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RHEOLOGICAL PROFILE OF RAW WHEY

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Abstract

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The results of raw whey rheological behavior investigation – particularly viscosity, dependence on temperature, time, and share rate, are presented. The whey samples have been examined under temperature ranging from 17 to 90 °C and under share rate ranging from 0.34 to 68 s^{-1}. The measurements have been performed using rotary digital viscometer (concentric cylinders geometry). The material was found to be temperature dependent (non-linearly), time dependent and shear thinning. Received data have been successfully characterized by several mathematical models (power, exponential, and polynomial) in MATLAB® software with satisfying correlations between experimental and computed results. Following correlations have been achieved: temperature dependence with $r^2 = 0.993$ using polynomial model, time dependence with $r^2 = 0.985$ using power model, and shear thinning behavior $r^2 = 0.998$ using power model. The results are quite useful for practical design of technological equipment such as pumps and piping.

whey, rheological behavior, modeling

Whey is the liquid remaining after milk has been curdled and strained; it is a by-product of the manufacture of cheese. Sweet whey (pH greater than or equal to 5.6) is manufactured during the making of rennet types of hard cheese like cheddar or Swiss cheese. Acid whey (pH less than or equal to 5.1) is obtained during the making of acid types of cheese such as cottage cheese.

Disposing of whey has long been a problem. For environmental reasons it cannot be discharged into lakes and rivers; for economical reasons it is not desirable to simply dump it to waste treatment facilities. Converting whey into powder has led to a number of products that it can be incorporated into. It is most desirable, if and where possible, to use it for human food, as it contains valuable protein component. It is also feasible to use it as animal feed (Samuelov et al., 1999). The whey contains fat, lactose, beta-lactoglobulin, alpha–lactalbumin, and water. The fat is generally removed by centrifugation and churned as whey cream or used in ice cream.

The knowledge of rheological and thermophysical properties of whey is a valuable tool in predicting the product stability during storage and in design of whey transport and processing technologies. In addition, accurate measurements of rheological data are necessary for the flow transport, as sizing of pumps and piping. Rheological and thermophysical properties of whey proteins can be influenced by novel food processing technologies (Krešić et al., 2008).

Generally, rheological properties are determined in order to define the behavior of solutions, suspensions and mixtures. Whey is an example of such material. The basic parameter, obtained during rheological study of liquid foods, is viscosity, used to characterize the fluid texture (Rao, 1977; Alonso et al., 1990; Rao and Cooley, 1992). As an example of application, chemical exchanges in foods frequently occur with time and may be studied by rheological methods. Another important factor is temperature, which frequently occurs in rheological equations (Rosen and Forster, 1978).

Process design for liquid foods with or without particulates requires accurate information on the flow behavior to arrive at processing conditions, which ensure safety and improve quality. In these continuous processes, rheological properties play a major role in describing the heat transfer or in the design, evaluation or/and modeling of the continuous treatment, such flow characteristics of pumpable liquids, viscous and semiliquid foods are dependent on material viscosity and density (Abdel-rahim et al., 1994; Herceg et al., 1999; Marcotte et al., 2001).

The rheological properties of whey protein concentrates and isolates have been studied by number of authors (Belmar–Beiny et al., 1993; Mleko et al. 2003; Camillo and Sabato, 2004; Herceg and Lelas, 2005; Patočka et al., 2006; Leng and Turgeon, 2007; Krešić et al., 2008), but information on rheological profile of raw whey (or concentrated raw whey) is just of general nature and restricted to simple description of its behavior.

Whey flow properties and viscosity should be also considered when designing spray drying technologies. Many authors have proposed various relationships between droplet size, physical properties (e.g. viscosity of concentrate) and technological parameters (e.g. nozzle pressure) (Schuck et al., 2005).

The objective of this work was to evaluate selected rheological properties of raw whey, to compare values of its viscosities under different shear rates and to describe the flow curves. The simple models to fit the flow curves and time and temperature dependencies have been also proposed.

MATERIALS AND METHODS

Whey samples

A raw concentrated sweet whey containing 48% of dry matter has been used to perform the experiments. The density of whey has been determined by picnometric method as 1200 kg.m^{-3}. The whey was produced as a by-product from skim milk (pH 6.2). The samples of whey have been received from a commercial producer (Eligo, a.s), manufacturing the whey powder. The whey was sampled directly from the production line – from the tank behind the expander.

