PHYTOCHEMICAL CONTENT, PHYSICOCHEMICAL AND MICROSTRUCTURAL PROPERTIES OF APPLE POWDER AS AFFECTED BY DRYING METHOD

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***Abstract*— Apple in forms of slice and juice dried through methods of freeze drying (FZD), microwave drying (MWD), oven drying (OVN), spray drying (SPD) and foam mat drying (FMD) and the obtained powders were characterized in terms of water activity, vitamin C (Vc), phenolic compounds (TP), anthocyanin (TA), density, porosity, color, glass transition temperature (Tg) and microstructure. The nutritional quality of apple powders expressed by the amount of Vc, TP and TA was found to be in the highest level in samples obtained after FZD followed by SPD. The minimum shift of color indexes from fresh apple observed for FZD followed by MWD. The highest and lowest bulk and true densities were noted after OVD and FMD, and FZD and SPD, respectively. DSC analysis showed the powders obtained from apple slice through FZD, MWD and OVD have significantly lower Tg than those of produced from apple juice, by SPD and FMD ($p<0.05$). Scanning electron micrograph confirmed the porous structure of FMD and FZD and the dense structure of OVD.**

***Keywords*— Apple powder, drying method, physicochemical properties, microstructure.**

I. INTRODUCTION

Apple (*Golden Delicious*) has amazing aroma and taste and contains soluble fibers, proteins, vitamins and minerals (Francini *et al*., 2017). As other high moisture agricultural products, apple is also exposed to malicious reactions resulted in losing its quality (Horuz *et al*., 2018; Santacatalina *et al*., 2016). Several preservation methods including drying and making compote are applied to increase its shelf life and provide availability all over the year (Doymaz., 2010).

In parallel with increase the people knowledge about the nutritional benefits of fruits and the necessity to inclusion them in daily diet, the researchers have been focused on development the methods could increase the shelf life of fruits while keep the highest quality. Accordingly, the drying of fruits bring about several profits such as shelf life increment and volume reduction. Several techniques have been used in order to obtain dried apple including hot air drying (Francini *et al*., 2017; Beigi, 2016; Kowalski and Pawłowski, 2015; Kutyla-Olesiuk *et al*., 2013), microwave drying (Al Juhaimi *et al*., 2016), microwave-hot air drying (Kutyla-Olesiuk *et al*., 2013; Horuz *et al*., 2018), oven drying (Al Juhaimi *et al*., 2016), vacuum drying (Michalska and Lech, 2018), freeze drying (Huang *et al*., 2012; Michalska and Lech, 2018), freeze drying combined microwave vacuum drying (Ando *et al*., 2019; Huang *et al*., 2012), spray drying (Michalska and Lech, 2018), Infrared drying (Kutyla-Olesiuk *et al*., 2013); ultrasound-hot air drying (Kowalski and Pawłowski, 2015; Santacatalina *et al*., 2016), high voltage electric field-air (Martynenko and Zheng, 2016) and pulse electric field assisted vacuum freeze drying (Parniakov *et al*., 2011).

The method by which the water of fruit is removed has a crucial effect on the physicochemical and nutritional properties of final product. Each drying method has been characterized through special time, temperature, heating medium, heat and mass transfer mechanism, physical state of final product, operation cost, etc., and a combination of these parameters in optimum mode should arrange together in order to achieve the product of interest. Herein, spray drying is relatively low cost-low temperature technique for drying the extract of fruits or plants at industrial scale in very low time while hot air is a simple-long process for drying of whole or sliced fruits (Rajabi *et al*., 2015; Kowalski and Pawłowski, 2015). FZD is desirable for the drying of heat-sensitive products. Firstly, the sample is frozen at temperatures between −90 and −40°C and then dried by direct sublimation under low pressure and reduced temperature (between −90 and −20°C). After drying, the brittle cake obtained can be broken into smaller pieces (Zuidam and Shimoni, 2010). The major disadvantages of freeze-drying are the high energy use, the long processing time, and the open porous structure obtained. MWD has several distinct advantages compared with conventional heat drying, including speed of operation, energy savings, precise process control, and faster start-up and shut-down times (Al Juhaimi *et al*., 2016). OVN is a low cost operation method and its equipment is simple. The heating period during OVD is long, resulted in quality loss of final dried products. FMD is another method that can produce the porous structure in foods. In FMD, foaming agent/agents let the fruit juice to form a foam structured mixture. One of the most difficult problems in the processing of foamed materials is the instability of the foam, which can occur both during the foaming and drying steps (Salahi *et al*., 2017).

