STUDIES ON THE GROWTH PERIOD AND SO₂ ABSORPTION PROCESS IN APRICOT FRUITS USING DIFFERENTIAL SCANNING CALORIMETRY

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ABSTRACT

The growth period and absorption process of sulphurdioxide in Hacýhalilo61u cultivar of apricot fruits have been investigated by differential scanning calorimeter, thermogravimetric analysis and differential thermal analysis with a scan rate of 2°C/min. in nitrogen atmosphere. The growth period of fruit and ripeness were followed by thermal analysis. Fruit ripeness period was rationalized in terms of the sugar content of the apricot fruit. The dependence of sulphur absorption in apricot fruit and the chemical composition change has been evaluated by means of thermal analytical techniques.

Key words: Apricot, Thermal analysis, Growth period, Fruit ripeness, DSC

INTRODUCTION

It has long been known that fruit generates heat by some process, but the quantitative determination of this evolution is a problem. A knowledge of the rate of heat production by apricot fruit in various stages of ripeness would be of value for both plant physiologist and other scientists in agriculture. The interest of the problem is that quantitative data might help to elucidate the nature of the reactions taking place in apricot fruits which involve the oxidation of sugar and other acids that result in evolution of carbon dioxide and sugars e.g., glucose, fructose, sucrose (Riva et al., 2005).

A number of reports on chemical composition of fresh apricots are available in the literature. (Munzuroglu et al., 2003; Bureau et al., 2009; Karata et al., 2007; Gurrieri et al., 2001), however data regarding quality and quantity of SO₂ content in dehydrated apricots and growth period of apricot fruit in terms of sugar contents are very scarce.

Dehydrated fruits are among the food products with highest sulphur dioxide content with permissible limit of, 2000 mg kg⁻¹; in particular SO₂ preserves the texture and colour that makes dehydrated apricots attractive to the consumer, and also preserves the characteristics taste of this product (Agüero et al., 2009; Rosello et al., 1994; Özkan and Cemero61u, 2002). In the treated products this preservative must exist in both free and combined forms, the relative proportions of these being determined by such factors as the composition of the food, its pH, and its temperature, all of which will play a part in determining the final stage of equilibrium attained (Willard et al., 1955).

The dehydrated food products are mostly preserved by means of absorption process in which sulphurization is predominantly used. The Rodríguez and Zatrisky (Rodriguez and ZarYtky 1986) modeled absorption of sulphur dioxide by means of a diffusive...
mass transfer equation. The deterioration of food products is prevented by the use of SO₂ because of its chemical properties. The most widely worked reactions of SO₂ in foods are rationalized with its effect on non-enzymatic browning of the Maillard and ascorbic acid types. Though the reactivity of SO₂ in model systems is known, the situation in most food products especially apricot is far from clear. This inhibitory effect is due to the ability of SO₂ to modify the course of complex chemical reactions which are induced by drying and which involve amino compounds, sugars, and organic acids (Willard et al., 1955; Petri et al., 2005).

Ingram and Vas (1950) found that unheated sucrose and fructose solutions did not combine with SO₂, and since apricots and peaches are sulphured at the relatively low temperatures between 25 and 50°C, the major reaction initially binding SO₂ in the fruit is likely to be that between glucose and SO₂ in order to find out the absorption process of SO₂ in apricots, DSC studies were performed to correlate the route of absorption by binding glucose and other sugars. World production of apricots is nearly 2.7 million tons and 45% of it is refined by food industry, and Turkey is the largest producer, this work is primarily carried out to figure the change in Hacıhalilolu cultivar apricot fruit during ripeness, and the change in chemical structure in terms of sugar moieties by means of differential scanning calorimeter.

**MATERIAL AND METHODS**

Apricots (Prunus armeniaca L.) were picked at commercial harvest and the most significant values of the chemical and physical characteristics of the initial raw material were evaluated (Table 1). During harvest season, 50 fruits were collected and their fruit characteristics were determined. The most representative apricot cultivar from Malatya, Hacıhalilolu, was used in this study.

Fruit samples were collected at different times of fruit development period after the blossoming. Analyses commenced on arrival of the samples in the laboratory and analysis was carried out in duplicates in order to obtain optimal results. Thermogravimetric analysis (TGA), differential thermal analysis (DTA) and differential scanning calorimeter (DSC) are used as thermoanalytical techniques for monitoring changes in physical and chemical properties of materials as a function of temperature by detecting the heat changes associated with such process. Samples (6-9 mg) were placed into aluminum DSC pans and hermetically sealed; an empty aluminum pan was used as the reference. Nitrogen or air at a rate of 2°C/min was used to flush continuously the measuring cell to prevent water condensation.

