Shelf stability of dhakki dates as influenced by water activity and headspace atmosphere

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ABSTRACT

Date palm (Phoenix dactylifera L.) is playing a vital role by providing food and shelter to millions. A prominent local cultivar "Dhakki" of Dera Ismail Khan is economically far more important for having jumbo size and weight with small stone, fine texture and delicious taste. However, being a late variety it is confronted with enormous environmental stresses. Stormy monsoon season coincidence with the period of dates ripening, unbalanced production/consumption, and lack of preservation technology are few extremely disturbing factors causing quality deterioration and excessive wastage. In this purview sorption isotherm for Dhakki dates was constructed in the range of 0.12 to 0.97 aw, and stability at 0.52, 0.56 and 0.75 aw under oxygen, air or nitrogen examined. Samples packed inside tinplate cans were stored for 4 months at elevated temperature of 40°C and quality evaluated monthly for darkening, pH, and titratable acidity, whereas slime appearance was examined twice daily. The sorption isotherm is sigmoid in shape, and water activity of 0.25 to 0.62 aw represented for the monolayer, whereas the level of 0.61±0.01 aw is regarded as the water activity of the freshly ripened Dhakki dates. The quality deterioration appeared as a function of both water activity and headspace atmosphere. Samples stored with water activities higher than 0.75 aw deteriorated rapidly by slime formation, whereas those with lower levels displayed proportionately greater stability and with 0.52 aw maintained characteristic color and flavor however gave a semi-dried look. The samples stored under the nitrogen afforded greatest stability. The rate of darkening, pH and titratable acidity was 2.2, 2.8 and 2.7 times higher respectively under oxygen than under the nitrogen. The impact of water activity and headspace atmosphere on quality parameter is statistically significant. In order to maintain freshness of the product with extended shelf life the Dhakki dates are to be stored under the inert atmosphere with a water activity close to its own level of 0.61±0.01 aw.

Keywords: Phoenix dactylifera L, water activity, inert atmosphere, quality changes, shelf stability.

INTRODUCTION

A few plant species has developed into an agricultural crop so closely connected with human life, as has the date palm (Phoenix dactylifera L.). Certainly the date palm imparts close and everlasting association with mankind, and is legend for the Arabic world and for the Muslims in particular. It has been referred to 20 places in the Holy Quran, and the Prophet Muhammad (Peace Be Upon Him) stressed upon his followers to honor it "a blessed tree", and since then the date palm has become an integral part of Muslim culture. Date palm nourishes millions all over the world and contributes significantly towards their development and prosperity particularly to those living in the Arabian deserts. The dates are nutritious being high in carbohydrates, fiber, potassium, and certain vitamins and minerals, but low in fat, and virtually free from cholesterol and sodium. Being excellent source of energy the dates are taken as a staple diet. During 'Ramadan', which is annual fasting month for Muslims, the daily fast is broken after sunset with a few dates before taking sips of water. Pakistan is considered 4th largest dates producing country in the world, and the date is our important cash crop and a good source of foreign exchange earnings. The total cultivated area of all types of dates in Pakistan exceeds 76.1 thousand hectares with its estimated annual production over 630 thousand tonnes, which constitutes about 11% of total world production (GOP 2002). Pakistan is exporting mostly dried dates worth Rs1.468 billion annually (GOP 2003). Cultivation of date palm in North West Frontier Province (N.W.F.P.) exceeds 1000 hectares with 6700 tonnes production out of which more than 50% is furnished from Dera Ismail Khan area. Most of the plantations in Dera Ismail Khan are concentrated in Panyala, Paharpur, Chowdhwan and Dhakki, where summer is hot, a climate responsible for early ripening of the date fruits.

