COMPARISON OF RHEOLOGICAL PROPERTIES OF HOPPED WORT AND MALT WORT

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Abstract


The aim of this work is determination rheological properties of hopped wort and malt wort and their comparison. In the paper following rheological properties has been described: the dependence of viscosity on a temperature of a sample and hysteresis loop test. The time dependence test was performed for a confirmation thixotropic behaviour. Based on measured values Arrhenius mathematical model has been applied. The activation energy was determined by using of this model. Tests have been carried out in the temperature range from 5 °C to 40 °C. Rheological tests proved that malt wort behaves as Newtonian fluid in all temperatures and hopped wort behaves as non-Newtonian fluid at low temperatures. Thixotropic behaviour is caused by the content of the rests of hops heads or malt scraps.

Keywords: beer, activation energy, rheology, experimental brewery

INTRODUCTION

The knowledge thermophysical and chemical properties of beer and various process products during beer brewing (such as mash, beer wort etc.) are very important for the design and evaluation of industrial processing equipment. Special category of physical properties is rheological behaviour of liquid products. For example viscosity, density or dependence shear rate on the shear stress can count between rheological properties. The measurement of rheological properties of substances is used in many branches such as waste management (Ratkovich et al., 2013; Trávníček et al., 2013), process liquid industry (Kumbár et al., 2013; Kumbár et al., 2014) and food processing industry (production of mayonnaise or ketchups, production of beverages). Rheology can be used in the brewing industry. For example the author Severa (Severa et al., 2009) states that the measurement of the viscosity is important in equipments, where are placed measuring systems with automatic measurement for controlling operation. Generally the measurement of viscosity is important in four phases: during of malt quality control, assessment of sweet wort quality, during of filtration processes and description of beer (Severa et al., 2009). Various rheological properties of process products during beer brewing and beers are determined in diverse works by different authors. The author Severa et al. deals by rheological properties of sweet wort for lager beer, hopped wort for light beer or viscosity of dark beer (Severa et al., 2009). The next authors deal by rheological properties of finished products – beer. For example authors Hlaváč and Božíková solves problematic of rheology dark beer (Hlaváč, 2007) or comparison of rheological and thermophysical properties of various beers (Hlaváč et al., 2012; Božíková et al. 2011).

However problematic of rheological behaviour of hopped wort and sweet wort is little discussed. The works of author Severa et al. is one of the exceptions. The aim of this work is supplement the knowledge about selected rheological properties of hopped wort and sweet wort and their comparison with each other.

MATERIAL AND METHODS

Samples

The samples of malt wort and hopped wort were used for the purpose of research of rheological
properties. These intermediate products arise during brewing of light lager beer. For brewing was used barley malt. The kind of fermentation was bottom fermentation. For brewing of malt wort was used infusion method.

The samples of malt wort and hopped wort were collected from laboratory brewery, which is located at Mendel University in Brno. The samples were transported to the laboratory at the same time. The density of individual samples was measured with use of pycnometer method. For this purpose pycnometers with volume of 50 ml and analytical balance Radwag AS 220/X (Poland) with an accuracy of 0.0001 g were used. For each sample of liquid the density value has been performed in three repetitions.

**Rheological Measurement**

Rheological measurement of substances for purpose of this paper was performed on the rheometr Anton Paar MCR 102 (Austria) with measuring geometry plate–plate. The diameter of the cone was 50 mm, the gap between plates was 0.5 mm. The flow curves were modelled by using Herschel-Bulkley model, which is given by equation:

\[ \tau = \tau_0 + K \dot{\gamma}^n, \]  

(1)

where

\( \tau \)..... shear stress [Pa],  
\( \tau_0 \) ... yield stress [Pa],  
\( K \) ... consistency coefficient [-],  
\( n \).... flow behaviour index [-],  
\( \dot{\gamma} \)..... shear rate [s\(^{-1}\)].

The change of dynamic viscosity in dependency on temperature was measured at temperature range 5–40 °C. Shear rate was constant with value 10 \( s^{-1} \). Where dynamic viscosity is given by equation:

\[ \eta = \frac{\tau}{\dot{\gamma}}, \]  

(2)

where

\( \tau \)..... shear stress [Pa],  
\( \dot{\gamma} \)..... shear rate [s\(^{-1}\)].

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

\[ \ln \eta = \ln \eta_0 + \frac{E_A}{R} \frac{T}{T_0}, \]  

(3)

where

\( \eta_0 \) ..... 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].