Viscosity measurement

The procedure of sample preparation for viscosity measurements corresponded to a typical sampling procedure. Since the whey was assumed to be a non-Newtonian, time dependent fluid (Steffe, 1996), special pre-experiment treatment was performed. The adequate volume (20 ml) of whey was put into the apparatus cuvette without previous heavy mixing or any other kind of preparation. Then the sample was pre-shared at 10 s^{-1} for 20 s.

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. Presented data have been obtained from measurements performed on laboratory digital viscometer Anton Paar DV–3 P (Austria) which is designed to measure dynamic or kinematic viscosity (ν, η), shear stress (τ), and shear rate ($\dot{\gamma}$). 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 [s^{-1}] and kinematic viscosity in [mm^2/s] speed of spindle in revolutions per minute [rpm]. The experiments have been performed with use of a low viscosity adapter with LCP spindle. The law viscosity adapter permits more accurate measurements than standard device equipped with another spindle type. Also the measuring range of viscometer can be extended to lower values. This extension is particularly advantageous when measuring materials where low shear rates data are required. Due to parallel cylinder geometry shear stress, except other values, can be determined.

The flow curves were obtained for raw whey shared at 0.34–68 s^{-1} and for the temperature range 17–90 °C.

Mathematical models

Mathematical models have been created with use of MATLAB® v. 7.1.0.246(R14) Service Pack 3, Curve fitting application (The MathWorks, Inc., USA). The suitability of the fitted models was evaluated by the determination of coefficient (r^2) and the significance level ($p < 0.05$).

RESULTS AND DUSCUSSION

Influence of temperature on kinematic viscosity

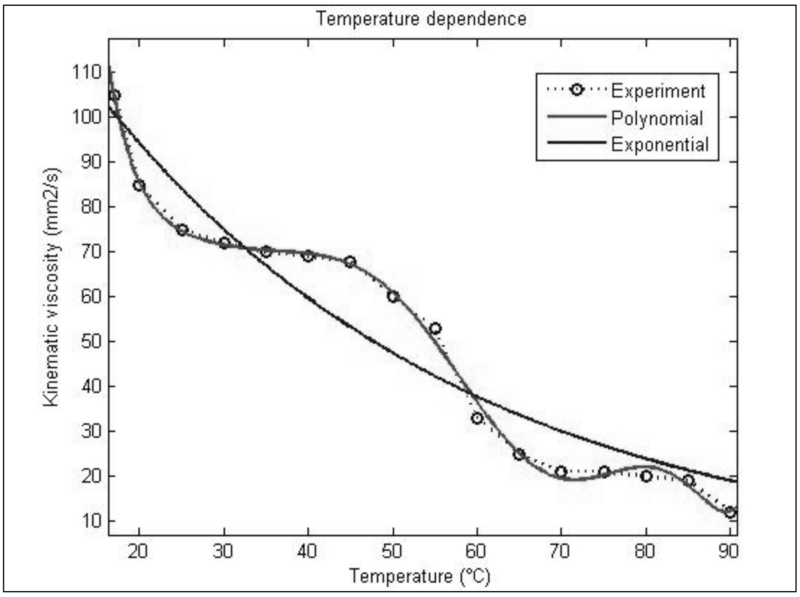
The values of raw condensed whey kinematic viscosity [mm^2/s] measured under different temperatures (17–90 °C) at share rate of 17 s^{-1} are listed in Table I.

Kinematic viscosity of whey is influenced by many factors. If we consider that whey acts as non-Newtonian fluid (Steffe, 1996), the important role, beside temperature, which will be discussed below in details, has the chemical composition, volume ratio of whey components, degree of crystallization and other factors. Higher solids content the higher viscosity in the concentrate, but also during the crystallization the viscosity undergoes deep changes, partly due to the changes in temperature, but also due to the crystallization itself.

