RHEOLOGICAL PROPERTIES OF HONEY FROM BURKINA FASO: LOSS MODULUS AND COMPLEX VISCOSITY MODELLING

Shortened title: Rheological properties of honey from Burkina Faso

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Abstract

This study evaluates the rheological behaviour of Burkina Faso honey and the use of exponential and polynomial models to predict the influence of chemical composition and temperature on the viscoelastic parameters: complex viscosity (η*) and loss modulus (G’’). Samples were first characterized evaluating: water activity, HMF, sugars (fructose, glucose and sucrose), electrical conductivity, moisture and colour. Dynamic rheological properties were obtained at different temperatures (5, 10, 15, 20, 25, 30 and 40°C). All the honeys displayed Newtonian behaviour. Complex viscosity and loss modulus can be predicted based on the chemical composition and temperature using polynomial models (R² > 98.00%).

Keywords: honey, rheology, complex viscosity, loss modulus
Introduction

In Burkina Faso, situated in West Africa, beekeeping activities have increased in the last years, thanks in part to the installation of beekeeping promotion centres, sponsored by beekeeper organizations [1]. These activities are helping in the production of honey and therefore, are playing an important role in society by creating sustainable livelihoods. The current development in Burkina honey production is reflected in the number of scientific papers published in recent years. For example, different authors studied the impact of storage conditions on the physicochemical characteristics of Burkina Faso honey [1]; the impact of climatic changes on nectar considering honey production by honeybee colonies in a specific zone of Burkina Faso [2]; the compliance of international standards related to the importation and sale of honey in Burkina Faso [2].

As far the authors know, there is no research related to the rheological properties of honey from this country. Knowledge about the rheological behaviour of viscous food stuff is useful in quality and process control [3]. The importance of measuring the rheological properties of honey is reflected in the volume of research published in the last decade about honey from different countries [4, 5]. For this reason, the aim of this study was to predict the influence of chemical composition and temperature on the viscoelastic parameters of honey (complex viscosity ($\eta^*$) and loss modulus ($G''$)) using the exponential model and the polynomial model. As honey rheology is directly related to different chemical parameters [3, 5, 6], samples were first characterized from a chemical point of view.

Materials and methods

Honey samples

Honey (18 samples) from three different places (Kampène, Bouroum-Bouroum and Passena) in the Poni region situated in the Southwestern region of Burkina Faso were provided by beekeepers. As
the rheological parameters of honeys can be influenced by the presence of crystals and air bubbles [7, 8], they were warmed up to 55 °C before being used, and kept in flasks at 30 °C to remove air bubbles that could interfere with rheological studies [4].

**Physicochemical analyses**

The physicochemical properties (HMF, moisture, electrical conductivity) and Pfund colour, were determined according to the harmonised methods of the international honey commission [9]. Water activity (aw) was measured at 25 °C (± 0.2 °C) using an electronic dewpoint water activity meter, Aqualab Series 4 model TE (Decagon Devices, Pullman, Washington, USA), equipped with a temperature-controlled system [10]. Sugars content (glucose, fructose and sucrose) were analysed in a HPAEC-PAD high-resolution ionic chromatograph with a pulsed amperometric detector (PAD) (Bioscan, Methrom, Switzerland) and a Metrosep Carb chromatographic column (styrene divinyl benzene copolymer, 4.6 × 250 mm). Carbohydrates were eluted with NaOH 0.1N at a flow rate of 1 mL min⁻¹ [11].

**Viscoelastic measurement**

A RheoStress 1 rheometer (Thermo Haake, Germany) was used to determine the dynamic rheological properties of honey samples at different temperatures (5, 10, 15, 20, 25, 30 and 40°C), by means of a parallel plate system (Ø 60 mm) with a gap of 500 µm. The measurement at each temperature was carried out twice using a fresh sample of honey. The sample was loaded, and left for 5 min to allow the sample to reach the desired temperature. With the aim of determining the linear viscoelastic range, stress sweeps were run at 1 Hz first. Then, the frequency sweeps were performed over the range ω=0.62–62.83 rad/s at 1 Pa stress. The 1 Pa stress was in the linear viscoelastic range. The experimental data were used to calculate storage (or elastic) modulus (G'),
Results and discussion

Physicochemical characterization

Different physicochemical parameters were analysed: HMF, moisture, electrical conductivity, Pfund colour, water activity content, and sugars content (glucose, fructose and sucrose).