It is obvious that choosing the drying methods of the best required to design a comprehensive research in which the most common techniques applied simultaneously to produce dried apple. In this study, we focused on the comparison of FZD, SPD, FMD, MWD and OVD to dehydrate apple slice and juice followed by assessing the produced powders in terms of moisture content, water activity, color, bulk and true densities, porosity, ascorbic acid, total anthocyanin and total phenolic content, crystalline structure and glass transition. The microstructural characteristics of apple powders were investigated through scanning electron microscopy.

II. METHODS

A. Materials

The size- and shape-sorted, firm with the same maturity and no surface injury apples (*GoldenDelicious*) were purchased from a shopping center in Babol (North of Iran) and transferred to the laboratory through cool bags followed by washing and storing in a refrigerator (4–8°C). Whey protein concentrate (WPC) (80% protein) was provided by Agri-Mark, Inc. (Lawrence, MA). Maltodextrin (MD) with a dextrose equivalent of 16.5-19, xanthan gum, Folin–Ciocalteu reagent, sodium carbonate and gallic acid were purchased from Sigma-Aldrich (Sigma-Aldrich Chemical Co., USA).

B. Sample preparation

In the case of oven, microwave and freeze drying, the same preparation method was used just before drying as follows. Apples were peeled manually by a stainless steel knife and sliced (25mm diameter, 1mm thickness) that were immediately placed on the hot water for blanching (80 °C, 1 min). For spray and foam mat drying, sample preparation was done just before drying as follows. Apples were peeled manually by a stainless steel knife and juiced through an electric juicer (Pars Khrazar Inc., Tehran, Iran) followed by centrifuging at 4000 rpm for 1 min (Digicen 21, Orto Alresa, Madrid, Spain).

C. Drying experiment

The drying conditions of each method were determined using data provided with pretest experiments (Data not given). Oven drying (OVD) of apple slices was carried out in a oven (Memmert Inc. Germany) at 85±2°C for 4h under air circulation.The obtained dried slices were then powdered with a hammer mill (AP-S, Hosokawa, Osaka, Japan) and kept at 20±1 °C in airtight Ziploc.

Microwave drying (MWD) of apple slices was fulfilled through a programmable domestic microwave oven (LG Intellocook, solardom Lightwave, SD 3859CR, maximum output of 900 W at 2450 MHz) at 450 w for 40 min. The obtained dried slices were then powdered with a hammer mill and kept at 20 °C in airtight Ziploc.

Freeze drying (FZD) of apple slices was conducted in a freeze drier (Operon-Korea) for 42 h (−86±5°C, 5 mbar).The obtained dried slices were then powdered with a hammer mill and kept at 20±1°C in airtight ziplock.

Spray drying (SPD) of apple juice (13.2±0.2 °Brix) was confirmed through adding 40% (weight/weight ratio) (w/w) maltodextrin (MD) to apple juice with the ratio of 1:3 (the ratio of juice solids to MD) and homogenization (Ultra-Turrax IKA® T25, Germany) at 10000 rpm for 1 min followed by transferring to the BUCHI mini spray-dryer (B-191, Switzerland). The total soluble solid content of apple juice was measured by a refractometer (Atago, Tokyo, Japan). The operation condition was set as follows. The inlet and outlet air temperature, airflow rate, feed flow rate and atomization pressure were maintained at 175 ± 5 °C, 95 ± 5 °C, 600 l/h, 4ml/min and 140 kPa, respectively. The produced powders were kept at 20 °C in airtight ziploc.

