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Original Research

Rheopectic Behavior of Rendered Fat

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Abstract

Waste fat is an integral part of the processing of animal by-products in rendering plants. The flow behavior and time-dependent flow properties of waste fat in the temperature range of 10ºC, 20ºC, 30ºC, and 62ºC was studied. Waste fat presented non-Newtonian behavior. Three mathematical models were used for prediction of the flow behavior of waste fat, including the Casson, Steiger-Ory, and Herschel-Bulkley models. The Herschel-Bulkley model sufficiently described the flow behavior of the waste fat at different temperatures. Several kinds of rheological curves were determinated for description of the flow behavior. Rheopectic behavior of rendered fat was determinated at temperatures lower than 30ºC.

Keywords: rheopexy, rendered fat, Herschel-Bulkley, activation energy

Introduction

Measurement of rheological properties is very important and applies to many fields of human activity. The rheological properties determination of substances is important, especially for the design of devices for transportation, pumping, and storing of these substances. Rheological properties identification also plays an important role in food rheology, where rheology relates to quality control or sensory properties [1]. Application of the rheology is commonly used, for example, in the polymer [2], building [3], metallurgy [4], biomass processing [5], geology, and mining industries [6, 7], etc. An important application also is the use of rheology in waste management [8, 9]. A significant part of the waste management system is animal by-product treatment in rendering plants. Liquid waste products are produced in the process, where rheological properties are not sufficiently described in current papers. For example, rendered fat belongs between these wastes. During processing of animal by-products the fats are separated from meat and bone meal by pressing, centrifugation, or extraction.

The rendered fat is cleaned using a decanter after separation of rendered fat from meat and bone meal. Then cleaned fat is pumped to a storage tank. The temperature of pumped rendered fat is approximately 60ºC. From here the fat can be pumped to a boiler house, where it is burned. Or the fat is pumped to trucks and transported to other facilities for processing. The content of fats and proteins in the dry matter of meat and bone meal is approximately 50% [10]. The european commission in reference documents of best available techniques presents that an average of 15% fat is received during pressing. Rendered fats belong to significant components that represent input of rendering plant. Rendered fat is interesting material that has high energetic potential. At this time rendered fat is subjected to analyses and experiments focused on transesterification and etherification for purposes of bio-fuel production [11, 12]. Transesterification is a process that consists of mixing of methanol with sodium hydroxide and material with content of lipids (oils, fats etc.). A product of transesterification is biodiesel and glycerine. Rendered fats mostly consist of lipids (cca 90%) and from cca 10% by proteins [13]. However, fats generally change rheological behavior with temperature change. The reason is a creation of crystals that influence rheological behavior of fats. A crystal size, shape, arrangement of crystals and ability to form aggre-

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gations are also very important from the point of view of rheology [14]. Triacylglycerols crystallize around 32ºC [15]; a different paper states 31ºC [14]. Triaglycerols have an ability to create aggregates at these temperatures. For this reason there is an assumption that rendered fat behaves as a non-Newtonian fluid at a temperature lower than 32ºC. Experiments were performed at various temperatures.

Materials and Methods

The samples were collected from a rendering plant that processes animal by-products. A sample of rendered fat was transported to the laboratory at the same time. The sample was heated at 70ºC in the laboratory. During the temperature crystals were created in a minimal amount. Further individual samples were cooled to required temperature, in which rheological measurements were performed.

Rheological measurements of substances for the purposes of this paper were performed on an Anton Paar MCR 102 rheometr (Austria) with measuring geometry cone-plate. The diameter of the cone was 50 mm, angle of cone was 1º. Samples of rendered fat were tested at temperatures 10ºC, 20ºC, 30ºC, and 62ºC. 62ºC is the temperature of pumped rendered fat in the selected rendering plant. The flow curves were modeled using the following models:

Herschel-Bulkley model:

$$\tau = \tau_0 + K \cdot \dot{\gamma}^n \qquad (1)$$

...where: τ – shear stress [Pa], τ_0 – yield stress [Pa], K– consistency coefficient [-], n – flow behavior index [-], $\dot{\gamma}$– shear rate [s^{-1}].

Casson model:

$$\tau^{\frac{1}{2}} = \tau_0^{\frac{1}{2}} + k^{\frac{1}{2}} \cdot \dot{\gamma}^{\frac{1}{2}} \qquad (2)$$

...where: τ – shear stress [Pa], τ_0 – yield stress [Pa], k – Casson model constant [-], $\dot{\gamma}$ – shear rate [s^{-1}].