**Sulphuration of the Fruit**

After harvest, the fruits were treated with sulphur dioxide by burning elemental sulphur in an enclosed chamber for two hours. Four different level of sulphurization doses were applied in order to find out the optimal sulphurization dose, sulphurization time and the change in fruit contents. After treatment with sulphur, fruits were dried in the sun, until moisture content was reduced to 25% threshold. The fruit skin color in dried was determined according to the Hunter method and was indicated as CIE L*a*b*. (Özkan, 2003). The sulphur content was determined according to the Monier Williams method.

**RESULTS AND DISCUSSION**

The characterization of apricots has been carried out using DSC, TGA and DTA. (Harwalkar and Ma 1990; Biliaderis and Seneviratne 1990; Dyszel et al., 1990). Fresh fruit and sulphurized fruits were analyzed for characteristics relating to their chemical composition in terms of sugars, polysaccharides and carbohydrate content. Computerized curve fitting data was demonstrated for a series of sugars. The first step in the decomposition process was the formation of levoglucosan. As shown in Figure 1, in general, carbohydrates at 360 °C have a loss of volatile products representing between 60 to 75% of the total...
Table 1: Fruit characteristics of Hacýhaic6lu apricot cultivar

<table>
<thead>
<tr>
<th>Properties</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fruit thickness (mm)</td>
<td>37.7 ± 2.1</td>
</tr>
<tr>
<td>Fruit breadth (mm)</td>
<td>36.4 ± 2.2</td>
</tr>
<tr>
<td>Fruit weight (mm)</td>
<td>38.5 ± 2.5</td>
</tr>
<tr>
<td>Fruit weight (g)</td>
<td>33.2 ± 0.7</td>
</tr>
<tr>
<td>Pit weight (g)</td>
<td>2.1 ± 0.04</td>
</tr>
<tr>
<td>Kernel weight (g)</td>
<td>0.6 ± 0.1</td>
</tr>
<tr>
<td>Soluble solids (%)</td>
<td>25.5 ± 0.6</td>
</tr>
<tr>
<td>Acidity (% malic)</td>
<td>0.45</td>
</tr>
<tr>
<td>pH</td>
<td>4.60</td>
</tr>
<tr>
<td>Fruit shape</td>
<td>Ovate</td>
</tr>
<tr>
<td>Pit shape</td>
<td>Ovate</td>
</tr>
<tr>
<td>Fruit taste</td>
<td>Sweet</td>
</tr>
<tr>
<td>Kernel flavor</td>
<td>Sweet</td>
</tr>
<tr>
<td>Skin color</td>
<td>Yellow</td>
</tr>
<tr>
<td>Skin color (CIE Lab)</td>
<td>L 76.3 a + 4,13 b + 51.00</td>
</tr>
<tr>
<td>Flash color</td>
<td>Yellow</td>
</tr>
</tbody>
</table>

mass and at 450 °C the remaining char is 25 to 30% by mass. The initiation temperature of the decomposition varies with sugar as shown in Figure 2. Fructose and lactose decomposes nearly 30 °C earlier than glucose. Glucose was observed to exhibit a single large decomposition step at 270 °C and 297 °C with 86.6% total weight loss and the char yield was 14.15%.

The disaccharides were found more stable than monosaccharides in general except where fructose was one of the pair and sugars with b-bonded glucoses were more stable than those a-bonded (Biliaderis and Seneviratne 1990).

Shifting focus from model compounds to actual food products fresh apricots and sulphurized apricot (Figure 3-6) reveals several interesting finding and applications of DSC and TGA. Since it is known that glucose combines with amino acids to form several different compounds (Harwalkar and Ma 1990), Maillard reaction was studied by thermogravimetry and DSC. As a result it was found that an average of 1 mole of amino acids reacted with 1,5 moles of glucose and cysteine and cysteine catalyzed the thermal decomposition of glucose. Amodori compounds are formed by the reaction of D-glucose and L-amino acids that undergo the Amodori rearrangement to form N-(1-deoxy-D-fructo-1-yl)L-amino acids (Harwalkar and Ma 1990). These are key products of the Maillard browning reaction which could be diminished after sulphur treatment. The sulphurized glucose and other sugars as well as sulphurized apricots were not found to exhibit characteristic Amodori reaction and Amodori rearrangement because sulphur is bonded to glucose molecule which prevents Maillard browning reaction. The DSC data supported these conclusions. The glucose itself showed endothermic peaks at 115 °C which is shifted to 140 °C after the sulphur content increased to 60%. and finally two endothermic peaks were observed at 90 and 120 °C. These were attributing to the unstable sulfate residues. Structure-activity relationships of carbohydrates in food products from analyses of the thermal and thermomechanical properties of common food ingredients in model systems was studied by differential scanning calorimetry (DSC). Because all materials synthetic and natural alike when observed in their physical solid state in the appropriate temperature range, exist in one of the several structural forms: completely crystalline, semicrystalline, partially crystalline, or completely amorphous. The term semicrystalline usually denotes materials of >50% crystallinity such as cellulose; the term partially crystalline refers to materials of <50% crystallinity, such as gelatin gel and native starch. Among various physical and chemical techniques applied to provide insights into the chemistry of the food ingredient, DSC and TGA methods have been widely used for detecting physicochemical transformations occurring during thermal degradation of carbohydrates. However, since TGA methods measure net changes in enthalpy and weight loss respectively, as a result of many reactions take place simultaneously, the real data are rather limited value in the elucidation of reaction
Fig. 1: DTA and TGA thermogram of Hacılıloolu Apricot Cultivar