Foam mat drying (FMD) of apple juice was performed by using xanthan gum and whey protein concentrate (WPC) as foaming agents. The optimum amount of each foaming agent based on the foam stability as well as drying conditions such as foam thickness and drying temprature were determined in pre-test expriment (Data not given). Accordingly, 0.15% (w/w) xanthan and 5% (w/w) WPC and apple juice were mixed vigorously using an electrical beater, poured in aluminium plate (4mm thikness) followed by oven drying at 60±4 °C. The produced powders were kept at 20 °C in airtight ziploc.

D. Sample analysis

1. Moisture content (Mc) and water activity (aw)

The powder moisture content (Mc) was determined by vacuum oven drying (Vaciotem, JP Selecta, Barcelona, Spain) at the temperature of 80 °C until reach constant weight (Rajabi *et al.*, 2015). Water activity (aw) was measured oninstruments Novasina LabMaster (Novasina AG Ltd., Lachen SZ, Switzerland) at the temperature of 25 °C. The powder wettability (Wt) test was done by pouring 1 g of sample in the surface of a 100 ml beaker contains 100 ml distilled water and the Wt was considered as the time required to disappear powder from the surface of water without any turbulence (Rajabi *et al*., 2015).

2. Bulk density, true density and porosity

The powder bulk density (ρ_b) was measured through pouring a specified weight of each sample inside a graduated cylinder followed by noting the occupied volume (Corrêa *et al*., 2016). The bulk density was expressed by the following Eq.

$$\rho_b = \frac{m}{v} \quad (1)$$

where m is the mass of powder (g) and V is the volume occupied in the cylinder (ml).

The powder true density (ρ_t) was determined by placing a specified weight of each sample inside a helium gas displacement pycnometer (AccuPyc 1330TM, Micromeritics, USA) (Corrêa *et al.*, 2016).

The powder porosity (ε) was calculated by the following Eq (Corrêa *et al*., 2016).

$$\varepsilon = 1 - \frac{\rho_b}{\rho_t} \quad (2)$$

3. Color

The color change of produced podwers as a function of drying method was observed through a commercial colorimeter (HunterLab Colorflex, Reston, VA, USA) and expressed by color indexes of L^*, a^*, and b^*.The scope of the changes of these indexes were from 0 (black) to 100 (white) for L^*, from -80 (green) to +80 (red) for a^* and from -80 (blue) to +80 (yellow) for b^* (Caparino *et al*., 2012). In order to compare the total color difference between fresh sample and produced powder (ΔE), the below Eq. was used.

$$\Delta E = \sqrt{\left(L_0^* - L_p^*\right)^2 + \left(a_0^* - a_p^*\right)^2 + \left(b_0^* - b_p^*\right)^2} \quad (3)$$

where the subscripts 0 and p represent the fresh and powdered sample, respectively. As it is clear, higher ΔE implies a greater color change of powders from the fresh apple.

4. Ascorbic acid content

Ascorbic acid content of samples on dry basis was calculated through 2,6-dichloro-indophenol titration method and expressed as milligrams per kilogram of dry product. The total vitamin C (Vc) content at the end of drying was calculated (Duan *et al*., 2013).

5. Determination of total anthocyanins

The pH differential method was conducted to quantify the total anthocyanins of samples as followes (Bouayed *et al*. 2011). Initially, two buffers with pH of 1.0 (KCl in water) and 4.5 ($CH_3CO_2Na.3H_2O$ in water) were prepared followed by adding 0.025 M of pH 1 buffer and 0.4 M of pH 4.5 separately in as-prepared methanolic extract of each sample in a 1:8 ratio of extract to buffer and terminated by reading the adsorbance of each mixture at both wavelengths of 510 and 700 nm. The total anthocyanin (TA) was expressed as cyanidin-3-glucoside equivalents, as follows.