The temperature during June - August normally ranges 38-48°C rising some times above 50°C with about 30-
cm rainfall. Among the local varieties "Dhakki" is the most promising cultivar with commercial importance. The date is quite popular for its extra large size (4-5 cm long and 2-3 cm thick) of small stone and heavy in weights (16-20 g/fruit). It has fine texture, relish taste (Baloch 1999) and fetches high price in the market. However, concurrence of monsoon season with date ripening period, the crop receives heavy damages by rainstorm and insect bites. The losses are even greater in case of Dhakki date, which is a late maturing variety and very susceptible at mature/ripened stage to hot humid climate. Moreover, during peak production period a large quantity of the fresh fruit is left over, and gluts the local market. Due to lack of appropriate processing and storage facilities the surplus produce is wasted.

A rapid darkening is also common in the dates on storage at the prevalent elevated summer temperature with high humidity, which causes much annoying situation for the date industry and calls for attention. Oxidation of phenolic compounds and involvement of sugar are the dominant factors causing darkening at elevated temperatures (Vandercook et al. 1979). Mechanism for the browning in model systems (Hodge 1953) and in fruits and vegetables (McWeeny et al. 1974; Wedzicha 1987) had been reviewed thoroughly. Packing under vacuum or inert gases (Rygg 1977; Moshen et al. 2003) or applying sulphite treatment (McWeeny et al. 1974) had also been suggested for storage to prolong shelf life of high moisture dates and other moist foods. Previously we have reported that the Dhakki dates have about 0.62 water activity lying at the segment covering intermediate moisture levels (Saleem et al. 1997). The information regarding the effect of storage atmosphere at elevated temperature as well as water activity on stability of dates in general and the Dhakki dates in particular is lacking. The objective of the present investigation is to explore the potential of inert atmosphere and optimize water activity close to freshly cured Dhakki dates in order to enhance storage stability at the elevated temperature of 40°C.

MATERIAL AND METHODS
Sample Preparation. Dhakki date at Khalaal stage having 200–250 mmHg cm² hardness Index (Baloch et al. 2003) was procured from the local market. Well-developed fruits having good appearance were taken while unwanted discarded. To retain normal color and flavor of the dates during curing/drying the fruits taken in a wire-mesh basket were dipped (1kg/L) for one minute in potassium metabisulfite (0.5 g/100 ml) solution at 70°C. The treated samples were allowed to drain, taken on to stainless steel trays with single layer loading of 6 kg/m², kept in a locally-made thermostatically controlled dehydrator equipped with hot air overflow system and then cured and dried at 40°C for 10 h until to about 24 % moisture contents. The dates were thoroughly mixed to ensure sample uniformity. Samples required for sorption studies were made into pulp after removing seeds, whereas whole cured fruits were used for further storage studies.

Sorption Isotherm and water activity evaluation
Pulp was macerated to obtain uniform mash, which was subjected to moisture equilibration with water activity in the range of 0.12 to 0.97 a_w at 40°C (Table 1). A 20-grm macerate was kept inside desiccators each containing saturated salt solution of required water activity. The sample was weighed twice daily until attainment of a constant weight. During equilibration for 5 days the solutions were maintained saturated by adding respective dry salt or distilled water as need arises. Equilibrium moisture content (EMC) of samples at each water activity was then determined using method of AOAC (1984). Sorption isotherm was constructed by plotting EMC against water activity using MSTATC package. Water activity of the date samples was then determined from the point of intersection with no change in weight of the sample and the sorption isotherm (Spiecl and Wolf 1987).

