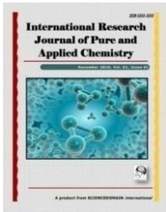

International Research Journal of Pure & Applied Chemistry
7(1): 18-33, 2015, Article no.IRJPAC.2015.051
ISSN: 2231-3443

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Physicochemical Characterization of Jordanian Air Dried Olive Fruits

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Author's contribution

The sole author designed, analyzed and interpreted and prepared the manuscript.

Article Information

DOI: 10.9734/IRJPAC/2015/15127
Editor(s):
(1) Hao-Yang Wang, Department of Analytical, Shanghai Institute of Organic Chemistry, Shanghai Mass Spectrometry Center, China.
Reviewers:
(1) Anonymous, Greece.
(2) Orwa Jaber Mahmoud Houshia, Chemistry Department, Arab American University, Palestine.
(3) Anonymous, Italy.
(4) Anonymous, Spain.
Complete Peer review History: http://www.sciencedomain.org/review-history.php?iid=959&id=7&aid=8270

Original Research Article

Received 8th November 2014
Accepted 31st January 2015
Published 26th February 2015

ABSTRACT

The effect of indoor air drying on the mass of irrigated and rain-fed green and black olives has been investigated in the present study. Mass loss data were collected over a drying period of about four months. Several measurements were carried out on the pit and pulp fractions of the dried samples. These measurements included the determination of: Mass percentages of pits and pulp fractions, mineral and fat contents, percentages of carbon, hydrogen and nitrogen, gross and net calorific values. Results based on using simultaneous thermogravimetry and differential thermal analysis, derivative thermogravimetry and differential scanning calorimetry are reported for pits derived from rain-fed green and black olives. The maximum average % mass loss was found to be 78.99% for irrigated green olives while the minimum average % mass loss was found to be 34.48% for rain-fed black olives. The percentages of pulp and pits for dry green olives fall in the range 57.59 - 65.18% and 33.91 - 39.98%, respectively. The corresponding ranges for the dry black olives are 65.13 - 76.70 and 20.65 - 33.76% for pulp and pits fractions. The gross calorific values are 21.609 and 21.745 kJ/g on dry basis for pits of rain-fed green and black olives. Soxhlet extraction with n-hexane of rain-fed olives gave extractives percentages of 23.39 and 21.84% for pits of green and black olives and 46.43 and 51.80% for pulp fraction of green and black olives, respectively. The pyrolysis thermograms gave residual masses of 0.29 and 0.27 at 600°C for pits

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of green and black rain-fed olives. Three peaks were identified on the derivative curves. Peak value, peak temperature and % remaining mass at the peak temperature were determined. The differential scanning calorimetric curves of the studied samples showed a series of exothermic humps in addition to the endothermic moisture peak.

Keywords: Air drying; dry olive fruits; extraction; heat of combustion; thermogravimetry.

1. INTRODUCTION

Food preservation had been realized as a necessity by mankind since ancient times. The need for food preservation arises when an excess of a crop cannot be totally consumed or sold in its harvest season or when direct access to fresh food sources is impossible. It is a fact that no plant can survive without water and no food can be preserved without removal of its water content. Removal of water inhibits the growth of bacteria, yeast, mold, and other microorganisms that usually cause deterioration of food. However, in most cases food drying requires a pretreatment step to deactivate enzymes. Before the advent of modern techniques of food drying, removal of water was achieved by sun drying. This process was found suitable for drying several types of fruits and vegetables such as figs, grapes, and tomatoes. This method of food drying is usually slow and inefficient in cloudy and humid climate; in addition to this, food contamination caused by dust and insects is very likely to take place. These drawbacks of sun drying are largely eliminated by using the modern techniques of electrical food dehydrators and freeze-drying. For a variety of food types, several methods for drying food at home have been described [1-2]. The common methods of food drying are: Sun drying, hot air drying, indoor air drying, food dehydrators, oven drying, solar drying, freeze-drying, and microwave drying. Several literature reports have dealt with description of a drying method, effect of the drying method on food quality, modeling and kinetics of water removal. For example Orphanides et al. [3] have studied the effect of drying method on the phenolic content and antioxidant capacity of spearmint; Ongen et al. [4] have used hot air drying for the preparation of dry pitted table olives suitable for human consumption as snack food; preparation of dry salt-cured ripe black table olives [5]; Mahdaoui et al. [6] have reported a study on microwave drying kinetics of olive fruit, and Marsilio et al. [7] have studied textural properties as related to pectic composition of oven-dried table olives. Information regarding the basic parts of the olive fruit and their characterization as well as stages of olive maturation has been reported [8-10]. Olive drying (with minimum exposure to morning and afternoon sun light) had been a common practice in Jordan as a pre-treatment step of ripe olives before taking the crop to the stone olive mills.

The main objective of the present work was to examine the effect of indoor air drying on the mass of fresh olive fruit samples and on the percentages of their pits and pulp fractions. Getting oil out of the dried olives was not an objective of the present work. However, the findings on mass loss can be considered as basis for further investigations aiming at assessing the advantages and disadvantages of olive drying on the quality of the produced oil or table olive. Since burning of olive pits is usually used for heat generation, certain measurements related to such application were also carried out. These measurements included the determination of heat of combustion, ash yield, and the pyrolysis thermograms.

2. MATERIALS AND EXPERIMENTAL PROCEDURES

Five fresh olive fruit samples were considered in the present study. The relevant information concerning these samples is given in Table 1. Three of these samples belong to the 2007 olive harvest season (samples with symbols: S, N and B) and two samples belong to the 2008 harvest season (samples with symbols: T1 and T2). As with regard to the olive quantities used in the present study, it was thought that about 50 fruit pieces per sample is an adequate quantity. This was the case for samples TI and T2. The other samples were donations with initial amounts less than 50 pieces per sample. Exclusion of damaged and brose fruits had resulted in the quantities reported in Table 1 for samples N, B, and S. The samples were spread on plain A4 paper and were left to dry out in a room of ambient temperature around 25°C. As will be explained later, the fruit pieces of a given sample were distributed into sub-groups based on fruit size, fruit shape, and fruit color. The mass of the olives of each sub group was determined every 3 to 4 weeks. The mass percent loss of olives was calculated at each mass measurement. The air drying of a sample was terminated when its mass no longer changes with time. The length of the air drying treatment falls in the range 156 to 118 days. As with regard to the length of air drying, the intention was to give longer time in order to reach the highest mass constancy especially for samples N and B.

The number of sub groups was dealt with as follows. In the case of samples S, N, and B, the number of sub groups is the same as the number of the olive pieces of the sample. This means that every olive piece was weighed individually during the air drying period. However, the olive pieces of samples T1 and T2 were divided into sub groups. Sample T1 has four sub groups with symbols Yu1, Yu2, Yu3, and Yu4 that contained 24, 24, 7, and 3 olive pieces, respectively. In the case of sample T2, the olives were divided into 14 sub groups with symbols Yu5 to Yu18. The four sub groups Yu5 to Yu8 contained 11, 11, 9, 12 olive pieces, respectively. The remaining 10 sub groups were single-fruit sub groups that carry the symbols Yu9 to Yu18.