Fig. 2: TGA thermogram of various sugars
Fig. 3: DSC thermogram of Fructose (a) and sulphurized fructose with 10g S (b), 30 g S (c) and 60g S (d)

Fig. 4: DSC thermogram of glucose (a) and sulphurized glucose with 10g S (b), 30 g S (c) and 60g S (d)
mechanisms. Nevertheless, these techniques are useful indicating the temperature range and the rate of pyrolytic process. It must be noted that pyrolysis of carbohydrates involves a sequence of concurrent and consecutive reactions, which are influenced by the prevailing conditions. Briefly, the suggested mechanisms for molecular rearrangement or transformations that take place include cleavage of glycosidic linkages via free radical formation or transglycosylation, formation of anhydrous sugars via transglycosylation, condensation and dehydration, and decomposition into carbonaceous char and volatiles via dehydration, disproportionation, and fission reactions. Some of these reactions are endothermic such as transglycosylation and volatilization while others exothermic in character dehydration and charring. Raemy and Schweizer, (1983) have carried of extensive calorimetric investigations on thermal degradation of a range of sugars and polysaccharides. Under the experimental conditions employed in our studies, the decomposition reactions yielded endothermic transitions temperature and enthalpy.

DSC analysis of the fruit development period in terms of sugar content are presented in Figure 7. All stone fruits, e.g. peach, apricot, plum, and cherry, and some nonstony fruits, e.g., fig, grape and currant show double growth curve, though the growth curves don't seem to distinctive for the different morphological type of fruits. The growth of fruit development could be explained in terms of fruit-growth rates which includes the type of growth period for all fruits. As the fruit reaches the growth period, it may undergo characteristic qualitative changes that are collectively referred to as ripening. The meaning of ripeness is different from the maturation, maturation refers to the process associated with a fruit reaching full size, whereas ripening refers to the process that qualitatively transform mature fruit. The
Fig. 6: TGA thermogram of sulphurized apricot.

Fig. 7: DSC Thermogram of Hacíhalíodoğulu Cultivar in terms of fruit development period
(a; May 5th, b; May 20th, c; June 5th, d; June 20th, e; July 5th)
general changes related with ripening is the hydrolytic conversion of storage materials in the fruit, and changes in pigments and flavor (Crowe et al 1984). Hydrolytic changes during ripening usually lead to formation of sugars. Various fruit show widely different rates and extents of such hydrolytic activities. Enzymatic changes in fruit include pigmentation and production of the other flavor materials (Vertucci, 1989). It was evident that sugar formation in terms of maturity increases with the time. The sample after 30 days of flowering, shows an endothermic peak over 100°C which was attributed to the carbohydrate formation (Fig. 7).

The peak intensity as well as other minor peaks was observed after the second period and the steady state was observed after 5th, July that is the usual harvesting time for apricot fruits. The carbohydrate content was maximized after 5th, July indicated that the best period of harvesting could be rationalized in terms of the soluble solid content which was nearly 24-28 wt %. Changes in enzyme components of the apricot were involved in the pigmentation during ripening and enzymatic browning reaction formed by the reaction of D-glucose and L-aminoacids to form N-(1-deoxy-D-fructo-1-yl)L-amino acids, key products of the Maillard browning reaction (Leopold, and Kriedemann 1975). As shown in Figure 8, the endotherm at 115 °C decreases steadily with the increasing sulphur content.

**CONCLUSION**

The analysis of apricots by thermal analysis techniques such as TGA, DSC and DTA covers a wide range of applications. Some of them are cited in the literature, however many more might be in use in commercial food laboratories. From studies of the ripening of apricot fruits and sulphurization of apricot fruits, the ripeness is associated with spectacular changes in sugar which was followed by thermal analysis and the change in growth period was rationalized with the
glucose, though we are aware of many other changes that could also be associated with the ripeness. 'Hacıhalidolu' cultivar apricot fruits sulphurized and changes were followed by DSC showed sulphur is mostly bonded to the glucose molecule and change the molecular structure in the dry fruit.

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REFERENCES