$$TA = \frac{A \times MW \times DF \times 1000}{\varepsilon}, \quad (4)$$

where A is the absorbance=$(A_{510} - A_{700})$ pH 1.0-$(A_{510} - A_{700})$pH 4.5; MW and ε are the molecular weight (449.2 g mol^{-1}) and molar absorptivity (26900 L mol^{-1} cm^{-1}) of cyanidin 3-O-glucoside (C3OG);1000 is conversion factor (g to mg); and DF is the dilution factor. TA was expressed as mg of C3OG equivalents per Kg of dried product (Bouayed *et al*., 2011).

6. Determination of total phenolic

The phenolic content (TF) of samples was measured using Folin-Ciocalteu colorimetric assay (Singleton and Rossi, 1965). Initially, fresh and dried samples (1 g of fresh and of 0.5 g of powdered apple) were extracted through mixing them separately in 10 ml aqueous methanol solution (80%, volume/volume ratio) followed by homogenization (T25 Digital, IKA, Germany) for 1 min. Extraction step was completed via mixing the resultant solution for 60 min at room temperature and centrifugation (3000 rpm for 10 min). Henceforth, 100 µL of the supernatant was mixed with 200 µL of phenol reagent, 2 mL of distilled water and 1 mL of 20% sodium bicarbonate and the resulted mixture allowed standing for 1 h in the dark to develop the color. The absorbance of mixture was read at 756 nm using a UV–Visible spectrophotometer (DR5000, Hach-Lange, Germany) and the concentration of total phenolic compounds was determined from a calibration curve that were attained by spotting different concentrations of standard gallic acid against absorbance at the same wavelength. Results were reported as milligrams of gallic acid equivalents per gram of dry mass (mg GAE/g ds).

7. Differential scanning calorimetry

The thermal behavior of samples was investigate through differential scanning calorimeter (DSC, 200 F3, NETZSCH, Germany) as described by Caparino *et al*. (2012). Calibration of instrument was done towards heat flow and temperature using standard indium and sapphire. Fifteen milligrams of each sample (fresh and dried apple) was precisely weighed and crimped in an aluminum pan while an empty pan (air) was applied as reference. The process was initiated by cooling down the temperature to -80 ºC at a heating rate of 10°C/min and followed by scanning from -80ºC to 80ºC at the same heating rate under a stream of nitrogen flowing at 50 mL/min. T_{gi}, T_{gm} and T_{ge} were obtained from diagram of heat flow against temperature.

8. Microstructure

In order to assess the microstructural characteristics of apple powders, field emission scanning electron microscope (FESEM, Tescan, Brno, Czech Republic) was employed. Each sample was attached to 2-sided adhesive tape aluminum stubs followed by gold coating. Finally the coated sample was visualized at 15 Kv.

E. Statistical analysis

The data analyzing were performed through MINITAB Release 17 (Minitab Inc., PA, USA) software. All experiments were triplicated and average values were reported. ANOVA procedure was employed for analyses of variance and mean values were considered at 95% confidence level.

III. RESULTS

A. Moisture content and water activity

The moisture content (MC) of the apple samples obtained using different drying method was varied in the range of 3.47-5.12% (Table 1).The type of drying method has the significant effect on MC of final product ($p < 0.05$) so the lowest and highest amount of MC were recorded in the case of samples dried with FZD and OVD, respectively. Similar trend reported by Caparino *et al*. (2012) on mango powder production using different drying. In comparison with the FZD, SPD and FMD, those produced with MWD have significantly lower MC. Ando *et al*. (2019) revealed that microwave irradiation because of its ability in penetrating inside of the sample followed by acting on the water molecules in a selective manner caused to increase the water removing from sample and achieving lower MC. On the other hand, the MC of powders produced from apple juice including FMD and SPD not only affect by drying type but also impressed by foaming agents and carrier, respectively, as reported by Moreira *et al*. (2013), who claimed that the type of drying