For the purpose of doing measurements other than mass loss, each dried fruit piece was fractioned into its pit and pulp components. The fruit pulp was hand-separated from its pit by using a sharp knife. Care was taken to minimize the handling loss during this process. The masses of pits and pulp fractions were determined in order to calculate the mass percentage of each fraction.

The oven drying experiments were carried out at 120°C by using a conventional drying oven. The pits and pulp samples used for the oven drying measurements were derived from samples S and N. The obtained samples were given the symbols KT18, KT19, KT20, KT21, and KT22. The details of the treatment of these samples are given in section 3.2.

Pits of samples T1 and T2 were used for determining the gross calorific value (GCV), the net calorific value (NCV) and the percentages of carbon, hydrogen, and nitrogen. These pit samples were given the symbols Yu19 and Yu20 for green and black olives, respectively. The heat of combustion measurements were carried out by using an adiabatic oxygen bomb calorimeter (IKA C 2000 Calorimeter System, IKA, Germany) with heat capacity of 8985 J/K. About one gram of the test sample was used and the reported value of GCV is the average of two runs. The elemental analyzer (Euro Ea 3000, Perkin Elmer, USA) was used for determining the % of carbon, hydrogen, and nitrogen. The reported percentages of the elements were based on duplicate analysis.

For the determination of the percentages of moisture, ash and fat material, the pits, seeds, and pulp fractions of samples T1 and T2 were used. These fractions were given the symbols Yu19, Yu20, Yu21, Yu22, and Yu23. The symbols stand for pits of green olives, pits of black olives, pulp of green olives, pulp of black olives, and seeds of green and black olives, respectively. The moisture content was determined by heating the sample in a conventional dying oven at 110°C for about 15 hours while the ash content was determined by burning about one gram of the sample in a muffle furnace at 600°C for five hours. The moisture content was based on duplicate runs while the content of ash was based on triplicate runs. The determination of fat content was accomplished by using a soxhlet extractor and n-hexane with 95% purity. About 5 g of the sample and 250 ml of n-hexane were used for each extraction experiment. The duration of an extraction run was about 48 hours. Other details of the extraction method were reported previously [11].

The pits samples Yu19 and Yu20 were used for the experiments involving simultaneous thermogravimetry and differential thermal analysis (TG/DTA) and differential scanning calorimetry (DSC). Nitrogen gas at a flow rate of 100 ml/min and a heating rate of 20°C/min were used. Aluminum crucibles provided with pierced lids were used. The thermogravimeter Netzsch TGA/DTA 409 PC Luxx (Netzsch, Germany) was used for conducting the TG pyrolysis experiments and Netzsch DSC 409 PC Luxx (Netzsch, Germany) was used for DSC measurements.

3. RESULTS AND DISCUSION

3.1 Results of Air Drying

3.1.1 Percentages of mass loss as function of air drying time

Since the number of olives is not the same in all sub-groups of samples T1 and T2, the statistical weighted mean formula was used for calculating a property pertaining to the whole olive sample. The properties calculated according to this formula were the mass loss at the end of a given

Table 1. Identification of the olive fruit samples used in the present study

Sample identity	N	B	S	T1	T2
Collection date	Nov 20, 2007	Oct 28, 2007	Dec 6, 2007	Oct 30, 2008	Nov 2, 2008
Olives number	24	10	23	58	53
Olives color	Green	Green	Black	Green	Black
Fruit source	Al-Shobak, Southern Jordan	Al-Bayader fruit market, Amman	Al-Shobak, Southern Jordan	Yarmouk University campus	Yarmouk University campus
Drying period / days	140	156	120	120	118
Cultivar	Nabali	Unknown	Nabali	Kfari baladi	Kfari baladi
Remarks on dried olives	Dark brown, rock hard, shrunk	Black/brown, hard, shrunk	Dark black, hard, shrunk	Black/brown, hard, shrunk	Dark black, hard, shrunk

drying period for both the sub-groups and the whole olive sample and the percentages of olive pits and olive pulp of a dry fruit at the end of the air drying treatment. The statistical formula used is given by Equation (1).

$$\% F = \sum_{1}^{z} \frac{n}{N} (\% f) \quad (1)$$

Where *F* is the weighted mean of a given property of the whole olive sample, *N* is the total number of olive fruit pieces of the sample, *z* is the number of sub-groups for a sample, *n* is the number of olive fruit pieces in a sub-group, and *f* is the value of the property for a given sub-group. To shed some light on the application of Equation (1) and to illustrate the distribution of the olives of a sample into sub-groups, sample T2was considered for these purposes.

Guided with differences in fruit size, shape, and color, the 53 olives of sample T2 were divided into 14 sub-groups; 10 sub-groups (yu9 – yu18 in the legend of Fig. 1) had just one fruit piece per sub-group while the other four sub-groups (yu5 – yu8 in the legend of Fig. 1) contained 11, 11, 9, and12 fruit pieces per sub-group. Fig. 1 shows a plot for data of sample T2 based on calculations according to Equation (1). As can be seen from Fig. 1, the % mass loss of the tested sample starts to level off at nearly 50 days of air drying. The last point on the plateau region was taken to represent the average maximum % mass loss of an olive sample. Following the same procedure used for sample T2, the 58 olives of sample T1 were distributed over four sub-groups (yu1 – yu4 in the legend of Fig. 2); the results of the mass loss calculations are shown in Fig. 2. The values of the average maximum % mass loss for the other olive samples were obtained in accord with Equation (1) with a modification *N* = *Z* and *n = 1*. The results for all samples are given in Table 2. For the sake of comparing the mass loss behavior of green and black olives, samples T1 and T2 were considered because they are the only pair that can be selected from Tale 1 with highest number of similar characteristics for two olive samples. The average percentages of mass loss data for these two samples are shown graphically in Fig. 3. According to this figure the mass loss of the green olives is higher than that of the black olives. By considering the scatter of data points in Figs. 1 and 2, we observe that Fig. 1 has the highest scatter. The values of the percent relative deviation, % R.D, (% R.D = mean of absolute deviations x 100/mean) are 11.85 and 2.08% for samples T2 and T1, respectively. It should be mentioned that the 58 olives of sample T1 were divided into 4 sub-groups none of them is a single-fruit sub-group, while the 53 olives of sample T2 were distribute into 14 sub-groups, 10 of them have one fruit per sub-group. For sample T2 the scatter reflects the fact that the individuality of the single-fruit sub-groups is dominating the value of R.D. The individual deviations of each fruit sample are manifestations of differences in the rates of physical processes governing the loss of water and other volatile organics during the drying period. Such rates are expected to depend on the degree of ripeness, the fruit surface area, and the pore structure of the fruit skin. The values of the % mass loss given in Table 2 indicate that the rain-fed samples (T1 and T2) have substantially lower mass percent loss as compared to the irrigated samples (N, S, and presumably B). As with regard to black vs. green comparison, the data of Table 2 indicate that the black fruits (samples S and T2) have lower mass percent losses as compared to their counterparts of green fruits (samples N and T1). These observations can be explained on the basis of the water content and the degree of ripeness of an olive fruit. Irrigated olives have higher vegetal water content and are expected to show higher mass loss than the rain-fed olives. Black olive fruits are ripe with high olive oil content and are expected to have lower mass loss as compared to the unripe green olive fruits.