The HMF content (widely recognized as an indicator of freshness) ranged between 1.02-35.60 mg/kg. All samples were in agreement with the Council Directive relating to honey [12], because in all cases the values of this parameter were lower than 40 mg/kg. However, in some cases the value was close to this limit, too high considering that they were raw honeys. These values were lower than those reported in honey from Burkina Faso [1, 2]. The moisture varied from 17.9 to 22.1 g/100g, in some samples exceeding the 20g/100g limit established by the Council Directive relating to honey [12]. The high electrical conductivity (between 683 and 1022 µS/cm) and Pfund colour values (91 to 150) of the samples indicates that the great majority of the analysed honeys could be considered to be honeydew. These values were in the same range with those reported by other authors in Burkina Faso honey [1, 2]. With respect to water activity, the values ranged between 0.61-0.66, higher than the values reported by other authors [13]. The inverted sugar and sucrose content had a range of 62-78 g/100g, and 1-2 g/100g, respectively, meeting the Council Directive relating to honey [12].

Rheological properties of honey

Figure 1 shows the rheograms for three honeys, each from one of the different areas studied in the Poni region of Burkina Faso: 1. Kampêne, 2. Bouroum-Bouroum and 3. Passena. It can be
observed that the rheological parameters analysed (complex viscosity (η*), loss modulus (G’’) and storage modulus (G’)) are strongly influenced by temperature. The values of the rheological parameters (G’, G’’, η) increased with the frequency applied to the sample, showing that G’’ had a greater magnitude than G’. Regarding the complex viscosity, the values were not influenced by the frequency applied. Therefore, it can be ascertain that the honey behaved as a Newtonian fluid (fig. 1) as in the case of honey from other countries such as Romania [4] and Spain [5, 14].

In general, G’ is less important than G’’ due to its low value with respect to G’’ (G’’ > G’) [15]. Consequently, different authors noted that the elastic behaviour of honey seems to be less important than its viscous behaviour [16]. The rheological properties of honey can also be affected by other factors such as sugars and other polymeric compounds [4, 17]. In particular, as these sugars have different rheological properties, the rheological behaviour can be greatly affect by the sugar content (glucose and fructose)

The data for loss modulus and viscosity will be used to obtain the best prediction model. Exponential and polynomial models will be applied, and presented below, to predict the influence of chemical composition and temperature on these two viscoelastic parameters.

**Viscosity modelling**

**Effect of Temperature**

The influence of temperature on the complex viscosity of honey is described using the Arrhenius model, which is:

\[ \eta^* = \eta_0^* \cdot \exp \left( - \frac{E_a}{RT} \right) \]  

(eq. 1)
Where: $\eta_0$ is a constant, $R$ is the gas constant [kJ·mol$^{-1}$·K$^{-1}$], and $E_a$ activation energy (an energy barrier to flowing) [kJ·mol$^{-1}$], $T$ – absolute temperature [K]. With respect to activation energies, their magnitude ranged between 41.07–48.58 kJ/mol. These values are strongly influenced by the moisture content; decreasing with the increase in the moisture content. The activation energies for the Burkina Faso honey presented in this study are smaller than those reported in the case of Romanian honeys [4] and in Spanish honeys [3, 5] due to the high moisture content of Burkina Faso honey to the honeys from Romania and Spain. The data were fitted well to the Arrhenius model (the regression coefficients are around 0.99).

