Modeling rheological of whey on function of shear rate, temperature and total solids concentration

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Abstract

The whey is the most abundant by-product of the dairy industry and its disposal in the environment without prior treatment is due to the lack of knowledge of its nutritional, physicochemical and phenomenological (rheological) characteristics of this by-product. The goal of this research was to study the rheological properties of whey as a function of temperature and concentration of total solids, for which viscous flow curves were developed in steady state with the increase in temperature (20 to 90°C) at different concentrations of total solids (25, 50, 75, 100%). The experimental data were measured with an Anton Paar MCR 301 rheometer and adjusted with the Rheoplus/32 V2. 81 software, obtaining the Herschel-Bulkley model as the rheological model that best describes the phenomenological behavior of whey. The results obtained showed that the whey is a non-Newtonian fluid with dilatant characteristics, where the viscosity increases with the increase in concentration and decreases with the increase in temperature. The design of factorial experiments 3k that allowed to determine the temperature as a factor of greater significant effect on the viscosity of the whey.

Keywords: Rheological models; Herschel-Bulkley; shear rate; temperature; concentration; whey.

Modelación reológica del suero de leche en función de la velocidad de corte, temperatura y concentración de sólidos totales

Resumen

El suero de leche es el subproducto más abundante de la industria láctea y su disposición en el medio ambiente sin un tratamiento previo se debe a la falta de conocimiento de sus características nutricionales, físicoquímicas y fenomenológicas (reológicas) de este subproducto. El objetivo de esta investigación fue estudiar las propiedades reológicas de suero de leche en función de la temperatura y concentración de sólidos totales, para ello se desarrollaron curvas de flujo viscoso en estado estacionario con el incremento de la temperatura (20 a 90°C) a diferentes concentraciones de sólidos totales (25, 50, 75, 100%). Los datos experimentales se midieron con un reómetro AntonPaar MCR 301 y se ajustaron con el software Rheoplus/32 V2. 81, obteniendo el modelo de Herschel-Bulkley como el modelo reológico que mejor describe el comportamiento fenomenológico del suero de leche. Los resultados obtenidos mostraron que el suero de leche es un fluido no Newtoniano con características dilatantes, donde la viscosidad aumenta con el incremento de la concentración y disminuye con el aumento de la temperatura. El diseño de experimentos factorial 3k permitió determinar a la temperatura como factor de mayor efecto significativo sobre la viscosidad del suero de leche.

Palabras clave: Modelos reológicos; Herschel-Bulkley; velocidad de corte; temperatura; concentración; suero de leche.
Introduction

Whey is a yellowish green liquid that results from the precipitation and removal of casein in the cheese making process [1]. This by-product of the dairy industry is an effluent containing mainly lactose and proteins as nutritionally important compounds, also minerals, vitamins, and fat. According to Guerra et al., [2] 1000 L of whey containing over 9 kg of proteins of high biological value, 50 kg of lactose and 3 kg of fat milk. In Mexico the traditional cheese factories, processed between 2000 and 10 000 L of milk per day [3], generating 90% of whey, which represents a significant loss of nutrients and valuable components. Rheology of food has been defined as the study of the deformation and flow of raw materials, intermediates and final products of the food industry [4]. Knowledge of the rheological properties is very useful for the preparation and handling of food involving fluid flow such as pasteurization, concentration, and dehydration [5] and in engineering applications that are related to the operations of process design, quality control, sensory evaluation, stability and consumer acceptance of a product [6]. Most liquid foods are complex rheological nature, because they are mixtures of liquid and solid [7], or dispersions of colloidal size, whose presence affects the stability and rheology of the fluid as result of interaction between suspended particles and the continuous medium. An example of this is dairy products, which are fat droplets, calcium phosphate particles of a colloidal size and different types of proteins that are suspended in a complex aqueous phase [8]. The rheological behavior of liquid foods can vary with some processing parameters, such as temperature and concentration, these being the most important and most studied factors, which gives rise to the need to establish mathematical correlations based on these variables, with the purpose of understanding the structure, mechanism and fluid flow behavior. The temperature effect is extensively studied because during processing, storage and transport the liquid food are subjected to different temperatures. Authors such as Cepeda & Villarán, [9]; Zainal et al., [10]; Arslan et al., [11]; Vandresen et al., [12]; and Karaman & Kayacier, [13] have described the effect of temperature on the viscosity at a specific shear rate by the Arrhenius model. While the effect of the concentration on viscosity, has been described by two equations, power and exponential, by Ibarz et al., [14]; Juszczak & Fortuna, [15]; da Silva et al., [16]; Rao, [17]; and Manayay & Ibarz, [18]. However, for engineering applications it is useful to obtain a single expression that can describe the combined effect of temperature and concentration on the viscosity. The goal of this study is to evaluate the effect of temperature and concentration on the rheological properties of whey from the production of cheese, with the purpose of using this by-product in a subsequent process.