**RESULTS AND DISCUSSION**

Measured chemical and physical properties of final product are given by Tab. I. Values of density of malt wort and hopped wort are showed in this table too. The dependence of dynamic viscosity on the temperature both substances are showed in Fig. 1. From this figure is evident that dynamic viscosity of hopped wort at 5 °C is several times higher. But values are parallel from temperature 20 °C. With highest probability this situation is caused by particles, which are contented in hopped wort in a greater extent and creates colloidal system. Particles consists above all from the rest of hops heads or malt scrap. According to different works the dynamic viscosity is depended above all on the temperature and content of \( \beta \)-glucans (Jonkova et al., 2013). The viscosity of malt wort is ranged from 1.75 to 2.1 mPa.s (Severa et al., 2009; Pazdro et al., 1997) and hopped wort is ranged about 1.8 mPa.s (Pazdro et al., 1997). These values are in accordance with values, which are measured. Here both values ranged about 1.7 mPa.s at temperature 20 °C. However values were significantly different at temperature 5 °C. Viscosity of hopped wort was 10.3 mPa.s and malt wort 2.7 mPa.s.

Afterwards the dependence of increasing temperature on viscosity was put to further mathematical analyses. For this analyses Arrhenius mathematical model has been used, which is shown in the equation (3). Logarithm of this equation is:

\[ \ln \eta = \ln \eta_0 + \frac{E_A}{R} \frac{T}{T_0}. \]

From this equation activation energy \( E_A \) was determined by using of regression analyses. Arrhenius model applied on the samples of malt wort and hopped wort are shown on Fig. 2. By using of regression analyses determination coefficient for individual samples was calculated and it reached following values: Malt wort – \( R^2 = 0.88 \), Hopped wort – \( R^2 = 0.90 \). The value of activation energy was following: Malt wort – 21.17 kJ\(·\)mol\(^{-1}\), Hopped wort – 42.8 kJ\(·\)mol\(^{-1}\).

<table>
<thead>
<tr>
<th>Parameter</th>
<th>Unit</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Weight alcohol</td>
<td>%</td>
<td>3.83</td>
</tr>
<tr>
<td>Volume alcohol</td>
<td>%</td>
<td>4.93</td>
</tr>
<tr>
<td>The original content of sugar in the malt wort</td>
<td>%</td>
<td>13.6</td>
</tr>
<tr>
<td>Degree of fermentation</td>
<td>%</td>
<td>72.02</td>
</tr>
<tr>
<td>True extract</td>
<td>%</td>
<td>5.80</td>
</tr>
<tr>
<td>Apparent extract</td>
<td>%</td>
<td>3.68</td>
</tr>
<tr>
<td>Density of lager beer</td>
<td>kg(·)m(^{-1})</td>
<td>1015.2</td>
</tr>
<tr>
<td>Color</td>
<td>Brix</td>
<td>8.09</td>
</tr>
<tr>
<td>Density of malt wort (20 °C)</td>
<td>kg(·)m(^{-1})</td>
<td>1019.1</td>
</tr>
<tr>
<td>Density of hopped wort (20 °C)</td>
<td>kg(·)m(^{-1})</td>
<td>1073.6</td>
</tr>
</tbody>
</table>
Fig. 3 and Fig. 4 describes hysteresis loop tests. This kind of rheological test is determined for evaluation of non-Newtonian fluids. From the Fig. 3 is evident that the dependence between shear stress and shear rate is linear. The curves overlap at increasing and decreasing shear rate. Exception is dependence, which are measured at temperature 5 °C. The small loop generated during the measurement. The similar situation is in the case of hopped wort too. With the difference that hysteresis loop of hopped wort measuring at temperature 5 °C is bigger. This difference is evident from the Tab. II. Here are stated values of hysteresis areas and hysteresis area of hopped wort is almost five times bigger than malt wort. This is due by content of particles, which change their position at low temperatures.

1: The dependence of dynamic viscosity on the temperature

2: Evaluation of Arrhenius model of malt wort and hopped wort

For evaluation of dependencies of shear stress on shear rate was chosen Herschel-Bulkley mathematical model. This model is used for the description of flow curve material with shear-thinning or shear-thickening behaviour. This model is often used for evaluation of rheological behaviour of various beverages, for example juices (Ahmed et al., 2007), or other foods such as mayonnaise (Ma et al., 1995), mustard (Bhattacharya et al., 1999), etc. This is reason why Herschel-bulkley model was used for evaluation of rheological behaviour of malt wort and hopped wort. The results of modelling are showed in the Tab. III. The consistency index \(k\) indicates the extrapolated shear stress at unit shear rate. The flow index is the rate of deviation from Newtonian behaviour; when \(n < 1\), the dynamic viscosity of the sample decreases, although
the dynamic viscosity of the sample increases when $n > 1$.