Figure 1 shows the experimental and computed data of viscosity–temperature dependence. Decrease of whey viscosity with increasing temperature was expected and corresponds with conclusions reported in literature (Herceg and Lelas, 2005; Krešić

I: *Kinematic viscosity of whey at different temperatures.*

Temperature [°C]	17	20	25	30	35	40	45	50	55	60	65	70	75	80	85	90
Kinematic viscosity [mm²/s]	105	85	75	72	70	69	68	60	53	33	25	21	21	20	19	12



1: *Temperature dependent viscosity, experimental and modeled data*

et al., 2008). It is obvious that dependence is far to be linear. The reason can be explained as an effect of chemical processes proceeding in the raw whey. In the native state, whey proteins are highly soluble. However, heating whey proteins can result in a loss of solubility due to denaturation of the proteins, especially in the pH range of 4.0 to 6.5. As the whey protein unfolds, hydrophobic amino acid residues are exposed. In their undenatured form, whey proteins can form rigid gels that hold water and fat, and provide structural support. The formation of disulfide bonds and ionic bonding controlled by calcium ions appears to determine gel structure (Leng and Turgeon, 2007).

Influence of temperature on whey kinematic viscosity was modeled. 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). Exponential model, often used for modeling of non-Newtonian fluids temperature dependencies is not perfectly suitable for whey behavior. Correlation of experimental and computed data has been calculated as $r^2 = 0.810$. Following general exponential model and coefficients have been used:

$$\nu = a\exp(b \cdot t) \qquad (1)$$

Coefficients: $a = 148.8$; $b = -0.02287$

Much better correlation ($r^2 = 0.993$) was achieved using polynomial model. Following parameters have been used:

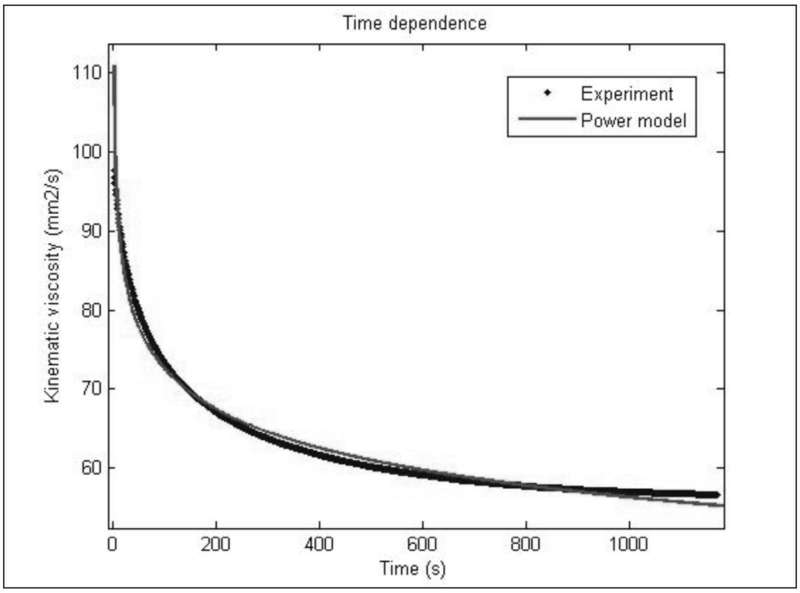
$$\nu = p1{*}t\text{^}8 + p2{*}t\text{^}7 + p3{*}t\text{^}6 + p4{*}t\text{^}5 + p5{*}t\text{^}4 + p6{*}t\text{^}3 + p7{*}t\text{^}2 + p8{*}t + p9 \qquad (2)$$

Coefficients: p1 = 7.567e – 011; p2 = –3.18e – 008; p3 = 5.636e – 006; p4 = –0.0005499; p5 = 0.03234; p6 = –1.179; p7 = 26.17; p8 = –325.9; p9 = 1830

The effect of temperature on viscosity of raw whey and whey protein concentrates is technologically important, since in most continuous heating processes, they will be subjected to a range of temperatures (0–60 °C). The similar mathematical relationship has been used by many researchers (Marcotte et al., 2001; Herceg and Lelas, 2005; Álvarez et al., 2006; Tavares et al., 2007; Severa and Los, 2008; Hlaváč, 2009) to describe the temperature dependency of rheological parameters. Tendency of viscosity decrease with increasing temperature was analogical in above mentioned works and presented study.