Material and methods

Samples of whey were collected from the dairy Plauchú S.A de C.V which is in the Camerino Z. Mendoza city, Veracruz, Mexico.

Rheological measurements, data analysis, and modeling

Rheological properties were determined at steady state using an Anton Paar MCR 301, rotational rheometer with a vane geometry ST22-4V-40 four blades. Initially, the shear stress was measured with increasing temperature (20 to 90 °C) and varying shear rate (0 to 1000 s⁻¹). The fitted rheological model was obtained by RheoPlus/32 V2. 81 software. Type of fluid was established as a base on the shear stress ratio and shear rate, defining its behavior with respect to the Herschel-Bulkley rheological model (Eq.1), which includes models such as Newtonian, Bingham, Ostwald-de-Waele (power Law), commonly used to describe the rheological properties of foodstuffs [22].

\[ \sigma = \sigma_0 + K \gamma^n \]  

(1)

where \( \sigma_0 \) (Pa): shear stress, \( \sigma_0 \) (Pa): yield stress (minimum force required for the fluid to move), and is related to the internal structure of the material to be broken [23]), \( K \) (Pa sⁿ): coefficient consistency (proporionality constant indicating the degree of non-Newtonian viscosity), \( n \) (1): shear rate and \( B (\cdot) \): index of rheological behavior (indicating the proximity of the fluid to a Newtonian fluid. For a Newtonian fluid \( n = 1 \), for a dilatant fluid \( n > 1 \) and pseudoplastic fluid \( n < 1 \).

Temperature and concentration effect on the apparent viscosity

Temperature effect on the viscosity was described by Arrhenius model (Eq.2) and the equation proposed by Košmerl et al., [24] (Eq. 3).

\[ \eta_a = \eta \exp \left( \frac{E}{RT} \right) \]  

(2)

\[ \ln \eta_a = a + \frac{b}{T} + \frac{c}{T^2} \]  

(3)
Two relationships, power (Eq. 4) and exponential (Eq. 5) described concentration effect on the viscosity. Whey samples were prepared in duplicate with a total solids concentration of 17, 34, 50 and 65 g/L i.e., 25, 50, 75 and 100% of the total solids presents in whey.

\[
\eta_a = \eta_0 C^{a_1} \quad \text{(4)}
\]

\[
\eta_a = \eta_0 e^{a_2 C} \quad \text{(5)}
\]

where \( \eta_a \) (Pa s) apparent viscosity at a given shear rate, \( \eta_0 \) (Pa s) zero-shear viscosity, Ea \((1/gmol)\) activation energy of flow, \( R \) \((J/gmol K)\) constant of gases, \( T \) (K) absolute temperature, \( a_1 \) (-), \( b \) (K), \( c \) (K2), \( a_2 \) (L/g) and \( C \) (g/L) concentration of total solids. Design of 32 factorial experiments was developed to evaluate which factor (temperature, concentration) significantly influence on the viscosity of whey. Factors were evaluated at 3 levels (low, medium and high) where the response variable is viscosity. Nine experiments were carried out with a replicate, giving a total of 18 experiments. Experimental data were analyzed statistically in NCSS 2007 software.

**Combined effects: shear rate-temperature, temperature-concentration on the viscosity**

The combined effect of the shear rate-temperature it was modeled by the equation proposed by Harper & Sahrigi, [25] (Eq. 6), in which \( \tilde{n} \) (-) is the rheological behavior index average based at all temperatures within the range studied. Viscosity was measured at three shear rates (300, 500 and 1000 s-1) and temperature (25, 50 and 90 °C).

\[
\eta_a = \eta_0 e^{(-\frac{E_a}{RT})/\tilde{n}^{n-1}} \quad \text{(6)}
\]

The combined effect of temperature-concentration was expressed by two models that combine Arrhenius model with exponential (Eq.7) and power(Eq.8) equation[26], where \( a_1 \) (L/g) and \( a_2 \) (-) are constants. Viscosity was measured at three different temperatures (20, 45 and 90 °C) and three different total solids concentrations (15, 30 and 60 g/L) at the shear rate fixed of 500 s-1.

\[
\eta_a = \eta_0 e^{-\frac{E_a}{RT}} C^{a_2} \quad \text{(7)}
\]

\[
\eta_a = \eta_0 e^{-\frac{E_a}{RT}} C^{a_1} \quad \text{(8)}
\]

**Effect of concentration on activation energy**

Variation of the activation energy with respect to the concentration was modeled using two functions: power (Eq.9) and exponential (Eq.10) types [27].

\[
E_a = A_1 C^{b_1} \quad \text{(9)}
\]

\[
E_a = A_2 e^{b_2 C} \quad \text{(10)}
\]

where \( A_1 \) (J/gmol L), \( A_2 \) (J/gmol), \( b_1 \) (-) and \( b_2 \) (L/g) are proportionality constants.