Table 1. Saturated salt solutions of required water activity at 40°C

<table>
<thead>
<tr>
<th>S. No</th>
<th>Name of salt</th>
<th>Formula</th>
<th>a_w</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Lithium chloride</td>
<td>LiCl₂</td>
<td>0.12</td>
</tr>
<tr>
<td>2</td>
<td>Potassium acetate</td>
<td>KCH₂COO</td>
<td>0.23</td>
</tr>
<tr>
<td>3</td>
<td>Magnesium chloride</td>
<td>MgCl₂</td>
<td>0.33</td>
</tr>
<tr>
<td>4</td>
<td>Potassium carbonate</td>
<td>K₂CO₃</td>
<td>0.44</td>
</tr>
<tr>
<td>5</td>
<td>Magnesium nitrate</td>
<td>Mg(NO₃)₂</td>
<td>0.52</td>
</tr>
<tr>
<td>6</td>
<td>Sodium bromide</td>
<td>NaBr</td>
<td>0.58</td>
</tr>
<tr>
<td>7</td>
<td>Sodium chloride</td>
<td>NaCl</td>
<td>0.75</td>
</tr>
<tr>
<td>8</td>
<td>Ammonium sulphate</td>
<td>(NH₄)₂SO₄</td>
<td>0.79</td>
</tr>
<tr>
<td>9</td>
<td>Potassium chloride</td>
<td>KCl</td>
<td>0.83</td>
</tr>
<tr>
<td>10</td>
<td>Potassium chromate</td>
<td>K₂CrO₄</td>
<td>0.88</td>
</tr>
<tr>
<td>11</td>
<td>Potassium nitrite</td>
<td>KNO₂</td>
<td>0.94</td>
</tr>
<tr>
<td>12</td>
<td>Potassium sulphate</td>
<td>K₂SO₄</td>
<td>0.97</td>
</tr>
</tbody>
</table>

Source: Troller and Christian (1978)

Evaluation for slime appearance
Cured date samples (100g) were maintained at water activity varying from 0.75-0.97 a_w for slime appearance
during the storage at 40°C by keeping inside glass desiccators each having saturated solution of different water activity. Slime formation was noted twice daily without opening the containers.

**Biochemical studies**

The samples were divided into three sets and water activity adjusted to 0.52, 0.58 or 0.75 \( a_w \). Each set was subdivided into three lots for storage under controlled atmosphere of oxygen, air and nitrogen. About 200 g of equilibrated samples were sealed hermetically inside A1 (315 mL) size tin-plated cans fitted with two nozzles (valve-built-in) on cross sides for gas flushing. The cans were evacuated (125mm Hg) for one minute and the required gas was filled in. To retain the required water activity the flushing gas was passed through the desiccators having saturated solution of the required water activity. The process was repeated 4-times before soldering the nozzle outlets. The sealed samples were then incubated for 4 months in an oven at 40°C.

Samples were taken out from the oven periodically after every month and analyzed for darkening, pH and titratable acidity. The dates after removing the pits were cut into small pieces, and ground into a uniform mash. The mash was extracted with distilled water or dilute acetic acid (2 g/100 ml) for the measurement of pH and titratable acidity, and for darkening evaluation respectively. The pH was measured potentiometrically using digital pH-meter (Model 3010, Jenway England) equipped with temperature control probe. The titratable acidity (expressed as citric acid, mg/g) was assessed after titrating sample extract against known (4.0g/L) concentration of sodium hydroxide using pH-meter. The darkening was determined on the clarified extract by measuring absorbance at wavelength of 420 nm (Baloch et al 1973) using spectronic-20 spectrophotometer (B-D, USA). The experiment was conducted simultaneously and the data analyzed statistically by means of MSTAT-C version 2-10 software package applying completely randomized design (MSTAT-C 1987). The means are separated by LSD test using the same package. Slope of the plots from linear regression trend between measured parameters and time was taken as a rate for the quality deterioration and the effectiveness of a treatment assessed.