Time dependence of viscosity

Whey viscosity can be declared as time dependent. Several repeated measurements confirmed such conclusion. The time-dependent viscosity of whey was measured at constant shear rate of $34\,s^{-1}$. Typical experiment results are shown in Figure 2. At a constant share rate, the kinematic viscosity decreases relatively slowly (when avoiding starting non–relevant values) for first 10–20 minutes and then approaches a constant value corresponding to equilibrium state. Similar dependence was observed for the majority of samples. The decrease can be attributed to partial internal structure influence. Detailed study of microstructure in relation to flow properties and processing is given in Walkenström and Hermansson (2002). The rate and extent of viscosity change depend on both, applied shear rate and pre-measuring treatment. From the longer time-period point of view the whey proteins can also be modified through processing or enzymatic treatments that alter their structure to provide enhanced functionality for gelation, emulsification and viscosity changes.



2: *Time dependence of whey viscosity, experimental and modeled data*

Received data were fitted into power model with satisfying result $r^2 = 0.985$ and following parameters:

$$\nu = a \cdot t^b + c \quad (3)$$

Coefficients: a = 188.2; b = –0.04967; c = –77.22

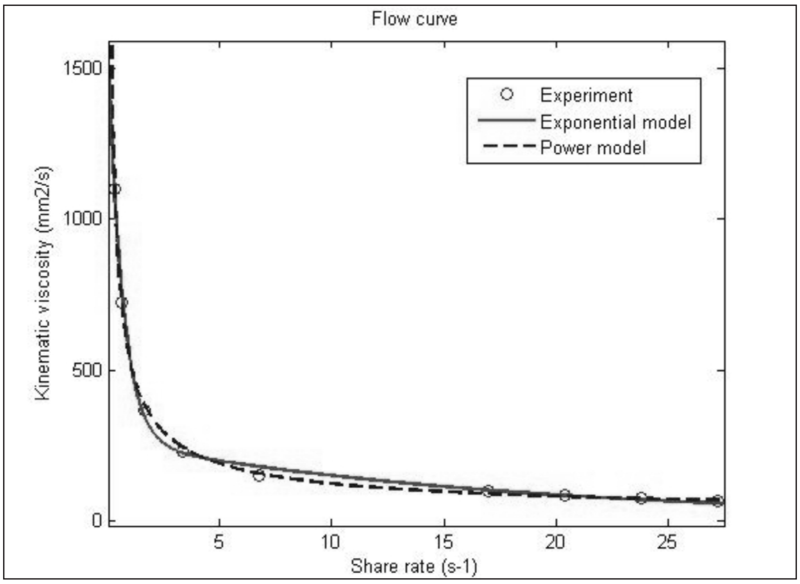
Similar behavior, time dependent thinning, was documented and described for other biological materials and/or semi-solid foodstuffs such as egg yolks (Atılgan et al., 2008; Severa et al., 2010), concentrated orange juices (Tavares et al., 2007), yogurts (Domagala et al., 2006), ketchups (Severa et al., 2005), mayonnaise (Figoni et al., 1983), and/or stallion ejaculate (Severa et al., 2008).

Shear thinning

The following research effort was focused on determining the rate dependence (0.34–68 s^{-1}) of viscosity. Such dependence is shown in Fig. 3. Fitted curves according to later mentioned equations show $r^2 = 0{,}997$ and $r^2 = 0{,}998$ correlation with measured data for exponential and power model, respectively.

II: *The values of kinematic viscosity as a function of share rate*

Share rate (s^{-1})	0.34	0.68	1.70	3.40	6.80	17.00	20.40	23.80	27.20	68.00
Kinematic viscosity (mm^2/s)	1100	726	365	230	150	96	83	76	67	64



3: *Shear dependence of whey viscosity, experimental and modeled data*

The Y-axis shows an average value of 5 measuring. Table II contains the experimental results.

Parameters of fitting models:

Exponential: $\nu = a\exp(b\cdot\dot{\gamma}) + c\exp(d\cdot\dot{\gamma})$ (4)

Coefficients: $a = 1405$; $b = -1.532$; $c = 261.1$; $d = -0.05635$

General Power: $\nu = a\cdot\dot{\gamma}b + c$ (5)

Coefficients: $a = 529$; $b = -0.678$; $c = 0.95$

According to Table II and Fig. 3. it may be observed that whey viscosity depends on shear rates, especially for values below approx. 5 s^{-1}. This indicates a range of non-Newtonian behavior and concentrated whey thus may be classified as shear thinning fluid. However, concerning whey protein isolate, Bazinet et al. (2004) reports that at 5 and 10% protein concentration (whatever the pH), the rheological behavior appeared to be a Newtonian, while at 20%, the rheological behavior appeared to be a non-Newtonian shear thinning.