Steiger-Ory model:

$$\dot{\gamma} = a_1 \cdot \tau + a_2 \cdot \tau^3 \qquad (3)$$

...where: $\dot{\gamma}$ – shear rate [s^{-1}], τ – shear stress [Pa], $a_{1,2}$ – constants.

The change of dynamic viscosity in dependency on temperature was measured at 10 to 70ºC. Shear rate was constant with value 50 s^{-1}. Where dynamic viscosity is given by equation:

$$\eta = \frac{\tau}{\dot{\gamma}} \quad [\mathrm{Pa \cdot s}] \qquad (4)$$

...where: τ – shear stress [Pa], $\dot{\gamma}$ – shear rate [s^{-1}].

For determination of mathematical dependency between viscosity and increasing temperature we used the Arrhenius mathematical model, which is given by equation:

$$\eta = \eta_0 \cdot e^{-\frac{E_A}{RT}} \quad [\mathrm{Pa \cdot s}] \qquad (5)$$

...where: η_0 – initial value of dynamic viscosity [Pa·s], E_A – activation energy [J], R– universal gas constant [J·K^{-1}·mol^{-1}], T– thermodynamic temperature [K].

Individual measurements were performed in three replications. The arithmetic average was counted from measured values. In addition, the data set was tested by Grubbs's test.

Results and Discussion

The hysteresis loop experiment was performed in the first part of this paper. As given by Fig. 1, the rendered fat creates hysteresis loop at lower temperatures. This is the most evident at 10ºC and 20ºC. The hysteresis loop gradually expires at higher temperatures. For this reason 30ºC seems to be a critical temperature. This is due to the fact that, individually, types of crystals gradually melt around this temperature [15]. For this reason rheological properties of the fat also change. At 10ºC and 20ºC there is non-linear increasing of shear stress with increasing shear rate.

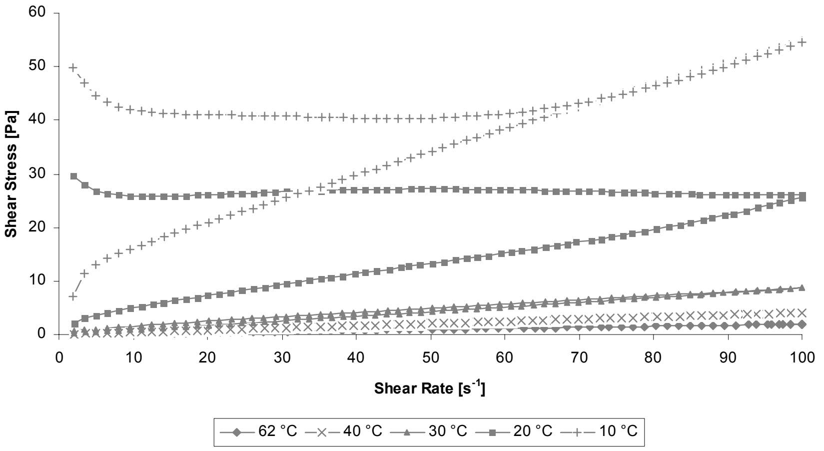

Fig. 1. Hysteresis loop of the flow curves of waste fat at different temperatures.

Table 1. Rheological parameters of the Steiger-Ory mathematical model.

Temperature [ºC]	R^2	a_1	a_2	Standard Deviation [s^{-1}]*
10	0.85994	0.062449	2.05E-05	10.865
20	0.93787	1.8337	0.00705	72.315
30	0.84448	7.6443	0.37014	11.441
62	0.99883	49.019	0.85071	0.99142

*relating to shear rate, a_1, a_2 – regression parameters (constants)

Table 2. Rheological parameters of the Casson mathematical model.

Temperature [ºC]	R^2	Yield Stress [Pa]	Casson Model Constant	Standard Deviation [Pa]*	η_{shear} [Pa·s]
10	0.98292	3.696	1.0183	57.288	10.369
20	0.96952	0.73123	0.42082	0.99628	0.17709
30	0.99742	0.25802	0.21766	0.086192	0.047375
62	0.99926	0.02531	0.13623	0.015475	0.018559

*relating to shear stress

Table 3. Rheological parameters of the Herschel-Bulkley mathematical model.

Temperature [°C]	R^2	Yield Stress [Pa]	Consistency Coefficient	*n*	Standard Deviation [Pa]*
10	0.99839	9.5765	9.2189	0.63627	17.603
20	0.99677	**	1.316	0.61578	0.32417
30	0.99906	0.25385	0.05838	1.0041	0.052018
62	0.99999	0.01184	0.01839	1.0129	0.0014992

*relating to shear stress, **makes no sense rheologically

When maximum shear rate value is achieved, subsequently the shear rate value decreases so values of the shear stress are lower compared to original values.