**Combined effect of shear rate-temperature-concentration on the viscosity**

The combined effect of shear rate-temperature-concentration was determined experimentally combined in a single expression [28].

\[
\eta_a = \eta_0 \tilde{n}^{n-1} e^{(-\frac{E_a}{RT})+d_1 C} \quad \text{(11)}
\]

\[
\eta_a = \eta_0 e^{-\frac{E_a}{RT} C^{d_2 \tilde{n}^{n-1}}} \quad \text{(12)}
\]

where, \( d_1 \) (L/g) and \( d_2 \) (-) are constants.

**Results and discussion**

**Rheological behavior whey**

Figure 1 shows the rheograms in different isotherms. Whey exhibits non-Newtonian behavior with dilatant characteristics, where the shear stress increases nonlinearly with shear rate increase. According to Tolbarz & Barbosa-Canovas [29], the dilatant behavior is due to the presence of particles of different sizes and shapes that are tightly packaged, making the flow more difficult, this be-
cause at a shear rate increase, the particles long and flexible are stretched. Therefore, the non-Newtonian behavior of whey is attributed to high molecular weight material (remaining proteins) that are suspended in the aqueous phase thus forming a complex solution.

Figure 1. Whey rheograms

Figure 2 shows the viscosity as a function of shear rate (flow curve), it is observed that the viscosity decreases with increasing temperature, this can be attributed to that molecules energy gain, which eventually forces weaken cohesion between them causing an increase in the intermolecular space and consequently increases the movement within the fluid [11,30]. Table 1 presents the Herschel-Bulkley models found experimentally for each isotherm. Models feature an appropriate adjustment ($R^2 > 0.98$). Yield stress parameter indicates the presence of soluble solids (sugars, proteins, and minerals), a typical characteristic of multiphase fluid [31]. Below the initial value of the yield stress ($\sigma_0$) whey is deformed as an elastic fluid, so it is concluded that the whey needs a small shear stress to behave as a viscous fluid. Index values of rheological behavior ($n$) indicate the effect of shear thickening during all tests at different temperatures.

Figure 2. Whey flow curves

| Table 1. Herschel-Bulkley experimental models for each isotherm |
|---------------------|----------------------|-------|
| T(°C) | Herschel-Bulkley experimental models (mPa) | $R^2$ |
| 20 | $\sigma = 30.746 + 0.099217\gamma^{1.843}$ | 0.9884 |
| 30 | $\sigma = 36.655 + 0.093253\gamma^{1.843}$ | 0.9864 |
| 40 | $\sigma = 46.37 + 0.075929\gamma^{1.859}$ | 0.9899 |
| 50 | $\sigma = 41.737 + 0.071000\gamma^{1.862}$ | 0.9859 |
| 60 | $\sigma = 48.416 + 0.063756\gamma^{1.870}$ | 0.9867 |
| 70 | $\sigma = 45.944 + 0.075479\gamma^{1.836}$ | 0.9891 |
| 80 | $\sigma = 51.014 + 0.099227\gamma^{1.789}$ | 0.9843 |
| 90 | $\sigma = 0.035091\gamma^{1.599}$ | 0.9651 |

Figure 3 shows that the increasing the temperature increases the yield stress of potential form, this is due to the presence of proteins remaining in the whey, that being heat denatured become more viscous solutions, this behavior was modeled by a function of potential type (Eq.13). Rheological behavior index remained constant slightly until a temperature of 60 °C, subsequently decreased sharply indicating that the increase in temperature reduces the dilatant behavior. Correlation between the index of rheological behavior in relation to temperature is modeled by a potential sigmoidal function (Eq.14).