**RESULTS AND DISCUSSION**

**Sorption Isotherm**

The date samples stored at water activity of 0.58 \( a_w \) or below started loosing weight, whereas gain in weight was observed in samples kept under water activity of 0.75 \( a_w \) and above. The loss or gain in weight was rapid during initial equilibration periods, which leveled off after 5 days of equilibration. The equilibrium moisture content (EMC) increased from 10.6% to 95.4% with respective increases in water activity level from 0.12 to 0.97 \( a_w \). A plot between EMC (%) and corresponding water activity values represents moisture sorption isotherms (Fig. 1). The figure depicts a typical sorption isotherm not segmented distinctly as frequently reported in theoretical representations. Heiss (1968) also reported a number of similar isotherms pertaining to fruits. The shape of the current isotherm indicates an overlap of moisture layers from one sorption region to the other. First segment of the isotherm extends to 0.25 \( a_w \) with relatively high rate of water uptake per unit change in water activity. The 2nd portion is larger in size approaching up to about 0.6 \( a_w \) and appears to be almost flat in shape. This portion most probably carries a moisture level for monolayer coverage. The last portion is enlarged one with highest slope for water uptake denoted for the region of vapor and capillary water. The isotherm depicts how the water activity interacts with food components and to its moisture, and thus helps in predicting stability of the dates during storage at various water activity levels.

![Fig. 1. Sorption isotherm and water activity of D Hawthorne dates at 40°C.](image)

Water activity of the sample at zero weight change, calculated from the point of intersection from the plot between water activity and loss or gain in weight (%).
was found to occur at about 0.61-0.62 $a_w$, and supposed to be the water activity of the Dhakki dates. This water activity is within the reported range for dehydrated semi moist fruits (Davies et al. 1978). The water activity of 0.61-0.62 $a_w$ corresponded to 24-25% equilibrium moisture contents.

**Studies on slime appearance**

Slime appearance was observed during the storage in samples maintained at water activity levels beyond 0.75 $a_w$. The period of slime formation decreased rapidly as the level of water activity increased. In samples at water activity close to 1.0 $a_w$ the mold growth became visible even prior to storage while the period of moisture equilibration. A plot between days prior to slime formation, and water activity represents mold free storage life of the dates (Fig. 2). The plot gives important information predicting mold free shelf life for the date fruits at various water activity levels during storage at the elevated temperature of 40°C. Safe shelf life of the date rapidly increased with the decrease in water activity. The results indicate that Dhakki dates can be kept much beyond 50 days without showing sign of slime formation provided it is stored at a water activity below 0.75 $a_w$.

**Biochemical studies**

Taking preliminary studies as well as the sorption isotherm of the dates into consideration three water activity levels of 0.52, 0.58 and 0.75 $a_w$ were selected to further examine the effect of storage on darkening, pH changes and titratable acidity of the dates. The chosen limit of water activity covers the water activity of the dates ($>0.52$ $a_w$) extends to the range of semi dried and moist foods stretching out to the sorption segment possibly intended for storage of freshly cured dates. Further, a temperature of 40°C was selected for storage studies so as to collect information at the elevated temperature. It is pertinent to note that the selected temperature lies within the range of most prevalent summer temperature corresponding with the high production season as well as rapid deterioration period of the freshly ripened dates.

**Darkening**

Irrespective of the environmental factors the darkening remained on the increase during storage at 40°C (Fig. 3). A maximum amount of darkening (0.089) was displayed by samples under oxygen at 0.75 $a_w$ whereas a minimum (0.059) under the nitrogen at 0.52 $a_w$. Mean values (Table 2) for samples as regard to storage atmosphere are statistically significant (P <0.05). The rate of darkening (12.1 x10⁻³/month) of samples stored with 0.75 $a_w$ under the oxygen headspace was twice that of nitrogen and 1.4 times under the air (Fig. 4). It clearly indicated that oxygen accelerated while the nitrogen retarded the darkening as compared to air.

The samples under the nitrogen resisted the deterioration and looked normal in color and flavor at end of the storage. Whereas those under the oxygen appeared dark brown and smelled like burnt sugar, and gave absorbance close to 0.1 units - an indication to the exhaustion of shelf life (Baloch et al. 1997; Baloch et al. 2000). Since cured dates of tamar stage possesses sugar carbohydrates, amino acids and tannin polyphenolic compounds (Sawaya et al. 1982), and moreover gives a continuous rise in the browning under any storage condition, testify the involvement of both oxidative and non-oxidative darkening at 40°C.

