Equilibrium Moisture Content Importance in Safe Maritime Transport of Black Tea

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ABSTRACT: In sea transport, a very important thing is an assignment of cargo to a particular class of storage climate conditions and it is carried out on the basis of the requirements that cargo places upon its storage atmosphere. The water content of black tea must not fall below 2%, as the product otherwise becomes hay-like and its essential oils readily volatilize, while on the other hand, it must not exceed 9% as it then has a tendency to grow mould and become musty. Therefore, tea requires particular temperature, humidity/moisture and possibly ventilation conditions. In this context, tea is a hygroscopic material that has the ability to absorb or desorb water in response to temperature and relative humidity of the atmosphere surrounding it. The moisture content of tea is one of the most important variables affecting its chemical and sensory properties. Therefore, to explore and predict the behaviour during transport of tea, its equilibrium moisture content must be determined for a range of transport temperatures and relative humidities. The present paper focuses on the evaluate the hygroscopic properties of tea from Rwanda with different degree of fragmentation based on isotherms of water vapour sorption and characteristics selected parameters of the surface microstructure determining transport conditions and therefor microbiological stability of teas.

1 INTRODUCTION

The knowledge and understanding of moisture sorption isotherms for foods is of great importance in food science and technology for many uses such as the design and optimization of processing as for instance in drying, for assessing the packaging and transporting problems, for modeling moisture changes which occur during drying, for predicting shelf life stability and for ingredient mixing predictions [Sinija and Mishra, 2008].

Tea leaves (Camellia sinensis L.) are the source of the world’s most popular beverage, and can be processed and fortified with different fruits, flowers and spices to fulfill specific features desired by the consumer. Tea is grown in countries with warm and humid climate mainly in China, India, Japan, Sri Lanka, but also in Rwanda and Argentina. Tea is one of the most popular beverages in the world, which can inhibit the development of cancer, lower the risk of cardiovascular disease, and improve cognitive health in human human [Chi-Wei et al., 2017, Chung et al., 2010]. It is a plant rich in polyphenols, flavonoids such as flavanols (catechins, procyanidins), flavonols (rutin, quercetin, kaempferol), and phenolic acids (gallic, caffeic). Polyphenolic compounds in tea leaves make up to 30% of green tea, but only 10% of black tea. The major catechins in tea are: (+)-catechin (C), (+)-epicatechin (EC), (+)-gallocatechin (GC), (+)-epicatechin gallate (ECG), (+)-epigallocatechin (EGC), and (-)-epigallocatechin gallate (EGCG). However, the major antioxidant in tea leaves is considered to be ECG, a
catechin compound with eight free hydroxyl groups (OH) which are decisive for its high antioxidant activity [Gramza-Michalowska et al., 2016]. In products’ (such tea, coffee) storage and transport, polyphenols are unstable under various conditions, such as presence of oxidative enzymes, high temperatures, pH level, moisture content, and presence of light and oxygen. Wang and Hellwell [2000] they were demonstrated that time of tea storage played a significant role in reducing the content of catechins. The contents of catechins in samples of tea after 60 days of storage were about 20% lower than in fresh leaves of tea – respectively from 363 mg/100ml to 317 mg/100ml for (+)-EGC and from 87.3mg/100ml to 71.5mg/100ml for (-)-EC and after 120 days of storage the content the catechins have moved to the level of 266mg/100ml and 62.3mg/100ml – respectively for (+)-EGC and (-)-EC.

In sea transport, a very important thing is an assignment of cargo to a particular class of storage climate conditions and it is carried out on the basis of the requirements that cargo places upon its storage atmosphere. Depending on the classification of the product, different parameters have to be set for the risk factors temperature, humidity/moisture and ventilation to prevent a reduction in product quality.