At this temperature it is time-dependent fluid. It is probable that the tested sample is rheopectic fluid at temperatures lower than 30ºC. The hysteresis loop is insignificant at 30ºC, and rendered fat behaves as Newtonian fluid with linear progression at 40ºC and 62ºC.

Rheological parameters of individual mathematical models are shown in Tables 1-3. The first model, Steiger-Ory model, is shown in Table 1. Steiger-Ory is used above all for describing of shear-thinning behavior. From this table it is evident that this model has relatively low values of determination coefficient R^2 for individual temperatures. But the Casson model attains higher values of determination coefficient R^2, and these values ranged from R^2 = 0.96952 at 20ºC to R^2 = 0.99926 at 62ºC. However, the Herschel-Bulkley mathematical model has the highest values of determination coefficient R^2 at each observed temperature (Fig. 3). The interval of values ranged from R^2 = 0.99677 to R^2 = 0.99999. Flow behaviour index *n* is one of the comparative parameters of Herschel-Bulkley. This index gives fluid behavior information. When index *n* is 1, the researched substance behaves as Newtonian fluid. However, when index *n* is more or less than 1, researched substances have properties of non-Newtonian fluids. Table 3 shows that rendered fat has index *n* approximatelly 1 at 30ºC and 62ºC. This means that rendered fat behaves as Newtonian fluid at these temperatures. But behavior of rendered fat is Non-Newtonian at 10ºC and 20ºC because the behavior flow index is less than 1. This index has similar values such as yellow grease. For example, Goodrum states that yellow grease has flow behavior index *n* = 0.64 at 23.9ºC [16].

The next important parameter is consistency index, which decreases with increasing temperature (Table 3). This is in accordance with the claim that the consistency index gives an idea of the viscosity of the fluid. The Herschel-Bulkley model is often used in food engineering. Applications of this model can determine yoghurt's rheological properties [17], buttermilk [18], or orange juice [19].

Viscosity dependency on increasing temperature is shown in Fig. 2, where it is evident that from approximately 26ºC to approximately 30ºC the viscosity suddenly changes. The cause of this is modification of the structure, where triacylglycerols crystals melt down. The density of some fats also changes from 26ºC [9]. The Arrhenius model

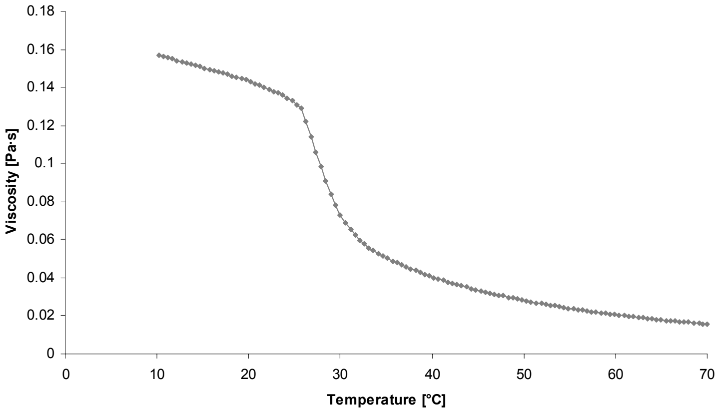

Fig. 2. Viscosity dependence on the increasing temperature of the waste fat.

was used to determine activation energy according to equation (5). The logarithm of this equation is:

$$\ln \eta = \ln \eta_0 + \frac{E_A}{R \cdot T}$$

Then function of dependency equals η = 4394.2/T – 17.098. This equation implies that the value of activation energy is $E_A = 36.5$ kJ·mol^{-1}.