Effect of Concentration

The influence of the concentration ($C$), expressed in °Brix, on the complex viscosity of honey was described by power-law (eq. 2):

$$\eta^* = \eta_1^* C^{a_1} \quad (eq. 2)$$

and exponential models (eq. 3) [15]:

$$\eta^* = \eta_2^* \exp(a_2 C) \quad (eq. 3)$$

Where: $C$ is the concentration in °Brix and $\eta_1, \eta_2, a_1, a_2$ are constants. The model parameters have been computed using non-linear regression. According to the regression coefficients values ($R^2$) both models are suitable for predicting the influence of concentration on complex viscosity of honey.

In order to calculate the model constants, the viscosity data were fitted to equations 2-3 by non-linear regression. The resulting values of the constants are presented in table 1. The coefficients of regression ($R^2$) are very similar, so the two models are suitable for describing the effect of the
soluble solids on honey viscosity. However, using the absolute average deviation it seems that the power law model is more suitable for predicting the influence of concentration on the complex viscosity of honey.

For a given temperature, the activation energy ($E_a$) for flow is influenced by soluble solid content, which can be described by several models [18]. In the present work, two models have been used (eq.4 and eq.5).

\[ E_a = A_1 C^{B_1} \]  
\[ E_a = A_2 \exp(B_2 C) \]  

Where, $A_1$, $A_2$, $B_1$ and $B_2$ are constants. The activation energies and the model parameters were computed by non-linear regression. The coefficients of regression ($R^2$) of the two models proposed above are the same. Computing the absolute average deviation of the activation energies, it can be observed that the exponential model was better than the power law model in describing the dependency of $E_a$ on $^\circ$Brix concentration.

**Combined effect of temperature and concentration**

In practise, it is useful to obtain a general equation of the combined influence of the temperature and concentration on complex viscosity of honey [19]. Figure 2 shows the combined influence of temperature and concentration on honey viscosity.

In this paper two models of complex viscosity of honey were investigated (eq. 6 and eq.7):

\[ \eta^* = \eta^*_3 \exp(E_1 C + E_a / RT) \]  
\[ \eta^* = \eta^*_4 C^{E_2} \exp(E_a / RT) \]  


The parameter data used in the two equations were fitted to these models by the non-linear regression, and the values of the model constants were determined. The complex viscosity predictions with temperature and °Brix concentration achieve coefficients of regression between 0.644 and 0.898 (table 2). The AAD certifies that the suitable model corresponds to eq. 6.

Therefore, for the interval of °Brix concentrations and temperatures (T) studied, the following equation (eq.8) is suggested for evaluating honey viscosity:

$$\eta^* = 3.98 \cdot 10^{-17} \cdot \exp(0.275 \cdot C + 420.03 / RT)$$  \hspace{1cm} (eq. 8)

Polynomial modelling of viscosity

The data model which predicts the complex viscosity of honey according to its chemical composition (sugars, non-sugars components, moisture content, etc.) and temperature was made using a 3rd degree polynomial equation with seven variables. The measured and predicted values were compared to check the appropriateness of the model. The equation of the model is as given (eq. 9):

$$\eta^*_\text{pred} = b_0 + \sum_{i=0}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} b_{ij} x_i x_j + \sum_{i<j}^{n} b_{ij} x_i x_j + \sum_{i<j}^{n} b_{ij} x_i x_j + \sum_{i<j}^{n} b_{ij} x_i x_j$$  \hspace{1cm} (eq. 9)

Where: $\eta^*_\text{pred}$ is the loss modulus predicted, $b_0$ is a constant that fixes the response at the central point of the experiments, $b_i$ – regression coefficient for the linear effect terms, $b_{ij}$ – interaction effect terms, $b_{ii}$ – quadratic effect terms and $b_{iii}$ – cubic effect terms. The operating region and the levels of the design variables, key factors, are shown as actual and coded values in table 3.