To elaborate on the data of average maximum mass loss given in Table 2, pairs of samples were considered. Samples S and N constitute a pair because they have the same cultivar, belong to the same geographical region, and were collected from irrigated olive trees. Also samples T1 and T2 constitute another pair because they have the same cultivar, same geographical region, and they were picked from rain-fed olive trees. Samples B and B* (B*not included in Table 1, represents 32 green olives, collected in October 2006, air dried for one year), might be considered as a pair because they were collected from the same fruit market nearly at the same time of the annual table olive season. Each one of these two samples contains olives of different size and shape but their cultivars were not known. In Table 2 samples N, B, and B* were classified as "table olive" because they were intended for making pickled olives, while samples S, T1 and T2 were classified as "oil olive" because they were intended for getting olive oil. The differences in mass loss between "table olive" and "oil olive" for the pairs S-N and T1-T2 can be explained on the assumptions that the oil/vegetal water ratio is higher in the "oil olives" and that the rate of water loss through the pores of the fruit skin is much faster than the rate of loss of olive oil. According to this reasoning sample N is expected to lose more weight than sample S. This reasoning explains the difference in mass loss between green and black olives evident in Fig. 3.

Unfortunately, due to the unknown initial mass of sample B*, there is no total mass loss entry for this sample. The inclusion of this sample in Table 2 was based on the fact that it has several properties in common with sample B. On geographical basis, the pairs N-S, B-B*, and T1-T2, belong to southern, central, and northern parts of Jordan, respectively. In southern Jordan water irrigation of olive trees is a must because of the low level of annual rain fall. However, in central Jordan olive trees are mostly rain-fed, while in northern Jordan olive trees are usually rain-fed.

3.1.2 Percentages of pits and pulp fractions of dried olive fruits

The percentages of pulp and pits given in Table 2 were calculated according to Equation (1) on the basis of the total dry mass of each one of the olive samples at the end of the air drying period. These percentages are weighted mean values. The symbols N and n appearing in Equation (1) can be replaced by the symbols W and w, which stand for the total mass of all the olives of the sample and to the total mass of the olives of a sub-group of the sample, respectively. It is evident in Table 2 that sample S has the highest % pulp and the lowest % pit; while the other samples have the percentages of their pulp and pits nearly in the sixties and thirties, respectively. It is interesting to notice that the degree of dryness caused by air drying, had no major effect on the percentages of pulp and pits fractions of the dried olives. The variation of the average percentages of pulp and pits of the irrigated black and green olives of samples S and N as a function of the mass of the dry olive fruit are given in Figs. 4 and 5, respectively. Fig. 4 was based on actual mass measurements for 23 olive fruit pieces (all fruits of sample S) and for their pit and pulp fractions. Because of the large % mass loss of sample N, some of its dry olives were so tiny. In this case several combined samples were made out of these tiny olives. As a result of this, Fig. 5 contains only 14 pairs of data instead of 24 points (the actual number of fruit pieces of sample N is 24). The scatter of points in Fig. 5 about their averages is quite noticeable when compared with data of sample S. To some extent, the same observation can be seen in Fig. 6 for green and black rain-fed olives of samples T1 and T2. However, when the data of sample B were graphed, large scatter in the percentages of pulp and pits was found. This scatter is most likely due to the fact that the olive fruit pieces of sample B were from different olive cultivars that might have substantial differences in their pulp and pits percentages.

Despite the slight variations in the mass percentages of both the pit and pulp fractions given in Fig. 4, the ripe olive fruits of sample S gave pulp to pit mass ratio nearly independent of the mass of the dry fruit. Such observation cannot be found in Fig. 5.

Assuming that the oil yield depends on the mass percent of the pulp, small olives are expected to give lower oil yield because the contribution of pulp, which contains the oil, to the fruit mass is low. The conclusion to be drawn from these

Table 2. Data for the percent averages of maximum mass loss, pits, and pulp fractions of dry olive fruit samples

Sample type	Average maximum mass loss (%)	Pulp average (%)	Pits average (%)	Pulp/Pits ratio	Handling loss (%)
Table olive (Sample N)	78.99	62.20	35.29	1.76	2.51
Table olive (Sample B)	60.46	57.59	39.98	1.44	2.43
Table olive (Sample [a]B*)	[b]n.d	59.56	36.80	1.62	3.64
Oil olive (Sample S)	61.12	76.70	20.65	3.71	2.65
Oil olive (Sample T1)	46.46	65.18	33.91	1.92	0.91
Oil olive (Sample T2)	34.48	65.13	33.67	1.93	1.20

[a]: Sample B was collected in 2006. Its history is the same as that of sample B1 and represents 32 green olive fruits intended for table olive, [b]: not determined*

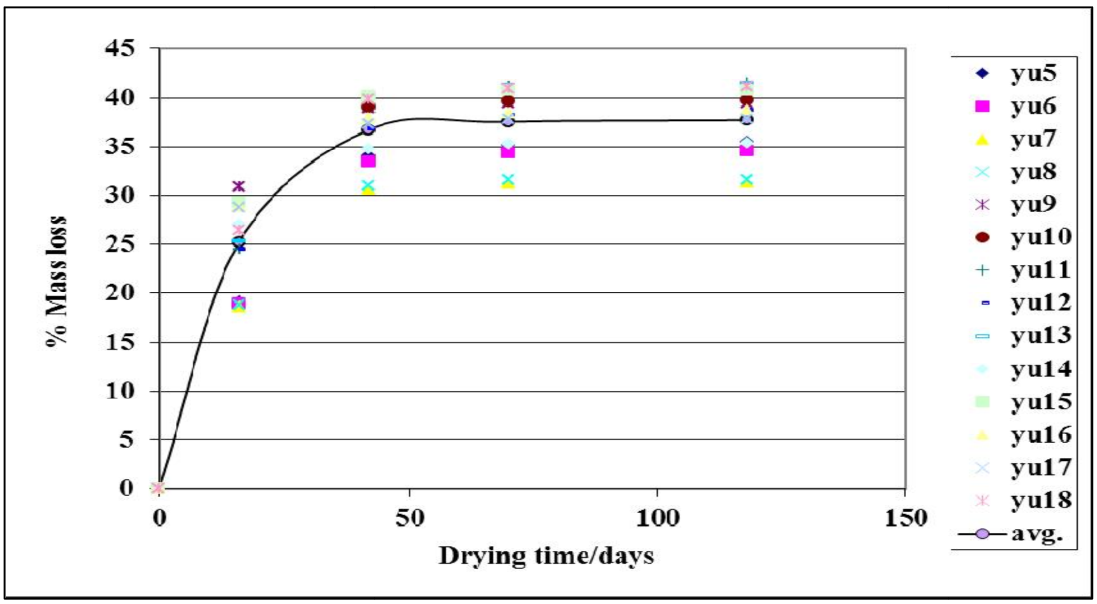

Fig. 1. Variation of the percentages of the mean mass loss with air drying period for sample T2 and its sub-groups

observations is that the degree of fruit ripeness is highest for samples S and T2 and their oil/vegetal water ratio is also the highest. Based on this conclusion, one can expect that the highest possible oil yield will be obtained from mature olives. The values of the pulp/pits ratio given in the fifth column of Table 2 indicate that the ratio for sample S is nearly twice the ratio for the other samples. Differences in the values of the pulp/pits ratio are very likely to be dependent on the type of olive cultivar and degree of ripeness of the olive fruit.

