Physicochemical Properties and Storability of Non-alcoholic Malt Drinks Prepared from Oat and Barley Malts

E. Hosseini¹, M. Kadivar¹*, and M. Shahedi¹

ABSTRACT

Non-alcoholic malt drinks are popular in many countries including Muslim countries. In Iran, these drinks are prepared in a manner similar to beer, but without fermentation and are generally produced using barley malt. In this study, malt drinks with ratios of 0:100, 25:75, 50:50, 75:25 and 100:0 of barley to oat malts, the latter obtained under optimum conditions in terms of its enzymes activity, were produced and their physicochemical properties along with their storability were evaluated during six months of storage. The results showed that with increasing the proportion of oat malt in drinks, total solids, ash, acidity, reducing and total sugars increased. The results also indicated that by increasing the oat proportion, bitterness, color, turbidity and foam instability increased, while the amount of foam decreased. It was evident that the oat malt had positive effects on color and bitterness as compared with that of barley, and had more antioxidant compounds.

Keywords: Malt drink, Oat malt, Chemical characteristic, Physical properties, Antioxidant content.

INTRODUCTION

Non-alcoholic malt drinks are consumed in many countries. There are many people who avoid alcohol because of their health. However, in Islamic countries, the main reason lies in the ban of alcohol in the faith. Malt drinks are classified based on the alcohol content as alcoholic (more than 1.2%), low alcoholic (0.5-1.2%) and with no alcohol (less than 0.5%). Non-alcoholic malt beverages are produced as non-fermentative or fermentative. In the fermentative type, alcohol is removed from the drink using physical techniques (by heating, dialysis and reverse osmosis) or biological methods (by selecting a low alcohol producing yeast strain and/or put an end to fermentation, by heating of the wort) (Briggs et al., 2004). Today, non-alcoholic malt drinks market in all over the world particularly in Islamic countries has expanded (Kamil, 2003). According to Islamic laws, the amount of inherent alcohol in food and drink should not exceed 0.5% and in some cases 0.1% (Riaz and Chaudry, 2004). Share of non-alcohol and low-alcohol malt drink in the world market has been about 2% and consumption has increased between the years 1994 and 2004 to 3.5% (Meussdoerffer and Zarnkow, 2009).

Malt drinks are generally produced by dissolving wort granulates in water, filtration, and adding pure hop aroma, followed by carbonation (Kamil, 2003). The drink has a lot of health benefits such as protection against coronary heart diseases, cancers and ulcers (Bamforth, 2002). Beer is normally produced with barley malt and in some cases from other sources such as oat (Briggs et al., 2004), which has a lot of nutritional value due to the large amounts of high quality protein, fat, β-glucan, minerals, vitamins and antioxidant (Kaukovirta–Norja et al., 2004). High fat and

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β-glucan content in oat and little changes in its protein content during the germination has limited its application as an independent source of malt in brewery. Activation of lipase during germination may cause hydrolysis and its subsequent oxidation leads to rancidity and development of bitterness in the final products (Lehtinen and Laakso, 2004).

It is believed that in general non-alcoholic malt drinks compared to alcoholic beers, have poor taste, mostly due to the lack of good mouth feel and imbalance of flavor elements which usually happens in the absence of alcohol (Malfliet et al., 2009). Taylor et al. (1998) showed that oat malt has a pleasant toasted biscuit aroma and a fairly strong mouth feel that can be felt when replaced with less than 10% barley in some alcoholic beers. There are several ways to improve the taste of non-alcoholic malt beverages, including adding other types of malt and higher levels of hops (Rehberger, 1999). To the best of our knowledge, production of non-alcoholic and non-fermentative malt drinks with higher proportion of oat malt has not been reported. In this study, various levels of oat and barley malts were used for the production of oat malt drinks, and their effects on physicochemical properties were studied.

MATERIALS AND METHODS

Oat (Avena sativa), barley malt as well as hops pellets were obtained from the Iranian Seed and Plant Improvement Institute, and Behnoush Company (Tehran, Iran), respectively. All the chemicals were purchased from Sigma (USA), Merck (Germany) and Scharlau (Spain) and were of analytic grade.

Preparation of Malt

Oat seeds were dehulled using a laboratory dehuller with the distance between rollers of 12mm (OSK, Japan). The seeds were then germinated in a dark incubator (at 16°C and relative humidity of 100%) according to Larson and Sandberg (1995), to find the best enzyme activity (i.e. the lowest lipase activity and the highest alpha-amylase and proteinase activity) (Table 1). The optimized germinated seeds were obtained at pH 5 and dried at 65-85°C for 19 hours and stored at 20°C until further processing (Heinio et al., 2001).