Tea requires particular temperature, humidity/moisture and possibly ventilation conditions (SC VI). This group includes goods with a low water content (WCC 2 – 1.5 – 30%), which is constantly determined by the humidity and temperature conditions of the ambient medium. This group includes goods with a low water content that is constantly determined by the humidity and temperature conditions of the ambient medium. The water content of black tea must not fall below 2%, as the product otherwise becomes hay-like and its essential oils readily volatilize, while on the other hand, it must not exceed 9% as it then has a tendency to grow mold and become musty. The sorption isotherms for these hygroscopic goods exhibit a continuous profile without sudden jumps. Undesirable changes occur as a function of relative humidity and temperature, in particular due to dampening (mold, rot, mildew stains, fermentation, deliquesce, self-heating) or desiccation (solidification, jamming/caking, fragmentation, drying-out). The goods in this group (also tea) do not have any particular requirements as to ventilation conditions, since they are dry for shipment and do not respire (BA 3 - goods in which respiration processes (external respiration) are suspended, but in which biochemical, microbial and other decomposition processes still proceed, such as meat, fish, processed grain products, dried fruits, spices, cocoa and coffee beans, tea, tobacco, expellers, fish meal). Other examples of goods in this group are foodstuffs (risk of dampening, drying-out and loss of aroma), green coffee beans, raw cocoa, green tobacco (risk of post-fermentation), dried fruits (risk of syrup formation and fermentation due to effect of humidity/moisture), furs, hides, packaging materials, natural fibers and fibrous materials, wood and wooden articles, furniture and musical instruments. Ventilation may possibly be necessary, if the required temperature and relative humidity parameters are to be achieved. Favorable travel temperature for tea ranged from 5 to 25°C. Tea must be stowed away from sources of heat in order to avoid the risk of desiccation and drying. Tea requires also particular humidity/moisture conditions in the range from 60 to 65%, because mould may easily develop on samples in the too high relative humidity environment. Tea is predominantly transported in standard containers, also known as general purpose containers. Containers intended for loading have to be watertight and must not be contaminated in any way. Containers which release a foreign odor, are contaminated by any substances or are too damp should be rejected. Below deck stowage is required to rule out the possibility of exposure to rain or seawater or of overheating by day and cooling at night. Tea in containers should be stowed away from sources of heat. In damp weather (rain, snow), the cargo must be protected from moisture, since moisture may lead to mold growth and mustiness. [www.tis-gdv.de; Ładunki okrętowe, 1994; Sharnow, 2000].

In this context, tea, as other plant materials (for example wood), is a hygroscopic material that has the ability to absorb or desorb water in response to temperature and relative humidity of the atmosphere surrounding it. This affinity of tea for water is caused by the hydroxyl groups accessible in the cell walls of tea. As a consequence, the moisture content of tea is one of the most important variables affecting its chemical (catechins) and sensory properties.

Generally, there are two types of water in tea leaves. The “water of constitution” is the water included in the chemical structure of wood and it is inherent to the organic nature of the cell walls. It cannot be removed without modifying the chemical composition of tea leaves. The second type of water comes in three forms: “bound” or “hygroscopic” water which is adsorbed by sorption sites in amorphous areas of cellulose and hemicellulloses present in the cell walls; “free” water which is liquid - like water in the cell lumen and voids; and “vapor” water which is present in voids and cell lumen.

As leaves of tea begin to lose moisture when exposed to ambient conditions in the transport, water leaves from voids and cell lumen first while the bound water content remains constant. The moisture content level which corresponds to lumen containing no free water (but will contain water vapor), while no bound water has been desorbed from the cell wall material, is known as the fiber saturation point. For most tea leaves, fiber saturation point is in the range 85-8%. As the moisture content of tea leaves decreases below fiber saturation point, bound water will begin to leave the cell wall material and different situation is observed when the moisture content of tea leaves increases more than fiber saturation point. Most of the chemical and sensory properties vary with moisture content below and above this point. At a certain point, equilibrium is attained between moisture in the leaf and that in the surrounding atmospheric environment, and this situation is the best for the tea transport conditions. This is where the tea leaves will not gain or lose any moisture with time and it is known as the equilibrium moisture content of the tea [Hartley and Hamza, 2016]. Simulation models for dryer design, dryer optimization and control for several agricultural products use the difference between the actual moisture content and the
equilibrium moisture as a measure for the driving force for drying. During the manufacture of black tea, the macerated leaf (termed “dhool”) which has undergone “fermentation” in tea terminology (actually enzymic oxidation) is then dried from around 70% w.b. moisture content to a target moisture content of 3% w.b. Some sorption of moisture during sorting and packing takes place so the packed product remains below 7% w.b. As the moisture content is reduced to such a low level compared to most agricultural products, equilibrium moisture content (EMC) plays a particularly important role at the end of drying and at transport condition [Temple and van Boxtel, 1999].

Knowledge of the moisture sorption characteristics of tea is important for predicting its stability during storage, transport and selecting appropriate packaging materials. Different materials have different equilibrium moisture contents (EMC). The EMC is dependent upon the temperature and related humidity of the environment as well as species, variety and maturity of the grain. The equilibrium moisture of tea can be used in modeling the transporting process [Sinija and Mishra, 2008; Ghodake et al., 2007].