Table 1. Moisture content (MC) and water activity (aw) of apple powder produced using different drying method

Drying method	Mc (%)	aw
FZD	3.66 ± 0.08^{d}	0.259 ± 0.005^{d}
OVD	5.12 ± 0.09^{a}	0.330 ± 0.003^{b}
SPD	4.58 ± 0.04^{b}	0.317 ± 0.009^{c}
FMD	4.39 ± 0.11^{c}	0.230 ± 0.002^{e}
MWD	3.47 ± 0.13^{e}	0.347 ± 0.004^{a}

Different superscripts represent significant differences in each row among the means ($p < 0.05$).

aid had significant effect on MC of the fruit powders.

Water activity (aw) was determined to be in the range of 0.230-0.347, respectively for the produced powder through FMD and MWD (Table 1). The low water activity of foam mat dried apple powders can demonstrated by this fact that aw is significantly influenced by the amount of total soluble content (TSC) specially gum because of their high water binding capacity (Fennema *et al*., 2017). Accordingly, addition of xanthan gum and WPC because of their role in increasing TSC resulted in dramatic decrease of aw in foam mat dried apple powders

B. Bulk density, true density and porosity

The bulk density variations were recorded to be in the range of 488g cm^{-3} (foam mat dried apple juice) to 586 g cm^{-3} (oven dried apple slice) (Table 2). In contrast to our results, Michalska and Lech (2018) reported that oven dried apple powder had the lower bulk desity than freeze and spray dried powder. This difference may be seen due to run oven drying under vacuum caused to form more crystalize structure resulted in increasing volume (Caparino *et al*., 2012). Several factors are rolled in changing of bulk density including MC, structure and particle size of powdered food materials. Accordingly, by increasing the MC of powders, their tendency to stick together is increased resulted in decreasing captive air followed by bulk density increasing (Goula and Adamopoulos, 2005; Salimi *et al*., 2018). Inclusion of foaming agents in the case of samples of FMD, as well as the bulky nature of foam mat dried powders cause to their bulk density to be significantly lower than others, as reported by Jakubczyka *et al*. (2011) on foam mat drying of apple.

As shown in Table 2, the true density of samples was in the range of 1321g cm^{-3} (spray dried apple juice) to 1516 g cm^{-3} (freeze dried apple slice). Drying condition had significant effect on the true density of samples ($p < 0.05$), so that the powders produced via FZD had the highest values followed by OVD, while the FMD gave out the powders which were lowest. It can be concluded that true density of those powders obtained from apple juice, i.e. SPD and FMD, was significantly lower than another one ($p < 0.05$). The lowest values of true density were recorded after SPD may be due to the inclusion of air with high temperature (180 °C) in drying chamber that could affect some of the apple components resulted in their breaking down or in formation of new components with lower true density (Michalska and Lech, 2018). On the other hand, the true density of maltodextrin (DE~19) is reported about 1250 g cm^{-3} (Takeiti *et al*., 2010), so incorporation of it in apple juice at 40% (w/w) cause to the true density of resulted powders to shift in that values.

Table 2. Bulk density, true density and porosity of apple powder produced using different drying method

Drying method	Bulk density (g cm^{-3})	True density (g cm^{-3})	Porosity
FZD	504 ± 6^{c}	1516 ± 2^{a}	0.667 ± 0.014^{a}
OVD	586 ± 9^{a}	1498 ± 4^{a}	0.608 ± 0.070^{d}
SPD	505 ± 7^{c}	1321 ± 5^{d}	0.617 ± 0.025^{d}
FMD	488 ± 5^{d}	1422 ± 4^{c}	0.656 ± 0.011^{b}
MWD	541 ± 11^{b}	1454 ± 7^{b}	0.627 ± 0.016^{c}

Different superscripts represent significant differences in each row among the means ($P < 0.05$).