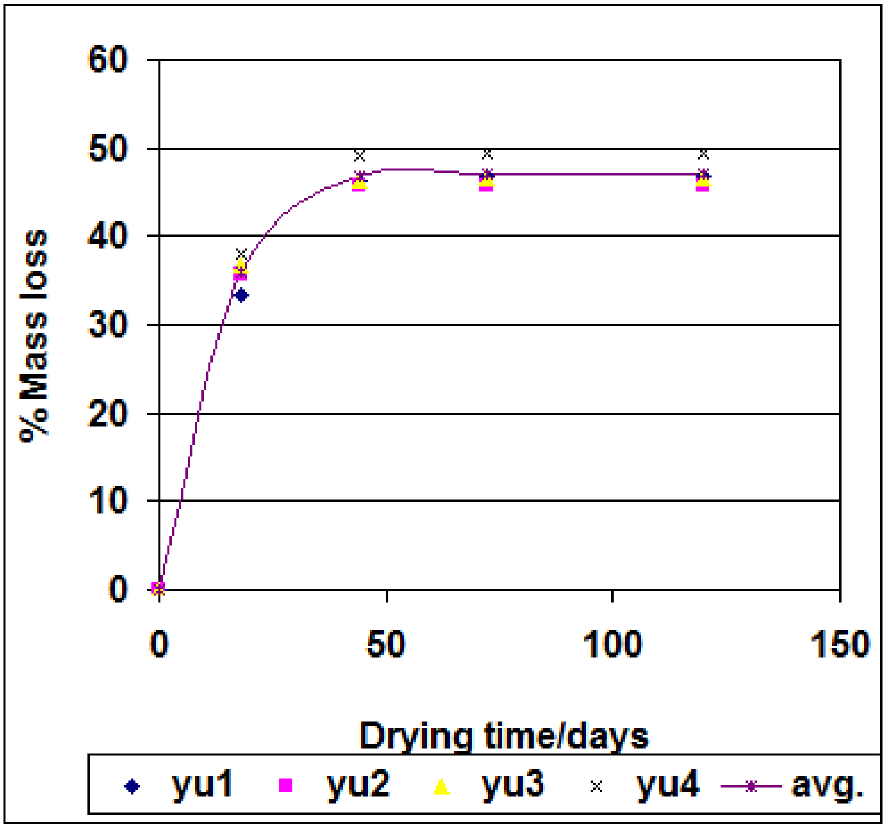

Fig. 2. Variation of the percentages of the mean mass loss with air drying period for sample T1 and its sub-groups

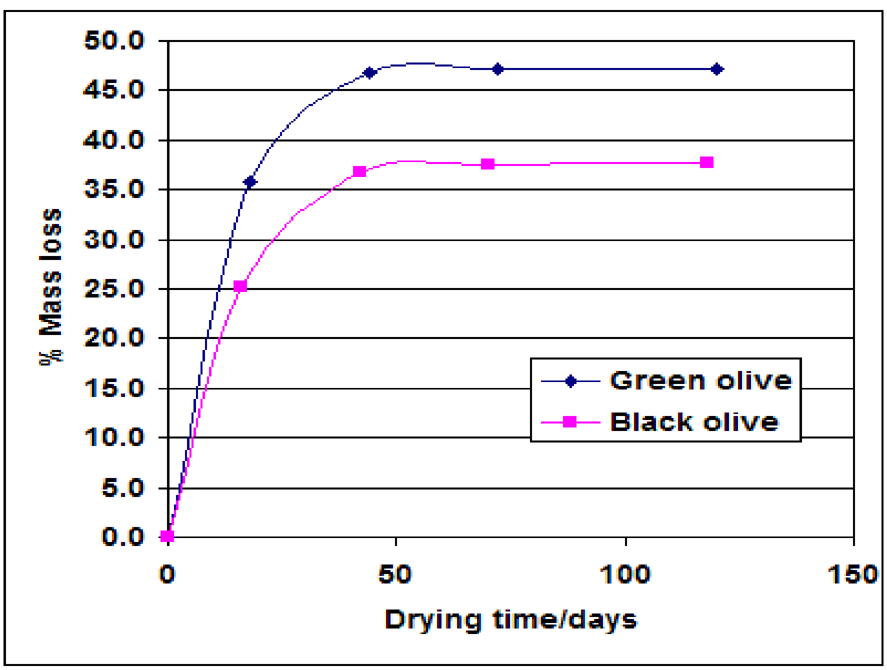

Fig. 3. Variation of average % mass loss with air drying time for rain-fed green and black olives

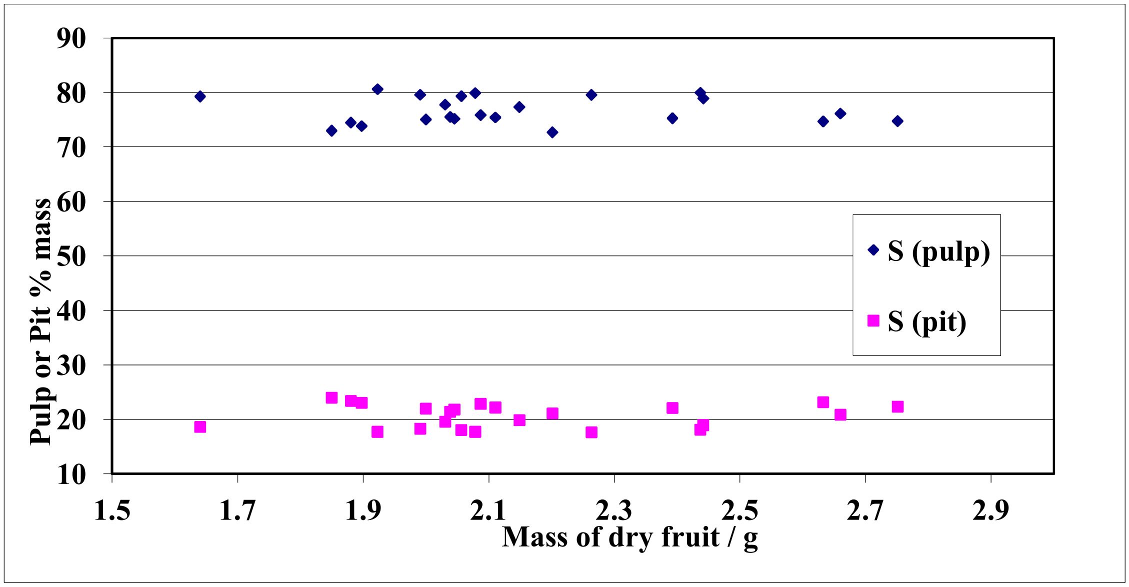

Fig. 4. Average mass percentages of pulp and pit components of irrigated black olives of sample S as function of the mass of the dry olive fruit