Figure 3. Parameters of Herschel-Bulkley model as a function of temperature. Shear stress and flow behavior index
\[ \sigma_0 = 12.77T^{0.3154} \quad R^2 = 0.80 \quad (13) \]

\[ n = \frac{1.855}{1+(0.01T)^{12.37}} \quad R^2 = 0.9836 \quad (14) \]

Temperature and concentration effect on apparent viscosity

The viscosity of liquids usually decreases with increasing temperature. Figure 4 shows that the temperature has a significant effect on viscosity whey, that is, the viscosity decreases with increasing temperature, and the equation proposed by Košmerl et al., [24] best describes this effect. Table 2 shows the experimental models of Equations 2 and 3. The low activation energy of Arrhenius model shows that whey has little variation in viscosity with increasing temperature since high values of activation energy of the flow indicate a rapid change of fluid viscosity with temperature [32].

\[ \text{Table 2. Experimental model of Arrhenius model and Košmerl et al., 2000 equation} \]

<table>
<thead>
<tr>
<th>Experimental model</th>
<th>Arrhenius</th>
<th>( \eta_a = 2.76e^{\frac{40.17}{RT}} )</th>
<th>0.93728</th>
</tr>
</thead>
<tbody>
<tr>
<td>Košmerl et al., 2000 equation</td>
<td>( \ln \eta_a = 11.798 - 51.04/T + 70.247/T^2 )</td>
<td>0.98921</td>
<td></td>
</tr>
</tbody>
</table>

Figure 5 shows that the viscosity of whey increases as increases the concentration of total solids, this is because with increasing solute concentration there is greater interaction between the solute and the continuous medium and as consequently there is a restriction on the movement of particles.

\[ \text{Figure 5. Concentration effect on viscosity of whey} \]

Table 3 presents the experimental models of Equations 4 and 5. Exponential model best represents the concentration effect; Juszczack & Fortuna, [15], reported the same phenomenon in cherry juice. Power model has been successful in mashed fruits and vegetables highly viscous, but for concentrated fruit juices, concentrated apple juice and in our case study the exponential model provides best settings. This is because according Hassan & Hobani, [33] the exponential model was found to produce a better fit than the power type relationship.

\[ \text{Table 3. Power and exponential experimental models} \]

<table>
<thead>
<tr>
<th>Experimental model</th>
<th>( \eta_a = 13.14e^{0.0689} )</th>
<th>0.96044</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Exponential</td>
<td>( \eta_a = 15.56e^{0.0092} )</td>
<td>0.97819</td>
</tr>
</tbody>
</table>

Table 4 presents the matrix of the 32 factorial design that was followed to evaluate the combined effect of temperature-concentration on the viscosity of the whey at a shear rate of 500 s\(^{-1}\).
Modeling rheological of whey, on function of shear rate, temperature and total solids concentration

Table 4.
Factors and levels used in the design of experiments

<table>
<thead>
<tr>
<th>Encoded factors</th>
<th>( \eta_i ) (mPa) at 500 s(^{-1} )</th>
<th>Factors</th>
<th>Factors levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>B</td>
<td>Run I</td>
<td>Run II</td>
</tr>
<tr>
<td>-1</td>
<td>-1</td>
<td>17.60</td>
<td>17.00</td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>14.45</td>
<td>14.40</td>
</tr>
<tr>
<td>1</td>
<td>-1</td>
<td>12.25</td>
<td>12.00</td>
</tr>
<tr>
<td>-1</td>
<td>0</td>
<td>17.15</td>
<td>17.45</td>
</tr>
<tr>
<td>0</td>
<td>0</td>
<td>14.60</td>
<td>14.65</td>
</tr>
<tr>
<td>1</td>
<td>0</td>
<td>12.35</td>
<td>12.60</td>
</tr>
<tr>
<td>0</td>
<td>-1</td>
<td>18.65</td>
<td>18.60</td>
</tr>
<tr>
<td>1</td>
<td>1</td>
<td>15.60</td>
<td>15.75</td>
</tr>
<tr>
<td></td>
<td>1</td>
<td>13.60</td>
<td>13.45</td>
</tr>
</tbody>
</table>

Table 5. Analysis of variance

<table>
<thead>
<tr>
<th>Factors</th>
<th>DF</th>
<th>Sum of Square</th>
<th>Mean of Square</th>
<th>F-Ratio</th>
<th>Prob Level</th>
<th>Power Alpha=0.05</th>
</tr>
</thead>
<tbody>
<tr>
<td>A: Temperature</td>
<td>2</td>
<td>76.4044</td>
<td>38.20222</td>
<td>1095.84</td>
<td>0.000000*</td>
<td>1.000000</td>
</tr>
<tr>
<td>B: Concentration</td>
<td>2</td>
<td>6.185278</td>
<td>3.092639</td>
<td>88.71</td>
<td>0.000001*</td>
<td>1.000000</td>
</tr>
<tr>
<td>AB</td>
<td>4</td>
<td>0.082222</td>
<td>0.020555</td>
<td>0.59</td>
<td>0.678709</td>
<td>0.136144</td>
</tr>
<tr>
<td>S</td>
<td>9</td>
<td>0.31375</td>
<td>0.034861</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total (Adjusted)</td>
<td>17</td>
<td>82.98569</td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Total</td>
<td>18</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