The porosity of samples was within 0.608-0.667, respectively for samples of OVD and FZD (Table 2). Because of process dependent of both densities, following the same trend for porosity was predictable. That way, the drying process had a crucial impact on porosity of apple powders. As expected, a correlation was observed between the values of bulk density and porosity in which the powders with the highest bulk density, gained the lowest porosity and vice versa. Accordingly, the processes of FZD and FMD are well known for producing porous dried products full of captive air (high porosity) with low bulk density. High values of porosity of microwave dried apple powder is related to the nature of process towards reducing shrinkage and thus provides a more porous structure (Huang *et al*., 2011; Drouzas *et al*., 1999). Contrastingly, Michalska and Lech (2018) obtained the highest porosity after spray dried apple maybe due to the difference between the concentration of maltodextrin added to apple juice than present work.

C. Color

The color indexes of apple powders produced through different drying methods are presented in Table 3. As it is clear, drying techniques had a meaningful effect on all three color indexes of L^*, a^*, and b^* ($p < 0.05$). The highest values of L^*, a^*, and b^* were recorded after SPD, FMD and MWD, respectively, while the lowest one were obtained after FMD, SPD and SPD, respectively. Al Juhaimi *et al*. (2016) revealed similar trend on the microwave and oven dried of apple slice. Several studies claimed that the drying of fruit using approaches in which low temperature-long time (freeze drying) or high temperature-low time (microwave drying, spray drying) applied cause to produce dried product with lowest level of color degradation (Lavelli and Vantaggi, 2009; Antal *et al*., 2015; Antal and Kerekes, 2016; Cuccurullo *et al*., 2018). Exerting high temperature in approaches such as oven drying resulted in development of golden brown color in surface of fruit which is shown by increasing the b^* as reported by Antal *et al*. (2015). In general, incorporation of foaming agents and wall material respectively for FMD and SPD caused to the color indexes of obtained powders to be located at the minimum or maximum values when compared with other ones revealed that drying aids materials based on the applied concentration, could have a crucial impact on color characteristics of final powders. Accordingly, SPD powders had highest amount of lightness, greenish and blueness as a result of adding maltodextrin to apple juice. Similarly, those powders

Table 3. Color indexes of dried apple (slice and juice) using different drying methods

Drying method	L^*	a^*	b^*	ΔE
FZD	84.23 ± 0.01 [b]	1.64 ± 0.03 [d]	20.29 ± 0.02 [b]	6.05 ± 0.79 [e]
OVD	81.10 ± 0.03 [c]	3.01 ± 0.02 [b]	24.53 ± 0.12 [a]	8.94 ± 1.24 [c]
SPD	86.05 ± 0.07 [a]	0.94 ± 0.02 [e]	14.07 ± 0.01 [c]	9.78 ± 1.08 [b]
FMD	72.83 ± 0.01 [e]	7.13 ± 0.04 [a]	25.18 ± 0.05 [a]	13.39 ± 1.84 [a]
MWD	80.08 ± 0.04 [d]	2.02 ± 0.02 [c]	25.26 ± 0.01 [a]	7.08 ± 0.93 [d]

Different superscripts represent significant differences in each row among the means ($p < 0.05$).

Table 5. Glass transition temperatures of apple powder produced using different drying method.

Drying method	Tg (°C)		H (J g^{-1})
	1st	2nd	
FZD	- 18.4 ± 1.8 [c]	39.8± 0.7[c]	11.76± 0.94[c]
OVD	- 19.1 ± 2.1[c]	38.1± 1.1[c]	12.52± 0.53[c]
SPD	- 7.8 ± 0.9[a]	79.6± 3.1[a]	14.83± 0.47[b]
FMD	- 13.6 ± 1.4[b]	51.3± 2.2[b]	20.78± 0.19[a]
MWD	- 20.5 ± 2.4[c]	40.5± 0.9[c]	11.60± 0.26[c]

Different superscripts represent significant differences in each row among the means ($p < 0.05$).