A 3rd order polynomial equation with 7 variables for viscosity was obtained as follows based on the design variables (eq.10):
\[
\log(\eta^\prime) = 0.59 - 1.53 \cdot X_1 + 1.36 \cdot X_2 - 0.34 \cdot X_3 + 0.05 \cdot X_1^2 + 0.13 \cdot X_1 \cdot X_3 - 0.10 \cdot X_2 \cdot X_3 - 0.16 \cdot X_3^2 + 0.38 \cdot X_1 \cdot X_3^2
\]

\[-0.33 \cdot X_1 \cdot X_1^2 + 1.27 \cdot X_1 \cdot X_3^2 + 1.07 \cdot X_1 \cdot X_3^2 \]

(eq. 10)

The coefficient of regression of the proposed model (P=0.005) represents 99.38% (R^2 adjusted 98.87%, ADD = 16.60). In figure 3 the measured and predicted values of viscosity are represented. According to equation 10, it can be observed that moisture content and non-sugar substances do not influence the equation. Fructose and temperature have a negatively linear influence while glucose has a positive one.

**Loss modulus modelling**

_Influence of Temperature_

The influence of temperature on honey loss modulus was also studied using the Arrhenius model.

\[
G'' = G_0'' \cdot \exp \left[ -\frac{E_a}{RT} \right] 
\]

(eq. 11)

Where: G_0 is a constant, R is the gas constant [kJ·mol\(^{-1}\)·K\(^{-1}\)], and E_a activation energy (the energy barrier to flowing) [kJ·mol\(^{-1}\)], T – absolute temperature [K]. The activation energy (E_a) values, calculated by the Arrhenius model ranged between 24.09 and 48.11 kJ/mol. G'' influenced the magnitude of the activation energy. The activation energy is negatively correlated with moisture. In terms of regression coefficients they were greater than 0.99 for all the samples analysed.

*Effect of Concentration*

The influence of the concentration (C, °Brix) on the honey loss modulus can be described by power-law (eq. 12):

\[
G'' = G_1'' C^{b_C}
\]

(eq. 12)
191 and the exponential model (eq.13) [15]:

192 \[ G^\infty = G_1^\infty \exp(b_1^\infty C) \]  

(eq. 13)

193 Where: \( C \) is the concentration in \(^{0}\)Brix and \( G_1^\infty, G_2^\infty, b_1^\infty, b_2^\infty \) are constants. With the aim of calculating the model constants, the loss modulus data were fitted to equations 12-13 by non-linear regression. The values of the parameters are presented in table 4. According to the ADD values, it seems that the power law model is more suitable for predicting the loss modulus evolution than the exponential model.

Considering the mean relative deviation, it appears that the exponential models are more suitable for predicting the influence of the concentration on the magnitude of loss modulus. For a given temperature, the activation energy for flow depends on the soluble solid content which can be described using several models [18]. In the present work, two models were applied (eq. 14 and eq. 15):

198 \[ E_a = A_1^\infty C^{b_1^\infty} \]  

(eq. 14)

199 \[ E_a = A_2^\infty \exp(B_2^\infty C) \]  

(eq. 15)

200 Where: \( A_1^\infty, A_2^\infty, B_1^\infty \) and \( B_2^\infty \) are constants. The \( E_a \) values and the concentration of the corresponding honey were fitted to equations 14 and 15 by nonlinear regression in order to determine the model parameter). The coefficients of regression (\( R^2 \)) of the two models proposed above are the same (\( R^2 =0.91 \)). The power law model is more suitable for predicting the activation energy value because of the much lower ADD values (12.55 in the case of equation 15, and 30.56 in the case of equation 14).

209 Combined effect of Temperature and Concentration
It is advantageous to obtain an equation describing the combined effect of temperature and concentration on the viscoelastic parameter [19]. The combined effect of temperature and concentration on loss modulus is shown in figure 4.