Similar findings appeared in the literature (Maier and Metzler 1965; Maier and Schiller 1960; 1961a, b). It is pointed out that the darkening was reduced by more than 30 % on storing the Dhakki dates under inert atmosphere at 40°C whereas a reduction of 20 % had been reported for Deglet Noor at 38°C (Maier and Schiller 1961a, b). The darkening was also influenced by water activity of the samples. The
mean values for water activity 0.52, 0.58 and 0.75 are statistically

Table 2. Mean values for darkening, pH and titratable acidity as affected by headspace atmosphere and water activity of Dhakki dates at 40°C for 4 months

<table>
<thead>
<tr>
<th>Factors</th>
<th>Parameters</th>
<th>Darkening</th>
<th>pH</th>
<th>Titratable acidity</th>
</tr>
</thead>
<tbody>
<tr>
<td>Headspace atmosphere</td>
<td>Oxygen</td>
<td>0.056 A</td>
<td>5.12 C</td>
<td>52.67 A</td>
</tr>
<tr>
<td></td>
<td>Nitrogen</td>
<td>0.049 C</td>
<td>5.79 A</td>
<td>32.01 C</td>
</tr>
<tr>
<td></td>
<td>Air</td>
<td>0.055 B</td>
<td>5.58 B</td>
<td>39.80 B</td>
</tr>
<tr>
<td></td>
<td>0.52</td>
<td>0.053 Y</td>
<td>5.58 X</td>
<td>38.92 X</td>
</tr>
<tr>
<td>Water activity (aw)</td>
<td>0.58</td>
<td>0.054 Y</td>
<td>5.52 Y</td>
<td>40.36 Y</td>
</tr>
<tr>
<td></td>
<td>0.75</td>
<td>0.056 X</td>
<td>5.34 Z</td>
<td>45.85 X</td>
</tr>
</tbody>
</table>

Mean values bearing different letters (A–C), (X–Z) in each column for every factor differ significantly (LSD, P ≤ 0.05).

significant (P < 0.05), whereas no significant effect appeared between 0.52 and 0.58 water activity under any headspace atmosphere (Table 2).

Adjusting the samples at the low water activity the stability increased under any atmosphere (Figs. 3, 4). The darkening rate was reduced by about 1.21 - 1.30 times on storing the samples at 0.52 instead of 0.75 aw. The samples stored under the atmosphere of nitrogen at the lowest water activity (0.52) were found most stable. The finding is in accord with the reported observations (Mullak and Mann 1984; Saleem et al. 1997).

A gradual decline in pH from 6.3 to 3.58 was seen during the storage, with a rapid decline when the samples were stored under oxygen and over higher water activities (Fig. 5). A drop in the pH of 2.72, 1.6 and 0.92 units was found for samples under oxygen, air and nitrogen with 0.75 aw respectively. A rate of fall (6.75×10^{-6} ΔpH/month, Δ stands for change) in pH corresponds to sample with 0.75 aw under oxygen was reduced by 1.74 and 3.11 times as a result of change in the atmosphere to air and nitrogen respectively (Fig.6).

Similar observations had been reported in case of Deglet Noor variety (Maier and Schiller 1961a). Mean pH values as affected by controlled atmosphere are statistically significant at P < 0.05 (Table 2). It is once again found that storage under inert atmosphere is the most effective technique for controlling the deterioration. A continuous fall in pH during storage under atmospheres of oxygen, air or nitrogen demonstrates that both oxidative and non-oxidative mechanisms are responsible causing pH changes, similar to that found in case of the darkening reactions.

