, for using of this simple mechanistic model, the equality of refraction indexes of both phases (EP, GP) must be ensured to prevent the light scattering. Generally, the GP has a higher index of refraction than the EP. The GP must be modified for example by water addition, which is also advantageous [8]. Water has the lowest index of refraction of all compounds present in the reaction mixture. It mixes with and diluts only the GP. At the suitable water content, the sample optically behaves like a homogeneous solution, although it is still heterogeneous from the chemical point of view. We have to note that we use this method of measurement and evaluation only in situations, that we study behaviour of the systems from the same raw materials. The only thing that we can assure is the fact that the addition of water is the same for all experiments. The exact amount of water to be added to each sample must be determined by titration of the RRM sample by water indicated by light absorption in this way: A weighed sample of RRM in a cuvette is put in the spectrophotometer and the sample is continually well mixed. The RRM with low water content is very opaque and by repeated water addition it becomes more transparent to a light. At the point the indexes of refraction are equalled, the mixture is optically transparent and light scattering is zero, absorption of light is at its minimum value, and the amount of water added is marked. With further water addition the mixture becomes opaque again.

Model formulation is now very easy: The optical beam passes through the sample of the RRM (Fig. 3) in the known distance h from the sample level. Great particles of the GP fall down more quickly than the small ones as it is formally depicted in Fig. 3 as sorted fractions of particles. The absorption of the sample changes every time, when one fraction of particles disappears from the optical beam. Absorption is linearly related to the concentration of the GP in the optical beam according to the Bouguer–Lambert–Beer's law. The concentration of the GP in the optical beam can be substituted by its volume fraction, and we can use distribution function.

The time course of light absorption $A(t)$ is given by the value of integration of differential distribution function $F(r)$ from 0 to r_t, where r_t is the fraction of the GP particles just disappeared from optical beam, calculated from the formula (4).

The constant includes the cuvette size parameters, transformation of concentration to relative volume and optical parameters of the GP (absorption coefficient g), mathematically written

$$A(t) = \varepsilon c_{GP} l = \varepsilon \frac{V_{GP}^{beam}}{V_{GP}^{beam} + V_{EP}^{beam}} l = const\, V_{GP}^{beam} = const \int_0^{r_1} F(r)\mathrm{d}r \qquad (22)$$

We can obtain the parameters of the suggested distribution function by non-linear regression of the integrated form (or the form by definition) of Eq. (22). The unknown constant present in this formula can be easily eliminated by dividing the whole formula by initial absorbance of the mixture, because the integral of distribution function in limits from 0 to infinity (no particle sedimented) has the value of 1 by definition. In this case as well in other cases there presented, fitted data are expressed in relative units $A(t)/A(t = 0)$, ranging from 0 to 1. Examples of standardized experimental data and data-fits by Model III are presented in Fig. 7.
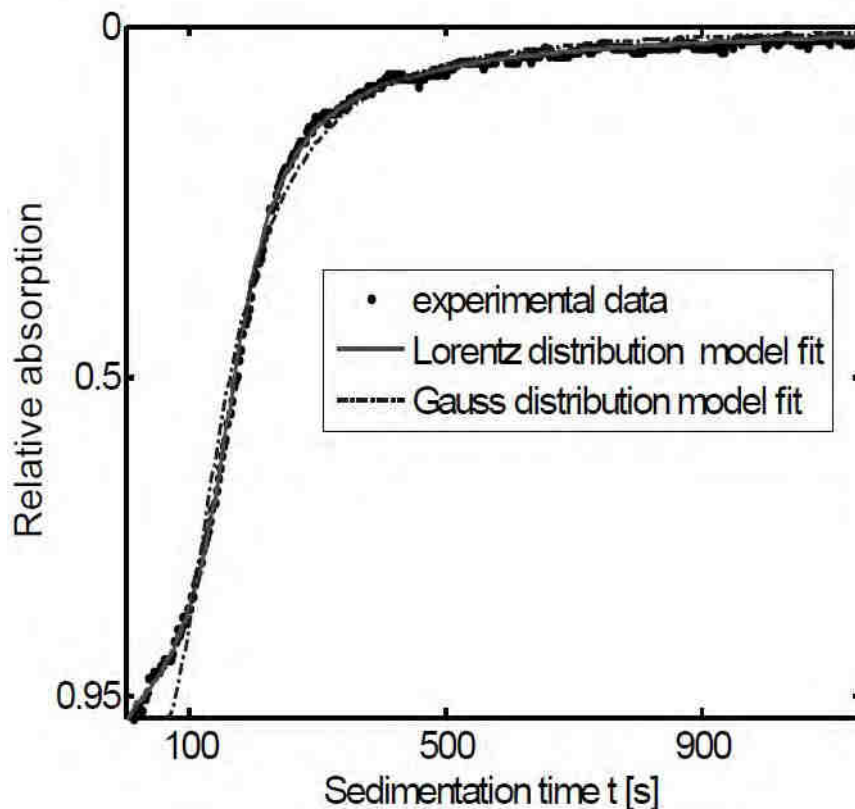

Fig. 7 Sedimentation absorption data fitted by the Model IV, with two proposed distribution functions, Gauss distribution model fitted with $R^2 = 0.9853$, the Lorentz distribution model with $R^2 = 0.9966$

Conclusion

This paper introduces several mathematical models developed in the research of the glycerol phase sedimentation in the biodiesel production. These models could serve as a tool for characterization and studying of sedimentation conditions in the purification step of the biodiesel production. The present authors suppose that this way of measurement and sedimentation data evaluation can be used in other liquid-liquid systems and sedimentation measurements. Great benefit of this work is non-derivative evaluation of the experimental sedimentation curves, suitable especially for noisy data. Two possible methods of measuring of sedimentation courses were used. The first is based on evaluation of camera records (Models I, II and III), the second uses spectrophotometer as measuring device (Model IV).

The first presented model (Model I), based on formal chemical kinetics, contains only three independent parameters. An approximative distribution function of the GP particles can be obtained from mathematical analysis of the fitted curve.

Remaining three models are based on one of proposed distribution functions combined with the concept of undisturbed sedimentation of spherical particles of the glycerol phase. Models I, II and IV are suitable only for fitting of monotonic curves of the amount of the GP on time.

The third model is most complicated and can also describe the data with non-ideal sediment layer formation. We can obtain information not only about sedimentation but also about sediment layer formation. The model is dependent on 5-6 parameters (according to the number of parameters of the used distribution function) necessary for the convenient description of measured sedimentation curves.

Limitation in usage of Model IV is the need of optical homogeneity of a sample, unifying of refractive indexes of the EP and the GP. The number of parameters to be evaluated is given only by the number of parameters in the distribution function used.

The correspondences of experimental data and model data fits were shown for each model.

Acknowledgement

Symbols

DF frequency distribution function
EP the ester phase
GP the glycerol phase
RRM raw reaction mixture

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