Malt Drink Production

Oat and barley malts were milled separately with a hammer mill (Achtung, Germany) to pass through sieve No.18 (1000µ). Milled barley and oat malt were mixed together at the ratios of 0:100, 25:75, 50:50, 75:25 and 100:0, respectively. Afterwards, distilled water (4:1, w/w, malt weight basis) was added. The slurry was heated according to a regular heat program (30 min at 48°C, 60 min at 68°C and 20 min at 76°C) and then malt extract was filtered using a cheese cloth and stored in a cold room for an hour to settle the suspended particles. The supernatant was then boiled for an hour, then hops pellets were added to the extract at the 45th minute. The wort was placed in the cold room for 24 hours and then filtered through the three successive polypropylene membrane filters with 5, 1 and 0.1 microns pore sizes (Bamforth, 2003).

To produce malt drink, the respective brix and pH of extracts were adjusted to 5 and 4. It was then transferred to 300 ml green Polyethylene Terephthalate (PET) bottles and 1.5 g dry ice was added to them. Upon completion of gas dissolution, drinks were pasteurized at 65°C for 30 minutes and then stored at room temperature before more analysis.

Measurement of the Total Phenolic Compounds

The total amount of phenolic compounds was measured using Folin-Ciocalteu phenol
reagent and spectrophotometer (UV Mini-1240 Shimadzu, Japan). Gallic acid was used as standard and the results in terms of mg gallic acid equivalent per liter (mg GAE/liter drink) were reported (Zhao et al., 2010).

### Physicochemical Evaluation

Physicochemical specifications of the malt drinks including specific gravity (Pycnometer), brix (Abbe refractometer, Abbe, Japan) pH (Corning pH meter, England), total solids and ash (Memmert electric furnace, Germany) were determined according to standard methods of American Official Analytical Chemists (AOAC, 2002) and European Brewery Convention (EBC, 2006). Total and reducing sugars were measured according to the Lane-Eynon method. Acidity was also measured by titration.

The foam height/amount was measured using the Hackbarth method (2006) with some modification. Prepared drinks were poured into a 500 ml cylinder (5 cm diameter) from a distance of 33 cm from the bottom of the cylinder through a funnel and their initial heights were immediately recorded. After 3 minutes, the height of liquid within the cylinder was subtracted from its initial height and was reported as the amount of foam.

Foam stability of the drinks was determined according to the EBC method 42-9, using an NIBEM-T meter (Haffmans, Germany). Foam stability was reported in seconds. Bitterness of the drinks was determined according to the EBC method 8-9, using a spectrophotometer (UV Mini-1240 Shimadzu, Japan). In this method, absorbance of the samples was measured at 270 nm against iso-octane as the reference. Turbidicity of the drinks was measured according to the EBC method 29-9, using a Hach turbidimeter (2100 P, Loveland Co., USA) and reported as Nephelos Turbidity Unit (NTU). Color of the drinks was measured according to the EBC method 2-7-4, using a Laviband.

<table>
<thead>
<tr>
<th>Enzyme</th>
<th>Without hull</th>
<th>With hull</th>
</tr>
</thead>
<tbody>
<tr>
<td>Amylase</td>
<td>19.70</td>
<td>20.30</td>
</tr>
<tr>
<td>α-amylase</td>
<td>20.30</td>
<td>20.70</td>
</tr>
<tr>
<td>Lipase</td>
<td>20.30</td>
<td>20.70</td>
</tr>
<tr>
<td>Protease</td>
<td>20.30</td>
<td>20.70</td>
</tr>
</tbody>
</table>

Table 1. Effects of hull and pH on the enzyme activity of oat during germination.

<table>
<thead>
<tr>
<th>Proteinase</th>
<th>With hull</th>
</tr>
</thead>
<tbody>
<tr>
<td>12.30</td>
<td>18.30</td>
</tr>
</tbody>
</table>

| Values with similar superscripts in rows do not differ significantly (P< 0.05). | 175 |

- *ml 0.1M NaOH/g.* Falling number. *Degree of hydrolysis.
colorimeter (PFX 195, England). To measure the pale color and full color of malt drinks, cells of 25 and 5 mm were used, respectively (EBC, 2006).

**Statistical Analysis**

Experiments were performed in duplicate by factorial experiment in a completely randomized design. Data were analyzed to compare significant differences between means by the least significant difference test (LSD) using SAS software at the significance level of p < 0.05.