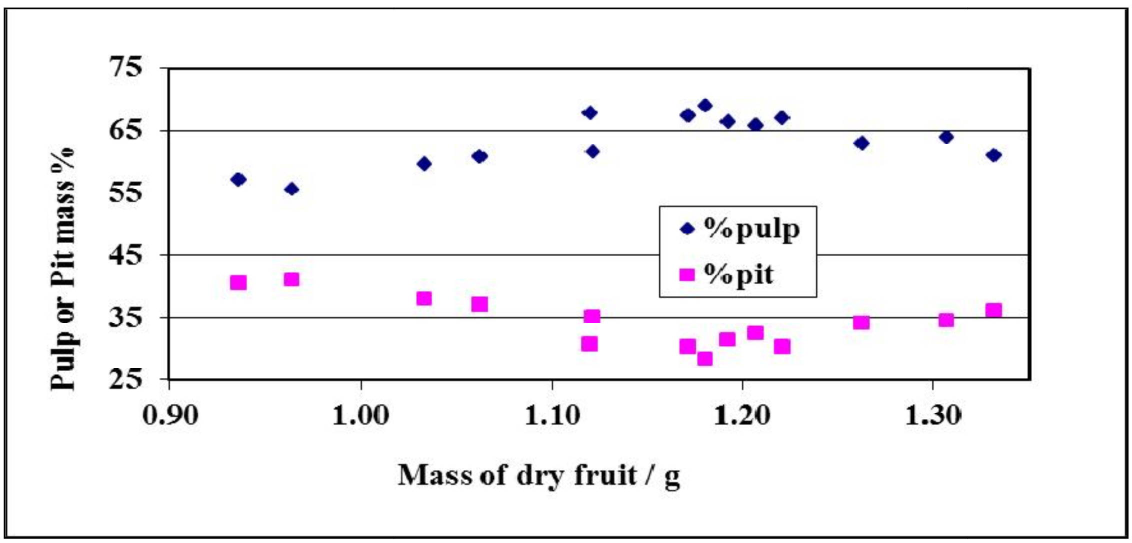

Fig. 5. Average mass percentages of pulp and pit components of irrigated green olives of sample N as function of the mass of the dry olive fruit

3.2 Oven Drying of Fragmented Dry Olives

To examine the behavior of the air dried pits and pulp upon grinding, a mixture of pits and pulp of six olive fruit pieces of sample S was prepared. When this mixture was ground in a metal mortar (household appliance), an appreciable amount of oil was released and further grinding resulted in oily dark brown slurry. Based on this observation, it was thought that heating might help in reducing the oil content of a sample; thereby a sample might be prepared in a powder form for further measurements. The temperature chosen for oven drying was 120°C. This temperature is close to the temperature usually adapted for moisture determination and well below the temperature of biomass torrefaction, which starts at about 200°C [12] and below the smoke temperature of extra virgin olive oil which is 160°C [13].

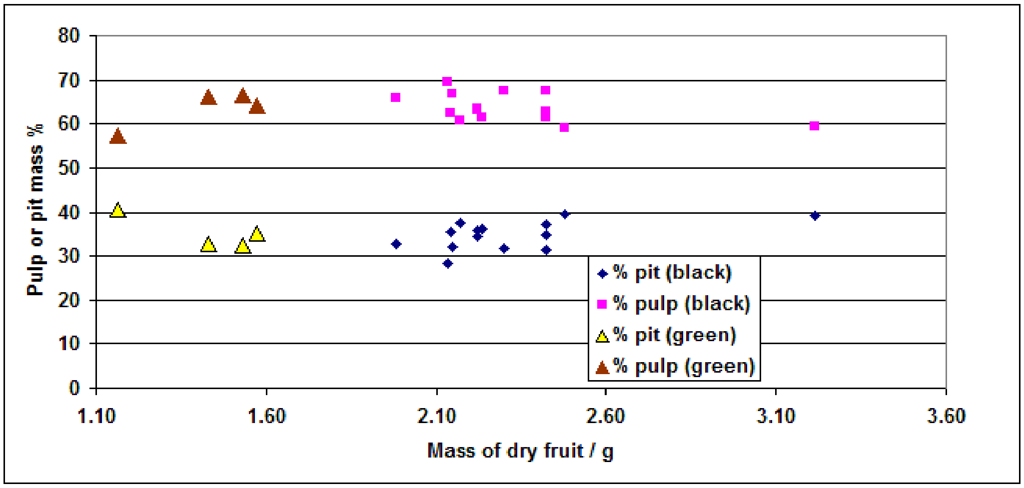

Fig. 6. Average mass percentages of pulp and pits components of rain-fed green and black olive fruit pieces of samples T1 and T2 as function of the mass of the dry olive fruit

The samples described in Table 3 were chosen for carrying out the oven drying experiments. As a pre-treatment, the samples were spread on paper sheets and were left to dry out in the laboratory environment for six weeks. During the oven drying treatment, the mass of each sample was recorded four times at 120°C over a period of 161 h. The accumulative mass loss percentages attained after the elapse of 161 hours of oven drying are given in Table 3 while the profile of mass loss upon heating is given in Fig. 7. According to this figure most of the mass loss occurs during the first 70 hours of the oven drying and beyond that the rate of mass loss becomes very slow. The mass loss data given in the last column of Table 3 indicate that the pits (samples KT19 and KT21) showed almost identical thermal behavior with percent mass losses higher than those of their pulp counterparts (samples KT18 and KT22). For the pits samples, the mass loss caused by the oven drying is larger than that caused by air drying by a factor of 5.8 for sample KT19 and by a factor of 3.9 for sample KT21.The high % of mass loss associated with pit samples is very likely to be due to the presence of adsorbed oil and oily fine pulp particles at the pit surface. Such oil is effectively driven off by heat rather than by air drying. As a matter of fact it was not possible to completely free the pit surface from oily brown fine pulp particles and traces of oil by scrubbing and wiping with tissue paper before starting the oven drying experiments. In the case of the pulp samples and the composite sample (KT20) the air drying was efficient in removing moisture and volatile organic matter. The pulp fraction was composed of several flakes with relatively large oil-containing surface in direct contact with the surrounding air. The last point concerning the data depicted in Fig. 7 is concerned with sample KT20. This sample is thought of as a "composite sample" made from a mixture of pits and pulp as given in Table 3. The exact position of the curve of sample KT20 in Fig. 7 was verified from the pit and pulp mass percentages (on handling loss-free basis) of the parent fruits (sample S) and the mass percent losses of samples KT18 and KT19 at a given time during the oven drying experiment. The formulas used for such calculation procedure are given below.

$$(\%\, L_s) = \sum_{i=1}^{i=4}\left(\frac{\%\, pulp}{100}\right)L_i + \sum_{j=1}^{j=4}\left(\frac{\%\, pits}{100}\right)L_j \quad (2)$$

$$M_s = M_o - L_s \quad (3)$$

Where $(\%\, L_s)$ is the calculated percentage of the accumulative mass loss of sample KT20 at a given oven drying time, L_i and L_j are the actual percentages of the accumulative mass loss of samples KT18 and KT19 at a given oven drying time, respectively. The $\%\, pulp$ and $\%\, pits$ are percentages of pulp and pits fractions of sample S as given in Table 2 but adjusted on handling loss-free basis. The adjusted values used in Equation (2) are 78.786% and 21.212% for pulp and pits, respectively. The symbol M_s is the calculated mass of sample KT20 at a given oven drying time, L_s is the calculated accumulative mass loss of sample KT20 while M_o is its initial mass (sum of masses of pits and pulp fractions).The calculated curve of sample KT20 is not evident in Fig. 7 because it coincides exactly with the experimentally determined curve.