The viscosity dependence on shear rate is shown on Fig. 4. On the graph it is evident that viscosity sharply decreases at the start of the experiment. The most significant decrease has rendered fat, which was tested at 10ºC. A contrarily insignificant decrease was measured at 30ºC, where viscosity is almost constant at all values of shear rate. At first sight the sample has shear-thinning behavior. According to some authors, fats (such as animal fats or their mixtures with oil)

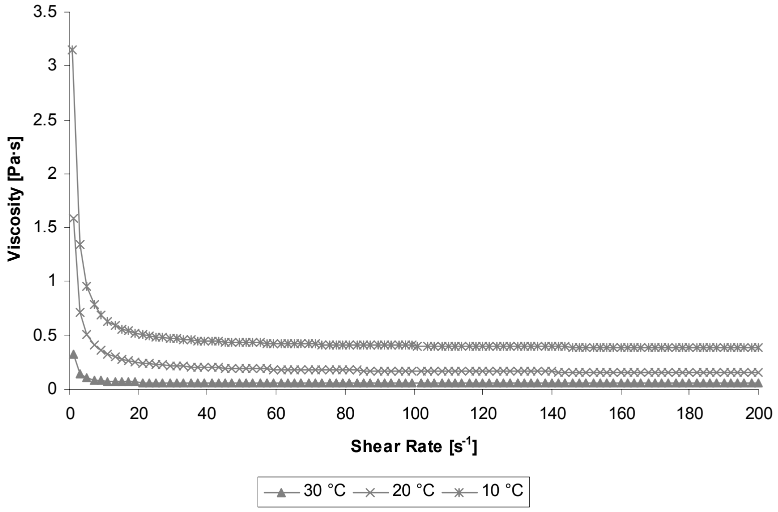

Fig. 3. Effect of the viscosity on the increasing shear rate at different temperatures.

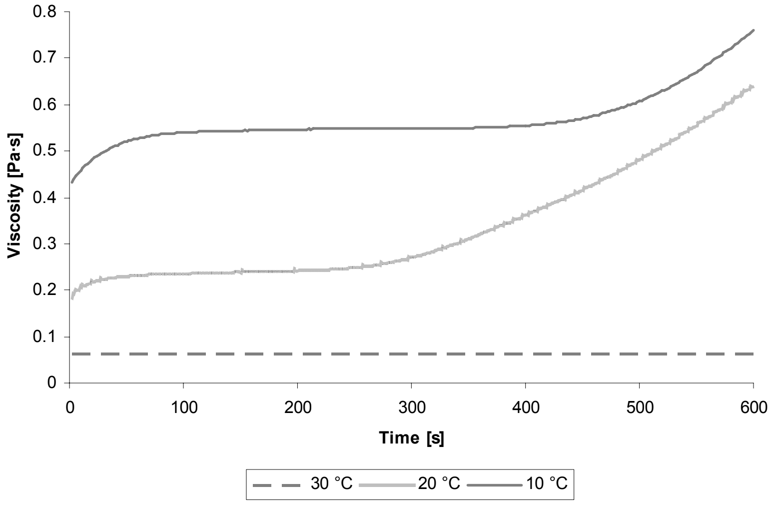

Fig. 4. Viscosity dependence on time shearing at different temperatures (measured without delay).

have shear-thinning behavior [20]. However, incorrect interpretation of rheological behavior can be frequent. For example, Goodrum describes rheological behavior of an animal fat and its mixture in [20], where fats have shear-thinning behavior. But the next rheological experiments are not performed (for example hysteresis loop). It cannot be said with certainty whether the behavior was really shear-thinning or behavior was, for example, thixotropic or rheopectic. However, testing of rendered fat (Fig. 1) shows that hysteresis loops are created and rheological behavior of tested samples is rheopectic. The next graphs (Figs. 4-7) shown viscosity dependency on time. At first the sample

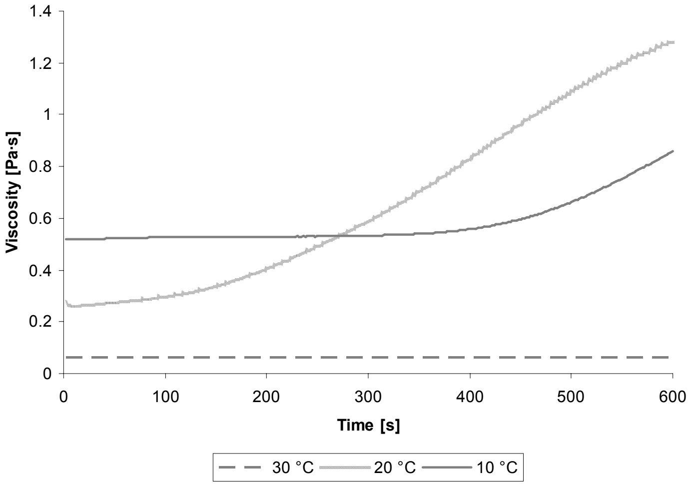

Fig. 5. Viscosity dependence on time shearing at different temperatures (measured with 5 min. delay).