**RESULTS AND DISCUSSION**

**Total phenolic Compounds**

By rising the proportion of oat malt, phenolic compounds were significantly increased (Figure 1) which could be an indication for higher antioxidant activity in the drinks. This is mainly due to the presence of heat resistant antioxidant compounds in oat, which are released during various stages of malt production and drink processing. The amount of measured phenolic compounds in this study was between 215 to 350 mg GAE/litant drink. The value is higher than that measured in beer by Zhao et al. (2010) and less than the value reported by Lugasi and Hovari (2003), which may be related to the use of different varieties.

The major phenolic compounds of oat are phenolic acids and Avenanthramide (AN), the latter is mostly found in dehusked grains (Emmons and Peterson, 1999) and particularly in dehulled oat (Collins, 1989). The amount of ANs is substantially increased during germination. Antioxidant activity of AN and its heat resistance are considerably higher than those of the phenolic acids; therefore remains after heat steaming would be detectable. It is reported that even heat processings such as drying (kilning) will increase ANs and phenolic acids (Dimberg et al., 1996).

A lot of phenolic compounds with antioxidant properties such as phenolic and ferulic acids, maillard reaction products and sulfites are present in beers and changes in their amounts in the drinks can consequently affect antioxidant activity (Pascoe et al., 2003). Since Folin-Ciocalteu reagent, which was used in this study, reacts with all phenolic compounds (Davalos et al., 2003), it could be suggested that the drinks with higher level of oat malt have more antioxidant property.

![Total phenolic compounds of produced drinks with oat and barley malts after six months of storage (mg GAE per liter of drink).](image1)

Figure1. Total phenolic compounds of produced drinks with oat and barley malts after six months of storage (mg GAE per liter of drink).
Physicochemical Characteristics of the Drinks

Physicochemical characteristics of the malt drinks immediately after production and storing for six months are shown in Table 2. Results indicate that by increasing the level of malt in the drinks, total solids, ash, reducing and total sugars as well as acidity are increased, whereas the amounts of brix, density and pH were almost constant.

Total solids are largely composed of sugar, dextrin, nitrogen compounds and salts (Anger et al., 2009), therefore, the parallel increase of ash, reducing and total sugars, and that of total solids seems to be reasonable. The higher sugar content of malt drinks at higher proportion of oat malt may be due to the optimization process during oat germination, in which the condition was set up to have the highest $\alpha$-amylase activity which was determined to be at pH 5 (Table 1) and therefore partial hydrolysis of its starch. On the other hand, increased acidity can also provide more diastase activity.

Among all parameters, only acidity and the reducing sugars were significantly increased after six months of storage, which in turn provides proper conditions for the hydrolysis of carbohydrates and lipids ($p \leq 0.05$).

Foam Height and its Stability

By increasing the oat in malt drinks, less foam with lower stability was observed which might be related to the greater amounts of lipids in such drinks (Table 3). Foam stability results from hops acids interacting with proteins with molecular weights higher than 5 KD, such as lipid transfer proteins (LTP), Z and those derived from hordein (Asano and Hashimoto, 1980). On the other hand, lipids may destroy the foam through interference with foam generating proteins and hops acids and also has competition with air (Roberts et al., 1978). However, there are
lipid binding proteins (LTP) which preserve the foam from destructive effects of lipids. Puroindoline and LTP1 in wheat, hordoindoline in barley (Cooper et al., 2002) as well as tryptophanins and avenoindolines in oat (Douliez et al., 2000) are of these types of proteins. Studies have also shown that basic amino acids are foam destabilizers (Honno et al., 1997). Oat that contains a higher level of arginine and lysine has shown lower foam stability than barley (Kent and Evers, 1994).

**Bitterness**

Significant increase in bitterness was observed as the proportion of oat was increased (Table 4). The bitterness of malt drinks might be also due to the presence of iso-alpha acids, produced from isomerization of hops alpha acids during boiling of the extract (Hughes, 2000). On this basis, factors such as oxidation of hops acids and fatty acids may have contributed to the fall and rise of the bitterness. A part of bitterness attributed to the drinks is the result of hydroxy acids formation from long-chain polyunsaturated fatty acids, which are produced due to the presence of peroxidase in drinks and extract (Lehtinen and Laakso, 2004). Bitterness in malt drinks may be related to the high amount of phenolic compounds and melanoidins that in turn lead to high antioxidant capacity of these drinks.

As shown in Table 4, the bitterness significantly decreased during the six months of storage. The same result has been reported by King and Duineveld (1999). It has been also demonstrated that the bitterness of beer is reduced due to iso-alpha acids oxidation. Such a reaction is enhanced under the influence of metal ions, hydrogen peroxide, light, oxygen and high temperature (Vanderhaegen et al., 2006). Accordingly, during drink storage, some phenolic compounds are consumed to neutralize free radicals and chelate metal ions and other oxidant factors, thereby contributing to the
Table 4. Effects of oat and barley malts on bitterness of the produced malt drinks (EBC).