Water activity of the samples also played a vital role governing pH changes, and samples with reduced water activity displayed greater resistance against the deterioration. The mean pH values with respect to water activity are statistically significant (P < 0.05, Table 2). About 29 - 38 % reduction in the rate of pH change occurred on reducing water activity from 0.75 to 0.52 aw. The manifestation that the samples with increased rate of darkening corresponded to increased rate of pH drop describes that the same process of quality deterioration are responsible for both phenomena (Baloch et al. 1977, Rygg 1977).
Fig. 5. Influence of oxygen, air and nitrogen as a headspace atmosphere on pH of Dhaliki dates equilibrated at 0.52, 0.58 and 0.75 water activity levels during storage at 40°C.

Fig. 6. Influence of water activity and headspace atmosphere on the rate of change in pH of Dhaliki dates during storage at 40°C.

Fig. 7. Influence of oxygen, air and nitrogen as a headspace atmosphere on titratable acidity of Dhaliki dates equilibrated at 0.52, 0.58 and 0.75 water activity levels during storage at 40°C.

Titratable acidity
A consistent rise in titratable acidity was observed for all the samples during the storage (Fig. 7). However, the rates were greatly influenced by storage atmosphere and water activity. Mean values of the determinant for both factors are statistically significant (P < 0.05, Table 2). Acidity of 22.15 x 10⁻² - 22.37 x 10⁻² mg/g prior to storage increased to 43.57 x 10⁻² - 100.95 x 10⁻² mg/g by keeping the equilibrated samples at 0.52 - 0.75 a_w for 4 month at 40°C (Fig 8). The rate of acid formation (19.14 mg/g month) for samples equilibrated with 0.75 a_w and stored under oxygen is about 1.76 and 2.86 times greater than for those under air or the nitrogen respectively, displaying highly significance difference (P < 0.05, Table 2). Moreover, it was found minimum of 5.43 (mg/g month) with 0.52 a_w and under nitrogen (Fig. 8). It is further noted that the samples yielding higher amount of darkening had produced greater amount of acidity and pH drop. It is therefore suggested that all such reactions have most likely a common reactive pool from where the determinants are emerging. Present findings are in line with those reported earlier (Saleem et al 1997; Saddozai et al 1998). Since water activity level of 0.62 a_w also touches to the segment of sorption isotherm containing capillary moisture range (Fig. 1), it can't give guarantee however, to the date fruit to remain unspoiled and safe over prolong storage at 40°C. Deterioration of dates may occur by the osmophilic yeast and xerophilic mold at water activity as low as 0.62 a_w and even by chemical degradation (Brockmann 1973).
Sorption isotherm of Dhakki dates is found to have sigmoid in shape similar to foods of high sugar contents. Water activity of Dhakki dates of 0.62 $a_w$ occurs on a segment of the isotherm of intermediate moisture and semi-moist foods encouraging deteriorative changes of chemical nature. The darkening and other associated changes responsible for quality degradation of Dhakki dates are function of storage atmosphere and water activity. The investigated parameters slow down considerably on packing the dates under nitrogen and at 0.52 $a_w$, and the measures taken proved useful to combat against the deteriorative changes. Since the samples were stored at elevated temperature of 40°C and at water activity within the range of intermediate moisture limits, the degradative reactions eventuated at very rapid rate, and possibly interacted with each other bringing alteration in the deteriorating process sequence. The higher deterioration rates at the higher water activity (0.75 $a_w$) are attributed to the increased mobility of the constituents involved in the deteriorative process, which were further promoted by the oxygen.

**Conclusions**

The rate of deterioration in Dhakki dates becomes significantly low by storing the samples at a lower water activity level and under inert atmosphere of nitrogen. However the samples stored at water activities lower than 0.58 $a_w$ suffer freshness and give hard texture. It is concluded that Dhakki dates preferably be stored under atmosphere free from oxygen and at relative humidity close to its own water activity level (0.60-0.61 $a_w$). Such pre-requisites will indeed provide sufficient stability and ensure for adequate shelf life of the Dhakki dates.

**REFERENCES**


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