As stated before, all our experiments have been conducted under room temperature (21 °C). It could be assumed that similar flow dependencies would be obtained for different experimental temperature conditions (obviously in different value levels). Presented data are in accordance with conclusions of Leng and Turgeon (2007) who used a Carreau model for shear-viscosity dependence description.

SUMMARY

The values of raw condensed whey kinematic viscosity, measured under different temperatures (17–90 °C) at share rate of 17 s^{-1}, show non-linear temperature dependence. The reason of this dependence can be explained as an effect of chemical processes proceeding in the raw whey concentrate. The dependence was mathematically fitted using polynomial model with satisfying correlation ($r^2 = 0.993$). Quantification of temperature dependence is technologically important. Since raw whey and whey protein concentrates are mostly subjected to heating processes in the range of 0–60 °C, it is critical to determine the material flow properties in this temperature region. The time-dependent viscosity of concentrated whey was measured at constant shear rate of 34 s^{-1}. Viscosity can be declared as time dependent. The kinematic viscosity decreases relatively slowly for first 10–20 minutes and then approaches a constant value corresponding to equilibrium state. Applied shear rate and premeasuring treatment influence both, the rate and extent of viscosity change. We can also conclude from the data presented in this study that the viscosity of concentrated raw whey is shear rate dependent, especially for values below approx. 5 s^{-1}. This indicates a range of non-Newtonian behavior and concentrated whey may be thus classified as shear thinning fluid. Correlation $r^2 = 0.998$ between experimental and computed data was achieved for power model. It can be also stated that there is an effect of a combined heat and shear treatment on the formation and rheological properties of fibrillar whey protein aggregates. Fibril growth is dependent on protein concentration (Akkermans et al., 2008). The results presented in this paper are quite useful for accurate design of technological equipment such as pumps and piping for raw whey shipping.

SOUHRN

Reologický profil surové syrovátky

Práce shrnuje výsledky měření reologických vlastností surové syrovátky, konkrétně její teplotní závislosti, časové závislosti a závislosti na rychlosti deformace. Vzorky syrovátky byly hodnoceny při teplotách od 17 do 90 °C a při rychlostech deformace v rozsahu 0,34 až 68 s^{-1}. Měření byla realizována na digitálním rotačním viskozimetru (s měřicí geometrií válec-válec). U materiálu byla zjištěna nelineární teplotní závislost, časová závislost a shear-thinning charakter. Teplotní závislost lze vysvětlit jako následek chemických procesů probíhajících v koncentrátu surové syrovátky. Závislost byla matematicky modelována za použití polynomového modelu, a to s uspokojivou shodou experimentu s modelem ($r^2 = 0{,}993$). Kvantifikace teplotní závislosti je technologicky významná. Vzhledem k tomu, že surová syrovátka a proteinové koncentráty jsou během technologického zpracování vystavovány především teplotám v rozsahu 0 až 60 °C, je velmi důležité stanovit jejich tokové vlastnosti právě v tomto teplotním rozsahu. Časová závislost byla hodnocena při rychlosti deformace 34 s^{-1}. Materiál byl shledán časově závislým. Kinematická viskozita klesala relativně pomalu během prvních 10 až 20 minut měření a následně dosáhla vyrovnané úrovně. Změny viskozity a jejich rychlost jsou ovlivněny zvolenou rychlostí deformace i přecházející manipulace se vzorkem. Závislost na rychlosti deformace je zvláště významná při hodnotách pod 5 s^{-1}. To ukazuje na ne-newtonowský charakter daného materiálu a surovou syrovátku lze prohlásit za shear-thinning kapalinu. Pomocí mocninného modelu bylo dosaženo korelace $r^2 = 0{,}998$ mezi experimentálními a modelovými daty. Výsledky prezentované v této práci mohou být využity při dimenzování a konstrukci technologických zařízení (např. čerpadel a potrubí) používaných pro manipulaci se surovou syrovátkou.

syrovátka, reologické vlastnosti, modelování

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