The following models for loss modulus were investigated (equations 16 and 17):

\[ G'' = G''_0 \exp\left(\frac{E''_1 C + E''_a}{RT}\right) \]  
(eq. 16)

\[ G'' = G''_1 C^{E''_2} \exp\left(\frac{E''_a}{RT}\right) \]  
(eq. 17)

The loss modulus, concentration, and temperature data were fitted to these models by the nonlinear regression and the values of the model constants were calculated. The values of these constants are shown in table 5. In the case of the loss modulus predictions, according to the temperature and concentration, the regression coefficients ranged between 0.550 and 0.908. The ADD value indicates that eq. 16 was the most appropriated model in the case of Spanish honey [3]. Therefore, for the interval of 0Brix concentrations and temperatures (T) studied, the following equation (eq. 18) is suggested to evaluate the loss modulus (G'') of honey:

\[ G'' = 4.22 \cdot 10^{-17} \cdot \exp(0.292 \cdot C + 43.178 / RT) \]  
(eq. 18)

**Polynomial modelling of loss modulus**

The data model for the prediction of loss modulus (G'') of honey according to the chemical composition, moisture content and temperature was made using a 3rd-degree polynomial equation with seven variables as in the case of honey viscosity. The equation of the model is (eq. 19):

\[ G''_{\text{pred}} = b_0 + \sum_{i=0}^{n} b_i x_i + \sum_{i=1}^{n} b_{ii} x_i^2 + \sum_{i=1}^{n} b_{iii} x_i^3 + \sum_{i=1}^{n} b_{ijk} x_i x_j x_k + \sum_{i=1}^{n} b_{ix} x_i x_j + \sum_{i=1}^{n} b_{ix^2} x_i^2 + \sum_{i=1}^{n} b_{ix^3} x_i^3 \]  
(eq. 19)
Where: \( G'_{\text{pred}} \) is the loss modulus predicted, \( b_0 \) is a constant that fixes the response at the central point of the experiments, \( b_i \) – regression coefficient for the linear effect terms, \( b_{ij} \) – interaction effect terms, \( b_{ii} \) – quadratic effect terms and \( b_{iii} \) – cubic effect terms. A 3rd order polynomial equation with 7 variables for loss modulus was obtained, based on the design variables (table 4) (eq. 20):

\[
G'' = 1.39 - 1.58 \cdot X_1 + 1.41 \cdot X_2 - 0.40 \cdot X_3 + 0.05 \cdot X_4^2 + 0.50 \cdot X_5 \cdot X_6 - 0.47 \cdot X_7 \cdot X_8 - 0.07 \cdot X_9 + 0.91 \cdot X_9 \cdot X_9^2 - 0.85 \cdot X_9^2 \cdot X_9^2
\]

(eq. 20)

The regression coefficient for the polynomial model is 98.87 (\( R^2 \) adjusted 97.94, \( P=0.005 \), ADD = 19.34). The measured and predicted values of loss modulus are plotted in figure 5. In the case of equation 20 it can be observed that fructose and temperature have a linear negative influence while glucose has a positive influence. The moisture content and non-sugar substances do not have an influence on the model.

**Conclusions**

The Burkina Faso honey displayed Newtonian behavior at all the temperatures analysed (5, 10, 15, 20, 25, 30 and 40 °C). The loss modulus had a higher magnitude than the storage modulus, displaying a solid-like behaviour. The response surface methodology was indeed a good tool for predicting complex viscosity and loss modulus; correlation coefficients higher than 98% were observed, 99.38% in the case of complex viscosity and 98.87% in the case of loss modulus. Fructose and temperature have a negative linear influence on loss modulus and complex viscosity, and therefore on the prediction of both of these factors, while glucose has a positive influence.
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**References**


Figure Captions

Figure 1. Rheological behaviour of honey from Burkina Faso. 1) Kampène, 2) Bouroum-Bouroum and 3) Passena. a) complex viscosity, b) loss modulus, c) elastic modulus

Figure 2. Influence of temperature and concentration on complex viscosity of honey from Burkina Faso

Figure 3. Measured vs. predicted values on complex viscosity of honey from Burkina Faso

Figure 4. Influence of temperature and concentration on loss modulus of honey from Burkina Faso

Figure 5. Measured vs. predicted values on loss modulus of honey from Burkina Faso