The measurement of physical properties of tea is important because they intrinsically affect its behaviour during storage, handling, processing and transport. The degree of fragmentation of tea and its behaviour under pressure, temperature and humidity are important in handling and processing operations, such as storage, transportation, formulation blending and packaging.

The present paper focuses on the evaluate the hygroscopic properties of tea from Rwanda with different degree of fragmentation based on isotherms of water vapor sorption and characteristics selected parameters of the surface microstructure determining transport conditions and therefor microbiological stability of teas.

2 METHODOLOGY

The research material was five black tea samples originated from Rwanda and differing by degree of fragmentation. Samples of orthodox black tea were as follows: FOP - Flowery Orange Pekoe, OP - Orange Pekoe, OPA - Orange Pekoe grade A, BOP - Broken Orange Pekoe and P - Pekoe.

The sorption method used was the static gravimetric technique, based on the use of saturated salt solutions to maintain a fixed relative humidity when the equilibrium is reached. The water activity of the food is identical to the relative humidity of the atmosphere at equilibrium conditions and the mass transfer between the product and the ambient atmosphere is assured by natural diffusion of the water vapor.

Tested black teas (I-V) were subjected to a preliminary analysis by the physico-chemical determination of the initial water content. Determinations of water content were taken by drying at 103°C [ISO 1573-1980 (E) Tea – Determination of loss in mass at 103 °C].

Isotherms of adsorption were determined by the static method, based on a moisture equilibrium between the tested product samples and the atmosphere of defined a relative humidity of, a regulated by means of the salt solutions [Gondek et al., 2013]. The determination of adsorption isotherms carried out at 25°C ± 1°C in a range of water activity \( a_w = 0.07\pm0.98 \). Time fixation equilibrium was 30 days. The sample for the study consisted of about 2 g of the product tested. The samples were weighing were placed in a dish measuring 15 mm in diameter to form a bed with a height of 2 - 3 mm and deployed in desiccators. Thymol was placed in the desiccators with water activity >0.7 in order to protect samples against the growth of microorganisms. Based on the initial weight of the product and the growth or loss of water content equilibrium water content was calculated and plotted sorption isotherms.

In order to describe empirically designated sorption isotherms have been restated the equation of Brunauer, Emmett and Teller (BET) [Brunauer et al., 1938], the range of water activity 0.07≤\(a_w\)≤0.33. The equation was characterized on the basis of the value of the coefficient of determination (R²), standard error (FitStdErr) and the value of statistics F.

Results achieved in respect of sorption properties were analysed with the computer software Jandel-Table Curve 2D v 5.01., which enabled determination of such parameters of the sorption process as: capacity of the monomolecular layer and energetic constant.

On the basis of water content estimated in the monolayer adsorbed at a temperature lower than the boiling temperature and the so-called “water crosssection”, the specific surface area of adsorbent was calculated according to the equation (2), [Paderewski, 1999]:

\[
a_{sp} = \alpha \frac{V}{M} N
\]

where:
\(a_{sp}\) – sorption specific surface, (m²/g d.m.), \(N\) – Avogadro number, (6.023×10²³ molecules /mol), \(M\) – water molecular weight, (18 g/mol); \(\alpha\) – water setting surface, (\(\alpha = 1.05\times10⁻¹⁹\) m²/molecule).

3 RESULTS AND DISCUSSION

The tea leaves are very hygroscopic plant material and very susceptible to water. As during transportation process of tea, the relative humidity of the surrounding air could be increased, leaves of tea tend to absorb water. On the other hand, as the relative
humidity decreases, the leaves of tea tend to desorb water. The basis for the assessment of the hygroscopicity of teas characterized by varying degree of fragmentation transported from Africa was the determination of the water content (Table 1).

<table>
<thead>
<tr>
<th>Samples of tea/ degree of fragmentation</th>
<th>Water content (g/100 g d.m.) mean ± SD</th>
</tr>
</thead>
<tbody>
<tr>
<td>I/ Flowery Orange Pekoe</td>
<td>6.88 ± 0.03</td>
</tr>
<tr>
<td>II/ Orange Pekoe</td>
<td>6.99 ± 0.04</td>
</tr>
<tr>
<td>III/ Broken Orange Pekoe</td>
<td>7.01 ± 0.04</td>
</tr>
<tr>
<td>IV/ Orange Pekoe grade A</td>
<td>7.13 ± 0.05</td>
</tr>
<tr>
<td>V/ Pekoe</td>
<td>7.12 ± 0.06</td>
</tr>
</tbody>
</table>

Abbreviation: SD – standard deviation
Source: Own study.