Table 3. Sample description and mass loss data for the samples used in oven drying at 120ºC

Sample identity	Sample source	Mass loss (%) after 6 weeks of air drying	Initial mass (g) for drying at 120°C	Mass loss (%) after 161 h at 120°C
KT18	Pulp of 8 olives of sample S	9.8	12.0	5.0
KT19	Pits of 8 olives of sample S	1.2	3.4	7.0
KT20	Pulp & pits of 9 olives of sample S	7.4	18.2	5.3
KT21	Pits of 24 olives of sample N	1.8	9.3	7.0
KT22	Pulp of 24 olives of sample N	5.4	15.8	6.2

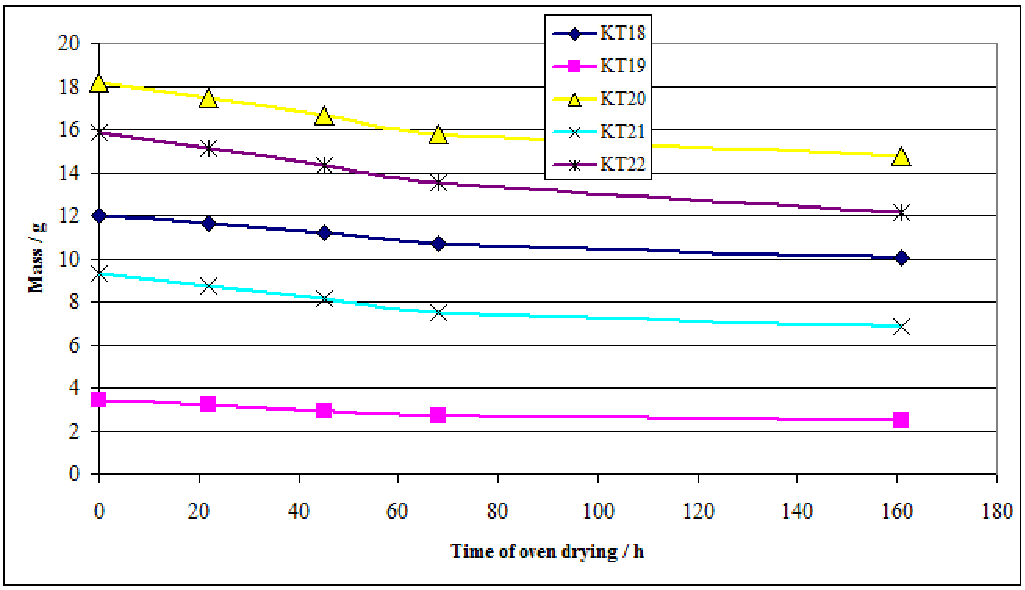

Fig. 7. Variation of sample mass with oven drying time at 120°C

3.3 Elemental Analysis, GCV, and NCV

The values of GCV and NCV as well as the percentages of moisture, carbon, hydrogen, and nitrogen of pits of rain-fed green and black olive fruit pieces are given in Table 4. The determination of the percentages of carbon, hydrogen and nitrogen is necessary for calculating the NCV of the burning of the pits samples according to Equation (4). As can be seen in Table 4, the samples nearly have the same values for percentages of carbon and hydrogen and the same values for GCV and NCV. The values of GCV reported in Table 4 can be compared with literature data reported on olive pits with a range of 19.9 - 21.1 kJ/g [14] and with the value 20.309 kJ/g for pits fraction of sun dried crude olive pomace [15]. Equation (4) was used for calculating NCV from GCV on dry basis with units of J/g.

$$NCV = GCV - \{(2442)\left(\frac{\%\,H}{100}\right)(9.01) + (92.7)(\%\,S) + (42.6)(\%\,N)\} \quad (4)$$

Equation (4) is based on the fact that the NCV of a fuel is less than its GCV. The terms: second, third, and fourth appearing on the right hand side of Equation (4) represent heat contributions that result from condensation of water coming from oxidation of sample hydrogen, heat of hydration of H_2SO_4 resulting from oxidation of sample sulfur, and heat of hydration of HNO_3 resulting from oxidation of sample nitrogen, respectively. These amounts of heat energy are unattainable when the fuel is burned under normal conditions of real life applications. Because of the low sulfur content of olive waste [16], the third term on the right hand side of Equation (4) was neglected from the calculation of NCV. Details on these thermochemical corrections can be found in our previous publication [11].

The present values of % C are close to 51.30, 51.04 and 51.14% reported for pits fraction, pits rich fraction, and fine fraction of crude olive pomace, respectively [15]. Also the % H and % N are somewhat less than those of crude olive pomace [15]. As with regard to % N, it was found that the % N of the pits of black olives is nearly half the value of the pits of green olives; presumably due to differences in the degree of fruit maturation. Differences in protein content for green and black table olives have been reported [17,18].

3.4 Ash and Fat Content of Rain-fed Olives

The description of the rain-fed samples used for determination of ash and fat content is given in Table 5.With the exception of sample Yu23, the % of ash and % fat for the other samples are given on dry basis. It is seen from Table 5 that whether the olives are green or black, burning of pulp produces more ash than the burning of pits. The same observation was noted for the pits and pulp fractions of crude olive pomace as well as for its pit rich and pulp rich fractions [15]. The data of Table 5 also indicate that the ash content of the olive fruit seeds is a little higher than that of pits but substantially lower than the ash of pulp. These observations imply that the metal containing compounds are highly concentrated in the pulp fraction of the olive fruit. The data of fat content reported in Table 5 follow the same pattern of ash data. This means that whether the pits come from green or black olives, there is no significant difference in their fat content. In support of this finding is the fact that the pits samples Yu 19 and Yu20 gave nearly the same GCV. It has been reported that differences in % hexane extractives had resulted in different GCV [11 - 15]. On the other hand, the fat content of the pulp of black olives is notably higher than the fat content of the pulp of green olives. This difference is very likely to be due to differences in fruit maturity which implies that the oil content of black olives is higher than that of green olives. This conclusion applies fairly well to olives of the same cultivar that share the same environment and growth history as the case of the T1-T2 olive trees.

3.5 TG, DTA, and DTG of Pits of Rain-fed Olives

The pits samples used in the TG experiments were Yu19 and Yu20 whose description is given in Table 5. Fig. 8 illustrates the TG pyrolysis curve of sample Yu20 and the DTA trace from room temperature up to about 600°C. The main features of the TG curve are the loss of about 60% of the sample mass in the temperature range 200-400°C and the non-steady slope of the curve in this temperature range. On the other hand, the DTA response indicates the occurrence of an endothermic process below 200°C which peaks at about 130°C followed by an exothermic process that becomes noticeable at about 300°C. After this temperature the DTA curve continues ascending until the exothermicity peaks at about 520°C then the curve bends downward. The significance of the DTA curve will be discussed in the next section which deals with the DSC measurements. The main features of the TG and DTA profiles of sample Yu19 were similar to those of sample Yu20. The DTG curves of samples Yu19 and Yu20 are given in Fig. 9. The symbols P1, P2, and P3 appearing in Fig. 9 denote the location of the three DTG maximums. The values of the *x* and *y* co-ordinates of these maximums are given in Table 6 for samples Yu19 and Yu20 based on the assumption that P1 is a moisture peak, P2 is a hemicellulose peak, and P3 is a cellulose peak. This assignment was followed in a previous publication that included DTG curves of wood and crude olive pomace samples [15]. Support for this assignment procedure can be found in several literature reports [19-23]. The resolution of the hemicellulose-cellulose DTG peaks as shown in Fig. 9 is better than that of olive pomace [15]. The data given in Table 6 indicate that the two samples have different peak temperatures and peak values for the loss of their moisture; but share the same % mass loss by the time the DTG maximum is attained. For hemicellulose decomposition, the two samples have different peak temperatures, while for cellulose decomposition the two samples have different peak temperatures and different peak values. Effects of heat and mass transfer usually associated with relatively large initial sample mass (sample Yu20 in our case) might be the cause of these differences.