Table1. Effect of °Brix concentration (C) on the complex viscosity of honey from Burkina Faso at different temperatures (T)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Power law</th>
<th>Exponential model</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\eta_1$</td>
<td>$a_1$</td>
</tr>
<tr>
<td>5</td>
<td>$3 \cdot 10^{-68}$</td>
<td>36.16</td>
</tr>
<tr>
<td>10</td>
<td>$8 \cdot 10^{-65}$</td>
<td>34.20</td>
</tr>
<tr>
<td>15</td>
<td>$6 \cdot 10^{-75}$</td>
<td>39.45</td>
</tr>
</tbody>
</table>
Table 2. Combined effect of °Brix concentration and temperature on the complex viscosity of honey from Burkina Faso

<table>
<thead>
<tr>
<th>Model</th>
<th>η [mPa·s]</th>
<th>E_i</th>
<th>E_a</th>
<th>R^2</th>
<th>AAD</th>
</tr>
</thead>
<tbody>
<tr>
<td>η^* = η_s exp(E_i C + E_a / RT)</td>
<td>3.98·10^{-17}</td>
<td>0.275</td>
<td>420.03</td>
<td>0.898</td>
<td>43.40</td>
</tr>
<tr>
<td>η^* = η_a C^{E_a} exp(E_a / RT)</td>
<td>7.10·10^{-15}</td>
<td>7.650</td>
<td>0.693</td>
<td>0.644</td>
<td>80.48</td>
</tr>
</tbody>
</table>

Table 3. Correspondence between actual and coded values of design variables

<table>
<thead>
<tr>
<th>Design variables</th>
<th>Symbol</th>
<th>Actual values of coded levels</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fructose (g/100g)</td>
<td>X_1</td>
<td>-1</td>
</tr>
<tr>
<td>Glucose (g/100g)</td>
<td>X_2</td>
<td></td>
</tr>
<tr>
<td>Sucrose (g/100g)</td>
<td>X_3</td>
<td></td>
</tr>
<tr>
<td>Sugars (g/100g)</td>
<td>X_4</td>
<td></td>
</tr>
<tr>
<td>Moisture content (g/100g)</td>
<td>X_5</td>
<td></td>
</tr>
<tr>
<td>Non-sugar substances (g/100g)</td>
<td>X_6</td>
<td></td>
</tr>
<tr>
<td>Temperature (°C)</td>
<td>X_7</td>
<td></td>
</tr>
</tbody>
</table>

Table 4. Effect of °Brix concentration (C) on the loss modulus of honey from Burkina Faso at different temperatures (T)

<table>
<thead>
<tr>
<th>Temperature (°C)</th>
<th>Power law model G'' = G''_1C^{b''_1}</th>
<th>Exponential model G'' = G''_2e^{b''_2C}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>G''_1 [mPa]</td>
<td>b''_1</td>
</tr>
<tr>
<td>5</td>
<td>2·10^{-67}</td>
<td>36.14</td>
</tr>
<tr>
<td>10</td>
<td>3·10^{-62}</td>
<td>33.23</td>
</tr>
<tr>
<td>15</td>
<td>3·10^{-74}</td>
<td>39.48</td>
</tr>
<tr>
<td>20</td>
<td>5·10^{-77}</td>
<td>40.88</td>
</tr>
<tr>
<td>25</td>
<td>3·10^{-76}</td>
<td>40.41</td>
</tr>
<tr>
<td></td>
<td>2·10-73</td>
<td>38.95</td>
</tr>
<tr>
<td>---</td>
<td>---------</td>
<td>-------</td>
</tr>
<tr>
<td>40</td>
<td>7·10^-6</td>
<td>3.22</td>
</tr>
<tr>
<td></td>
<td><strong>D - mean</strong></td>
<td></td>
</tr>
</tbody>
</table>

Figure1.
Figure 2.
Figure 3.

log(\(\eta^*\)) (Pa\(\cdot\)s) - measured

log(\(\eta^*\)) (Pa\(\cdot\)s) - predicted
Figure 4.
Figure 5.