Based on the assessment, it was found that the obtained values of the initial water content of all samples of tea satisfied the requirements of the standard [PN-ISO 1573:1996] and did not exceed the recommended content of 8%, which was consistent with the literature determining the water content in tea at the level of 4–18% [Górecka et al., 2004] similar test results obtained by and Dmowski and Ruszkowska [2016] in samples of leaf tea from China and Sri Lanka. The highest content of water occurred in OPA, Pekoe and BOP samples of tea (oldest, broken and fannings leaves of tea) - 7.13 g/100 g d.m.; 7.12 g/100 g d.m. and 7.01 g/100 g d.m. respectively. The lowest level was found in Flowery Orange Pekoe tea (young leaf tea harvested from top of Camellia sinensis tree). The oldest samples of tea contained more water than younger, leaves tea. On the basis of the obtained results of the initial water content in the assessed tea, it can be assumed that the water content was determined primarily by the size of tea leaves, associated with the stage of collective maturity, resulting from the location of leaves on the bush and the technological process, that in the case of BOP sample of tea included the process of mechanical cutting of tea leaves during production.

At the same time, based on the conducted tests, it was found that a relatively high content of dry matter, in the assessed morphological forms of teas with different degree of disintegration, indicated the appropriate quality of the raw material and a high content of ingredients with valuable flavours.

Ensuring high transport and storage durability of teas characterized by different degree of disintegration (morphological form), requires understanding the hygroscopic properties of raw materials. The source of information on the water content in the product are sorption isotherms. Equilibrium moisture content is defined as the moisture content of a hygroscopic material in equilibrium with a particular environment (temperature and relative humidity). Values from equilibrium moisture studies are important for knowing how a material absorbs and loses moisture during storage and for defining the transport and storage conditions in order to obtain the best quality product [Temple and van Boxtel, 1999; Kędzierska and Palacha, 2011].

Hygrosopic properties of all samples of teas are determined by comparing the relative positions of water vapor adsorption isotherms (Fig. 1).

Figure 1. The sorption isotherm of water vapor product I - IV, determined after 30 days of storage in an environment with aw=0.07-0.98.

Sorption isotherms determined empirically in tested teas I–V, were characterized by sigmoidal in shape and, according to the classification of Brunauer, showed similarity to the isotherms of type II. The sigmoidal shape of the sorption isotherms is related to the occurrence of the range of monolayer adsorption in the low water activity (aw<0.3), the multilayer adsorption range (0.3<aw<0.7) and the capillary condensation area (aw>0.7). Designated sorption isotherms in tested teas, characterized by continuity in the course of the entire range of water activity (0.07–0.98) with increasing water activity increased water content in the analyzed teas.

In the area of water activity 0.07<aw<0.44, corresponding to the range of monomolecular desorption, the highest hygroscopicity (sorption capacity) was characterized by samples of FOP, BOP, OPA and OP tea and for OP tea. The same situation, it can be seen in OP samples of tea in the range of water activity from 0.07 to 0.55.

After exceeding the water activity respectively 0.44 and 0.55, the upper limit of the range of multilayer adsorption and capillary condensation the all samples of tea were characterized by the higher hygroscopicity. It can be assumed that above of level aw>0.75, the capillary condensation phenomenon was observed in the tested samples, which can be equated with exceeding the critical moisture level. It can be observed at the inflection point of the sorption isotherms and probably indicated the initiation of the capillary condensation phenomenon. This phenomenon is identified by exceeding the level of critical humidity, that can determined the loss of the product's ability to continue transport and storage.

Designated sorption isotherms in tested teas, characterized by continuity in the course of the entire range of water activity (0.75–0.93) with increasing water activity increased water content in the analyzed OPA tea.

The use of adsorption isotherms as an indicator of the storage stability of the product is based inter alia on the basis of a calculation capacity monolayer (vm), that corresponds to a single layer of adsorbed water.
vapour molecules. The theoretically defined water content in the product corresponding to this monolayer is the optimum water content in this product. The excess water, in relation to the monomolecular layer, leads to critical humidity, which can cause undesired changes in the product, for example: undesirable taste and flavor, loss of aroma and microbial growth [Mathlouthi, 2001; Ociezek and Klopotek 2013].