* Term significant at alpha = 0.05

Analysis of variance (Anova) (Table 5) shows that the factor A (Temperature) and B (Concentration) have significant effects on the viscosity since it shows a value lower than 0.05, the value set for the level of significance (\( \alpha = 0.05 \)). Factor A (temperature) have the greatest effect on the viscosity of the whey, i.e. apparent viscosity is more sensitive to temperature than to concentration. According to Anova, the interaction between the factors is not significant since its values of significance are above the established level of significance.

Combined effect: shear rate-temperature, temperature-concentration on apparent viscosity

Figure 6 shows that the viscosity of whey increases with increasing the shear rate and decreases with increasing temperature, the shear rate being the most significant factor on this property of the fluid. The model found experimentally (Eq.15) adequately predicts the combined effect of shear rate and temperature by presenting an appropriate correlation coefficient.
\[ n = 6.0926 \times e^{(-0.5324x + 0.2967y)} \quad R^2 = 0.9856 \quad (15) \]

Figure 7 shows the response surface with experimental model 16, and figure 8 with experimental model 17, in both figures it can be observed that increasing concentration and decreasing temperature increase the viscosity whey, same effect as authors found as Cepeda & Villarán, [9]; Chin et al., [34] working with liquid foods. Both experimental models present a correlation coefficient suitable to model whey viscosity as a function of temperature and concentration.

\[ n = 2.85e^{(-0.0024x + 0.0012y)} \quad R^2 = 0.97196 \quad (16) \]

\[ n = 2.46e^{(-0.00328x + 0.00128y)} \quad R^2 = 0.96162 \quad (17) \]

**Concentration effect on the flow activation energy**

Figure 9 shows the relationship between the concentration and the activation energy, the calculated value \( E_a \) low concentration was highest indicating that the viscosity is more affected by the temperature at low concentration, i.e., the activation energy decreased with increasing concentration. Saravacos [35] and Grigelmo-Migué et al., [36] reported that the flow activation energy decreases with the presence of suspended particles, this is because as the concentration increases the number of collisions of particles in the fluid increases and consequently it increases the movement in the fluid. The \( E_a \) values were found was between 450.94 and 3867.74 J/gmol.

![Figure 8. Combined effect temperature concentration on the viscosity of whey (Eq.16)](image)

![Figure 9. Combined effect temperature concentration on the viscosity of whey (Eq.17)](image)

![Figure 9. Concentration effect on the flow activation energy](image)

Table 6 shows the experimental models found of the equations 9 and 10. The potential model is the one that best describes the relationship between concentration and flow activation energy.

<table>
<thead>
<tr>
<th>Experimental model</th>
<th>( E_a )</th>
<th>( R^2 )</th>
</tr>
</thead>
<tbody>
<tr>
<td>Power</td>
<td>( 6065.20C^{-0.11136} )</td>
<td>0.97346</td>
</tr>
<tr>
<td>Exponential</td>
<td>( 4658.57e^{-0.00328C} )</td>
<td>0.81457</td>
</tr>
</tbody>
</table>

Finally, two rheological models were found experimentally, these models adequately describe the apparent viscosity of whey according to the shear rate, temperature and concentration by presenting a correlation coefficient \( R^2 = 0.99 \). These models will be a useful tool for engineering applications later in the design process, as well as quality control and sensory evaluation.

\[ n = 0.0187x^{0.03166}e^{(-0.5324x + 0.2967y)} \quad R^2 = 0.9938 \quad (18) \]

\[ n = 5.0474e^{(-0.0024x + 0.0012y)} \quad R^2 = 0.9941 \quad (19) \]
Conclusions

Modeling provides a means of representing a large quantity of rheological data in terms of a simple mathematical expression. Whey in the range of temperatures and concentrations studied showed non-Newtonian behavior with dilatant characteristics that can be described by the rheological model of Herschel-Bulkley. The viscosity of the whey is directly affected by the temperature and concentration, decreasing with increasing temperature, and increasing with increasing concentration. Arrhenius equation adequately modeled the effect of temperature on the apparent viscosity but does not follow the trend of experimental data so that is the equation proposed by Koršmel; better described the rheological behavior whey regarding temperature. Effect of concentration on the variation of the apparent viscosity of whey adequately described by the exponential model. The flow activation energy varied from 4505.94 to 3867.74 J/gmol to a variation of 15 to 60 g/L total solids.

References


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