On the base of knowledge obtained by measurements both kinds of fluids behave as non-Newtonian substance at 5 °C. Specifically these substances behave as thixotropic fluid. However here is probability that these substances behave as shear-thinning or shear-thickening fluid. Differences between this phenomenon are much discussed. However fundamental difference

### II: Hysteresis areas at various temperatures

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature</th>
<th>5 °C</th>
<th>15 °C</th>
<th>25 °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malt wort</td>
<td>0.21 Pa·s⁻¹·ml⁻¹</td>
<td>0.1 Pa·s⁻¹·ml⁻¹</td>
<td>0.01 Pa·s⁻¹·ml⁻¹</td>
<td></td>
</tr>
<tr>
<td>Hopped wort</td>
<td>1.59 Pa·s⁻¹·ml⁻¹</td>
<td>0.07 Pa·s⁻¹·ml⁻¹</td>
<td>0.06 Pa·s⁻¹·ml⁻¹</td>
<td></td>
</tr>
</tbody>
</table>

### III: Rheological parameters of the Herschel-Bulkley mathematical model

<table>
<thead>
<tr>
<th>Sample</th>
<th>Temperature [°C]</th>
<th>$R^2$</th>
<th>$n$</th>
<th>$k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Malt wort</td>
<td>5</td>
<td>0.9990</td>
<td>0.92</td>
<td>0.0042</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.9981</td>
<td>0.86</td>
<td>0.0037</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.9969</td>
<td>0.99</td>
<td>0.0015</td>
</tr>
<tr>
<td>Hopped wort</td>
<td>5</td>
<td>0.9148</td>
<td>0.99</td>
<td>0.0036</td>
</tr>
<tr>
<td></td>
<td>15</td>
<td>0.9963</td>
<td>0.94</td>
<td>0.0025</td>
</tr>
<tr>
<td></td>
<td>25</td>
<td>0.9975</td>
<td>1.04</td>
<td>0.0013</td>
</tr>
</tbody>
</table>
between these types of fluids is that shear-thinning and shear-thickening behaviour of materials are time independent rheological behaviour. On the other hand thixotropy or rheopectic behaviour is time dependent rheological behaviour. From the reason time dependence test must be performed to conjectures could be confirmed or disproved.

The next rheological test deals with time-dependency of measured substance. This test describes the dependence of viscosity on the time. The results of tests are given by Fig. 5 and Fig. 6. From these graphs is evident that only curve of hopped wort has increasing tendency at temperature 5 °C. The other curves are approximately constant. The fluctuations of measuring values are given by ambient conditions. The gap between plates of rheometer is relatively big and the viscosity is low. From the reason the substance can be pulled by centrifugal force down and it can temporarily cause decreasing of shear stress.

Based on the facts the hopped wort has thixotropic behaviour at 5 °C. The rheological behaviour changes on the Newtonian fluid, if the temperature increases. But border between thixotropic and Newtonian behaviour are very close. The same is applies to the malt wort. This sample has small hysteresis area at temperature 5 °C. But viscosity is constant with the time. However values of hysteresis area are so low that this type of sample can be evaluated as Newtonian fluid at all temperatures.
CONCLUSION

Determination of rheological properties of products during of bewaring of beer is very important for quality control of output product or filtration processes. Rheological properties of beers were determined in detail, but the flow properties of semi-products arising during of bewaring of beer are not described in detail. These products include malt wort and hopped wort too. Generally hopped wort has higher viscosity than malt wort and has different flow properties. This difference is evident above all at low temperatures. For example hopped wort shows thixotropic behaviour at temperature 5 °C. Where the hysteresis loop was created during testing and in the next experiment was demonstrated that it is time dependence substance. When temperatures were higher the non-Newtonian behaviour changed to Newtonian behaviour. Whereas the malt wort shows Newtonian behaviour at all temperatures. This situation is caused by the content of small particles in hopped wort, which are created colloidal system. The particles consist from above all from the rest of hops heads or malt scrap, which have tendency to agglomeration. Agglomerated particles separate during force action on the fluid and viscosity decreases. When force action stops, separated particles again agglomerate and viscosity increases.

REFERENCES