3.6 DSC of Pits of Rain-fed Olives

The DSC curve given in Fig. 10 for sample Yu20 indicates an endothermic peak with peak

Table 4. Moisture content, elemental analysis and values of GCV and NCV for pits of rain-fed green and black olive fruit pieces. Elemental analysis, GCV, and NCV are given on dry basis

Sample	Moisture %	C %	H %	N %	GCV (kJ/g)	NCV (kJ/g)
YU19	4.74±0.26	49.772±0.059	5.969±0.017	0.740±0.050	21.609±0.010	20.264±0.010
YU20	6.52±0.01	49.994±0.152	6.108±0.124	0.423±0.054	21.745±0.010	20.383±0.010

Table 5. Moisture, ash, and fat contents of pits, pulp, and seeds of rain-fed green and black olive fruit pieces

Sample no.	Sample source	% Moisture	% Ash	% Fat
Yu19	Pits of green olives (sample T1)	4.74±0.26	1.03±0.02	[a]23.39
Yu20	Pits of black olives (sample T2)	6.52±0.01	0.81±0.03	[a]21.84
Yu21	Pulp of green olives (sample T1)	7.76±0.42	8.34±0.06	46.43±2.33
Yu22	Pulp of black olives (sample T2)	8.36±0.06	7.71±0.14	51.80±3.10
Yu23	Seeds of green and black olives	n.d	2.14±0.04	n.d

[a]: Values are based on one run; n.d: not determined

Table 6. Maximum rate of mass loss and peak temperature of major derivatives on the DTG curves of pits of rain-fed green and black olive fruit samples. Rates are given on dry basis

Sample identity	Yu19	Yu20
Initial mass of sample (mg)	16.52	40.06
Moisture peak temperature (°C)	95	101
Moisture peak value (%/min)	0.62	0.82
% of remaining mass at T1	98.54	98.28
Hemicellulose peak temperature (°C)	285	296
Hemicellulose peak value (% / min)	11.52	11.50
% of remaining mass at T2	81.45	80.54
Cellulose peak temperature (°C)	350	356
Cellulose peak value (%/min)	12.81	15.00
% of remaining mass at T3	51.82	53.28
TG mass fraction at 600°C	0.29	0.27

temperature at 114.8°C. This peak is due to removal of sample moisture. The corresponding temperature values on the DTG curve of Fig. 9 and on the DTA curve of Fig. 8 are 101 and 130°C, respectively. The moisture peak is followed by a thermally dormant stage up to about 220°C as can be seen on the DSC and the first derivative of DSC (DDSC) curves in Fig. 10. This temperature is nearly the onset temperature for the decomposition of lignocelluloses on the DTG curves of Fig. 9. At point P2 in this figure, the peak temperature for hemicellulose decomposition of sample Yu 20 is 296°C (see Table 6); the hump at 302°C in Fig. 10 is believed to be for exothermic decomposition of hemicellulose. The sharp peak at point P3 in Fig. 9 with peak temperature of 356°C was assigned for cellulose decomposition; for endothermic decomposition of cellulose, the peak at 354.5°C on the DSC curve is believed to represents such decomposition. Above 400°C, the high temperature diminishing part of the DTG curve, the ascending part of the DTA curve in Fig. 8 which peaks at 520°C, and the peaks at 384 and 443.9°C on the DSC curve are believed to be due to the slow decomposition of lignin.

The DSC curves had been used for calculating the calorific requirements for biomass pyrolysis by adapting a four-stage scheme. The scheme suggested by He et al. [24] is given as follows: a) Drying of biomass which accounts for removal of moisture, b) Heating of biomass where no mass loss takes place, c) Degradation of biomass, d) heating and aggregation of char. In our case stage (b) Is identified as a dormant stage because no mass loss and no heat effects took place up to 220°C. The events that took place after the onset temperature of 220°C were specifically discussed in the present work. The assignment of the DSC peaks as reported in the present work was based on literature information. Yang et al. [25] have shown that decomposition of lignin and xylan (a substitute for hemicellulose in lignocellulosic studies) is exothermic while decomposition of cellulose is endothermic. It should be mentioned that several unpublished DSC curves were obtained in our laboratory for olive pomace and pits of pickled olives. Some of these curves had their 302 and 384°C humps well above the 0.0 mW/mg ordinate. However, in all cases the curves maintained the same features evident in Fig. 10.

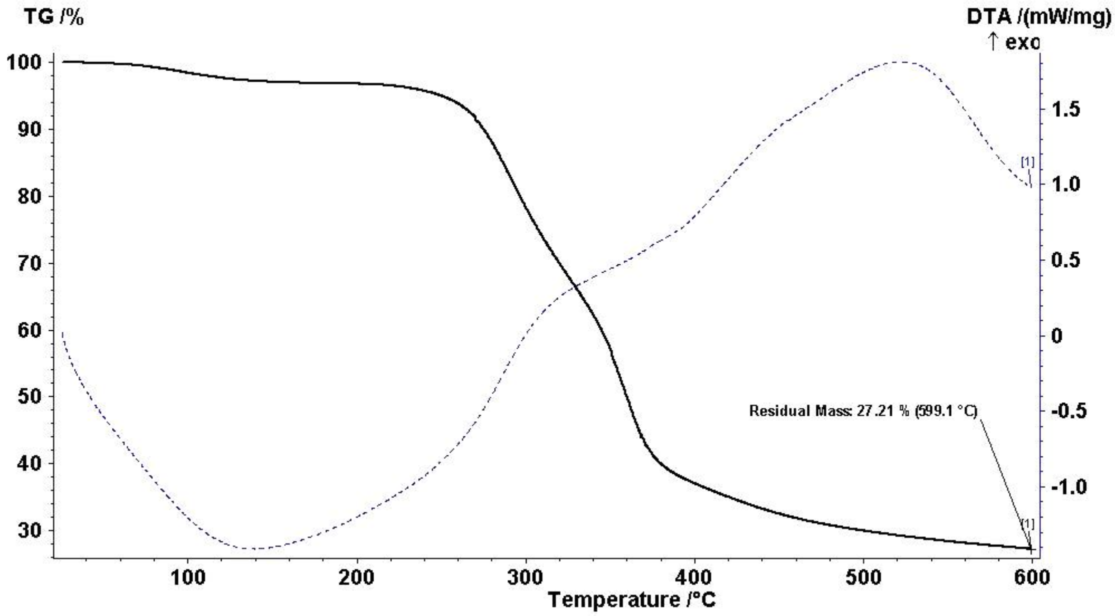

Fig. 8. Simultaneous TG /DTA pyrolysis curves of pits of rain-fed black olive fruit pieces (sample Yu20)