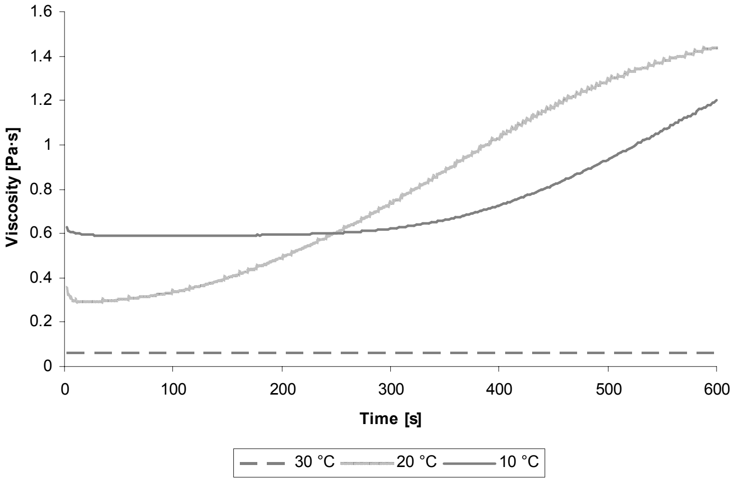

Fig. 6. Viscosity dependence on time shearing at different temperatures (measured with 10 min. delay).

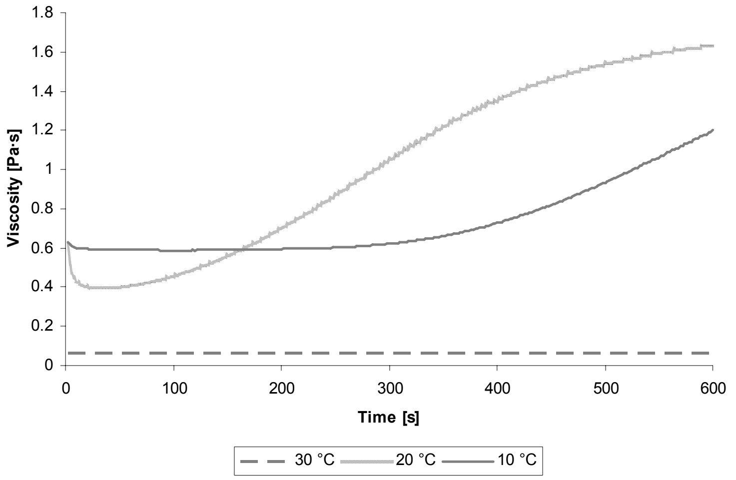

Fig. 7. Viscosity dependence on time shearing at different temperatures (measured with 15 min. delay).

was tested without delay (Fig. 4). Here it gradually increases viscosity, which is in accordance with the assumption about rheopectic behavior of the tested sample. Rheopectic behavior is probably caused by the creation of floccules in the sample. Furthermore, the sample was tested with 5, 10, and 15 minutes delay. During the time delay viscosity always increases because floccules created from the previous testing have no time for decomposition. At first during the short time interval there occurs a sharp increase of viscosity (this is especially evident at 20ºC). This effect is caused by measuring geometry of a rheometr. The destruction of parts of floccules occurs when starting up the rheometr. However, floccules create again after stabilization of shear rate. Direction of curve, which showed an increase of viscosity at 20ºC, is higher than the direction of the curve which showed an increase of viscosity at 10ºC. Values of viscosity at 20ºC are from a certain time period (in the case of a 5-minute delay it is 280 s) higher than viscosity values at 10ºC. The time interval when curves intersect together is shorter with increased delay time. However, the absolute value of viscosity at 10ºC is higher than the absolute value of viscosity at 20ºC. This effect is probably caused by the fact that velocity of molecules is higher at higher temperatures. For this reason the creation of floccules is faster.

Conclusion

Rendered fat from the rendering plant had non-Newtonian behavior. This rendered fat was described by three mathematical models: Casson, Steiger-Ory, and Herschel-Bulkley. On the basis of determining coefficient R^2, it was determined that Herschel-Bulkley is the most suitable model. In the interval from 26ºC to 30ºC we found that viscosity rapidly increases. This effect was caused by the fact that crystals start to melt. Activation energy was determined on the basis of dependency of viscosity on temperature and the Arrhenius mathematical model. After determination of individual flow curves the rendered fat was characterized as fluid with rheopectic behavior. The results of this work are very important for operators of rendering plants. Rheological behavior substances have a direct impact on the operation of various devices (for example pumps, mixers) and pipe design. Efficient operation of these devices has a direct impact on the economics of a rendering plant.

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