<table>
<thead>
<tr>
<th>Drink type</th>
<th>100% barley</th>
<th>75% barley, 25% oat</th>
<th>50% barley, 50% oat</th>
<th>25% barley, 75% oat</th>
<th>100% oat</th>
</tr>
</thead>
<tbody>
<tr>
<td>Production time</td>
<td>9.10±0.85</td>
<td>9.70±0.28</td>
<td>10.80±0.57</td>
<td>11.60±0.42</td>
<td>14.10±0.56</td>
</tr>
<tr>
<td>After 2 months</td>
<td>6.80±0.42</td>
<td>7.50±0.42</td>
<td>8.25±0.64</td>
<td>9.80±0.42</td>
<td>12.50±0.14</td>
</tr>
<tr>
<td>After 4 months</td>
<td>4.30±0.14</td>
<td>4.40±0.14</td>
<td>4.90±0.28</td>
<td>7.30±0.28</td>
<td>9.80±0.14</td>
</tr>
<tr>
<td>After 6 months</td>
<td>3.40±0.14</td>
<td>3.40±0.14</td>
<td>3.80±0.56</td>
<td>5.90±0.56</td>
<td>7.90±0.71</td>
</tr>
</tbody>
</table>

* Values with similar small or capital letters in rows or columns, respectively, do not differ significantly (p≤ 0.05).

reduction in the antioxidant potency of the drink.

### Turbidity

Results indicated that the turbidity of malt drinks is significantly increased over the time (Table 5). Turbidity of beer is due to several factors, the most important of which is the reaction between certain types of polyphenols and proteins. In beer, proline-rich polypeptides originated from hordein and flavanol polyphenols are the main causes of turbidity (Siebert et al., 1996). The actual mechanisms of flavanoides and proteins bonding are not fully known, but it is proposed that initially simple flavanoides are polymerized as non-enzymatic and enzymatic oxidation during mashing and boiling and then they bind the proteins to form turbidity (Kaneda et al., 1990). In addition, polyphenols with at least two adjacent hydroxyl groups in their rings can bond with proteins.

Greater turbidity of oat malt drinks, compared to that of ordinary beers, might be due to several reasons among which too much lipid has been cited as the major reason (Briggs et al., 2004). Beers produced by the large amounts of oat create a typical and stable turbidity so that the production of clear malt beer from this kind of malt is almost impossible (Meussdoerffer and Zarnkow, 2009). Oat protein content and its dominant protein are different from those of barley. Considering the lower amount of prolams in oat, proteins originated from other proteins especially globulin may have
caused the turbidity in various stages of malt and drink preparation. According to the study of Silbereisen and Plomann (1963), reactions between globulins and phenolic acids such as digallate acid will generate considerable turbidity in beer.

Higher turbidity in drinks with greater proportions of oat can be also due to greater viscosity in malt extract and malt drinks (Meussdoeroffer and Zarnkow, 2009), which is in turn due to higher amount of β-glucan and arabinoxylan. These materials can also affect the opacity of the product (Baxter and Hughes, 2001).

**Color**

During storage, color of the drink gradually became darker (Table 5). Beer color is generally affected by the hops and malt components. Maillard browning reactions produce melanoidins, creating yellow, orange, red and brown pigments (Shellhammer and Bamforth, 2008). Studies have shown that oat malt produces more color than barley malt (Meussdoeroffer and Zarnkow, 2009). The main reason for this phenomenon may be due to the formation of larger amounts of melanoidins and other color compounds during malt drying as oat malt has more proteins and reducing sugars than barley malt (Table 2).

Beer color is also affected by the processing steps. In mashing, large amounts of oxygen enter the extract (Rakotozafy et al., 2002). Oxygen in its ground state is inactive, but with converting to its active species such as superoxide, its activity is

promoted (Bamforth, 2001). Peroxy radicals are the most known active species of oxygen radicals entrapped non-enzymatically by polyphenols which oxidize and trigger polymerization and consequently color formation (Stephenson et al., 2003). Color is also under the effect of temperature, boiling time, pH of the extract, concentration of free amino nitrogen and sugars (Shellhammer and Bamforth, 2008).

**CONCLUSIONS**

Non-alcoholic malt drinks are rich in nutrients and have considerable phenolic compounds, which are thought to act as antioxidants. The present study showed that by increasing the oat proportion in the drink, bitterness, color, turbidity and foam instability are increased. Since phenolic contents of the oat malt and its drinks are considerably higher than that of barley malt, it may be considered as a more bioactive food with better color development.

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