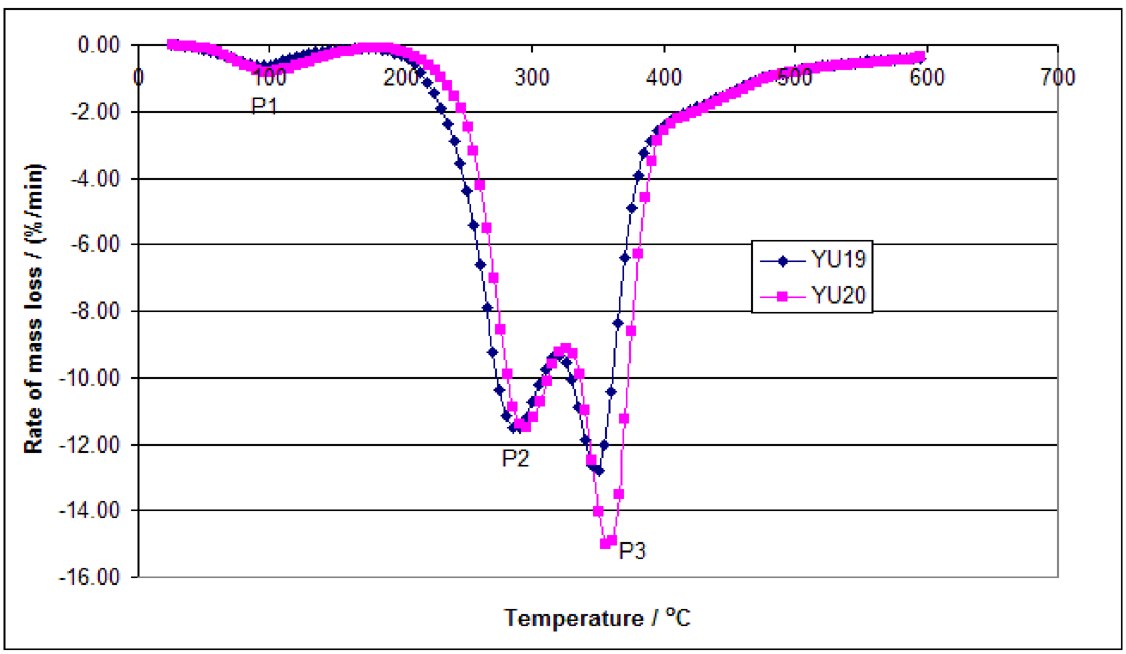

Fig. 9. DTG of pyrolysis curves of pits of rain-fed green and black olive fruit pieces (samples Yu19 & Yu20)

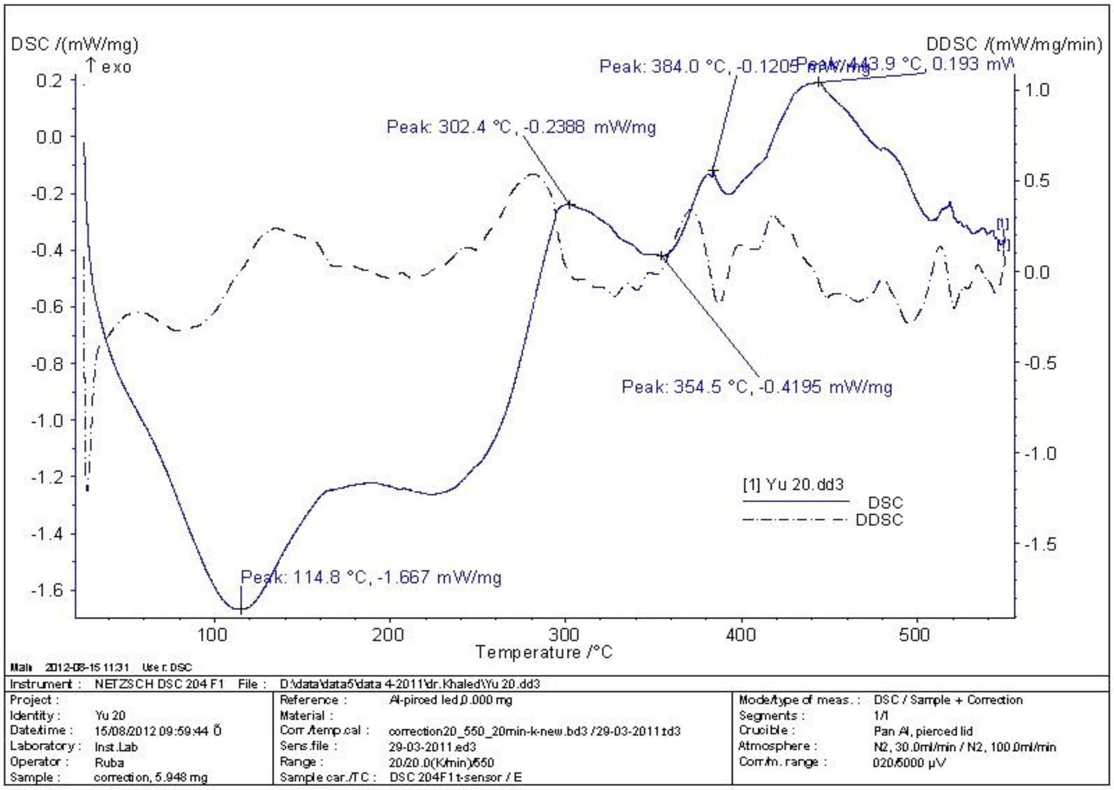

Fig. 10. DSC and DDSC pyrolysis curves of pits of rain-fed black olive fruit pieces (sample Yu20)

4. CONCLUSION

In nearly seven weeks, indoor air drying efficiently removes the moisture content of fresh green and black olives. When compared with rain-fed olives, the irrigated olives lose higher percentages of vegetal water. The protein content (as judged from % N) of black olives is lower than that of green olives. The fat content of dry black olives is higher than the fat content of dry green olives for fruits of the same cultivar. The relatively large mass loss reported in the present study for olive fruits drying indicates that the natural balance between the water phase and the oil phase in the pulp cells is dramatically disturbed. In view of this result, the effect of olive drying on the quality of the produced oil or table olive need to be officially evaluated by the Ministry of Agriculture in Jordan in order to avoid any possible health hazards. Based on their calorific value, pits of dry olives are potential energy source. Also the low ash yield resulting from their burning is an attractive property for choosing them for heat generation. Pits of olives of the same cultivar have the same GCV and nearly the same fat content. The metal content of the pulp fraction is higher than that of the pit fraction. The DSC and DTA analyses of pits fraction of olive fruits indicate the occurrence of exothermic and endothermic processes that can be linked to the components of their lignocellulosic part. The pyrolysis of the pits of dried olives resulted in residual masses with values comparable to those of olive pomace.

ACKNOWLEDGEMENTS

The author is grateful to Yarmouk University for the financial support of the present work (Grant 28/2010). The assistance of Miss Ayshyh Subeh in the ash and fat determinations is highly appreciated.

COMPETING INTEREST

Author has declared that no competing interests exist.

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