To the estimate the surface microstructure and phenomenon of sorption, the course of sorption isotherms in the water activity range of \( a_w = 0.07 \pm 0.33 \) enabled determining parameters of the BET equation (\( v_m \)) by assaying the degree of its fit \( (R^2, \text{FitStdErr}, F_{stat}) \) to empirical data. Respective results were presented in Table 2.

Table 2. The BET equation parameters

<table>
<thead>
<tr>
<th>Product</th>
<th>( v_m )</th>
<th>( c_e )</th>
<th>( R^2 )</th>
<th>FitStdErr</th>
<th>Fstat</th>
<th>Specific Surface of sorption ( m^2/g )</th>
</tr>
</thead>
<tbody>
<tr>
<td>I/FOP</td>
<td>4.154</td>
<td>119.22</td>
<td>0.951</td>
<td>0.251</td>
<td>38.706</td>
<td>145.96</td>
</tr>
<tr>
<td>II/OP</td>
<td>4.164</td>
<td>168.87</td>
<td>0.955</td>
<td>0.229</td>
<td>42.354</td>
<td>146.30</td>
</tr>
<tr>
<td>III/BOP</td>
<td>4.226</td>
<td>149.29</td>
<td>0.967</td>
<td>0.202</td>
<td>58.899</td>
<td>148.47</td>
</tr>
<tr>
<td>IV/OP/A</td>
<td>4.451</td>
<td>152.17</td>
<td>0.944</td>
<td>0.254</td>
<td>34.035</td>
<td>156.39</td>
</tr>
<tr>
<td>V/P</td>
<td>4.497</td>
<td>171.50</td>
<td>0.940</td>
<td>0.285</td>
<td>31.517</td>
<td>157.99</td>
</tr>
</tbody>
</table>

where: \( R^2 \) - determination coefficient; 
\( \text{FitStdErr} \) - standard error; 
\( F_{stat} \) – statystyka F; 
Source: Own correlation

The studied teas I–V were different in terms of size monolayer. The tea V (Pekoe) was characterized by the highest capacity monolayer. It can be assumed that water was bonded stronger in this type of tea than in other types. Similar capacity of monolayers was characterized by the remaining samples of Orange Pekoe tea. It can be assumed that the most defragmentation of tea (V / Pekoe), more strongly bounded water compared to other products.

Probably, it resulted from differences in the surface structure determined by the degree of defragmentation of this sample of tea, that was the fannings type.

The monolayer moisture content \( v_m \) is recognized as the optimum moisture content for good storage stability. This \( v_m \) value is the critical moisture content for tea to keep flavour and quality [Chen and Weng, 2010]. The average value of \( v_m \) ranged from 4.15% to 4.49%, was recommended as the optimum moisture content. The corresponding ERH at this monolayer moisture content value is nearly 60%.

This situation was confirmed by the estimated values of monolayer capacity \( (v_m) \) based on the BET model, which formed the basis for calculating the specific surface area of sorption, the highest value of which was determined in fannings tea (V) - 157.99 m\(^2\)/g, and the smallest in tea leaf tea (I) - 145.96 m\(^2\)/g.

4 SUMMARY

Based on the conducted research, it was found that evaluated samples of black tea was characterized by a different initial water content, determined by the degree of disintegration.

The evaluation of hygroscopic properties of the black tea samples showed that the sorption isotherms of its were characterized by sigmoidal in shape and, according to the classification of Brunauer, showed similarity to the isotherms of type II.

In the area of water activity \( 0.07 < a_w < 0.44 \) corresponding to the range of monomolecular desorption, the highest hygroscopicity (sorption capacity) was characterized by samples of FOP, BOP, OPA and P tea and for OP tea. The same situation, it can be seen in OP samples of tea in the range of water activity from 0.07 to 0.55. While, in the area of water activity \( 0.69 < a_w < 0.98 \) corresponding to the range of monomolecular adsorption, the highest hygroscopicity was characterized by all tea samples. In water activity range from 0.75 to 0.93, the highest level of hygroscopicity in OPA tea sample were determined.

Designated sorption isotherms in tested teas, characterized by continuity in the course of the entire range of water activity (0.75-0.93) with increasing water activity increased water content in the analyzed OPA tea.

Water activity is an alternative method of describing equilibrium relative humidity, and is expressed as a percentage. The corresponding ERH is about 60% for long-term transport and storage of all researched samples of black tea.

Assessing the quality and transport durability of black teas, based on the parameters of the monomolecular layer’s capacity and the specific surface area of sorption, it was found that especially fannings tea (no. V) was the least susceptible to changes in the transport conditions.

REFERENCES