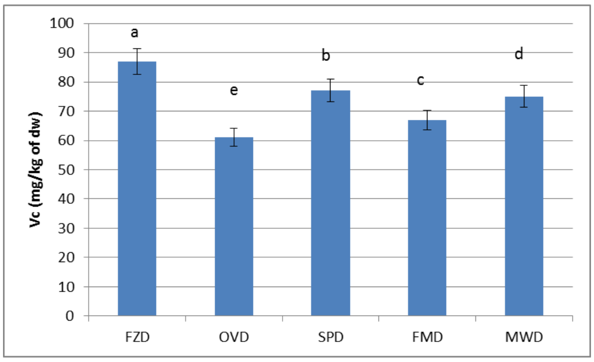

Figure 1. Ascorbic acid (Vc) content of apple powder produced using different drying method.

produced via FMD, had the lowest lightness and highest amount of redness and yellowness.

The color change level of sample than fresh apple was determined by calculating ΔE, that is widely used for monitoring of food color variation during drying. As shown in Table 3, drying method had also profound effect on ΔE ($p < 0.05$), so that the minimum and maximum total color differences were obtained for FZD and FMD, respectively. In accordance with our finding, Antal and Kerekes (2016) reported that the lowest color change than fresh apple was seen after freeze dried apple by the values of 5.01. The FZD process runs in a very low temperature, resulted in diminishing the food damages towards the color and bioactive components makes final products physicochemical properties as same as fresh one. The microwave dried apple powders have statistically significantly lower ΔE than those of FMD, SPD and OVD. Cuccurullo *et al.* (2018) reported that the microwave drying method reduce the surface overheating, resulted in minimizing the surface color change. In the case of high ΔE values, as mentioned before, the powders produced from apple juice because of presence drying-aid materials had significantly lower or higher color indexes than those produced via apple cubes, caused to their ΔE were also statistically significant higher than others.

D. Ascorbic acid

The amount of vitamin C (Vc) in dried samples was determined in the range of 61 mg/kg of dw (for the dried sample using OVD) to 87 mg/kg of dw (for the dried sample using FZD) (Fig. 1). Ascorbic acid is known by its heat sensitivity and destroyed easily when expose to thermal processing methods (Peleg *et al.*, 2018). So, it was predictable that FZD process could keep the highest amount of Vc, while the lowest retention obtained after OVD. In SPD process, a thin protective film is formed around each droplet immediately after the feed is sprayed in drying chamber, causes the bioactive and heat-labile components to be retained and protected during drying process (Rajabi *et al*., 2015). On the other hand, the time in that each droplet expose to heat medium is very low. These circumstances resulted in higher retention of Vc in final product. High amount of Vc was also observed in the case of microwave dried apple powders, mainly due to the short time of drying process as reported by Huang *et al*. (2011).

E. Total anthocyanin

Analysis of total anthocyanin (TA) showed these compounds were varied in the range of 5.8 mg C3OG/Kg dry matter (ds) (for the dried apple using OVD) to 7.1 mg C3OG/Kg ds (for the dried apple using FZD) (Fig. 2).As it can be predictable, FZD due to work under very low temperature was offered the highest amount of TA. Drying technique had the crucial role on retention of TA in final powder so with increasing the temperature as well as time of process, TA degradation was dramatically increased ($p < 0.05$). Yan and Kerr (2013) reported similar result on the TA content of dried apple using different methods. These researchers revealed that by increasing the drying temperature, the TA content of dried apple was significantly decreased. In the case of SPD, formation of a protective film around the apple juice during the drying was preventing the bioactive components to be destroyed by heat. This reason along with the short process time helps the final product to meet the highest quality indexes (Rajabi *et al*., 2015). Microwave drying is known for its short dehydration process and so, as mentioned above, bioactive components being held in final product bringing high quality powders (Zielinska and Michalska, 2016). Similar results reported by Kwok *et al*. (2004) on microwave drying of berries. On the other hand, in comparison with above-mentioned approaches, the process of OVD duo to apply longer process time and higher temperature, converts to an undesirable drying method, caused to the produced powders had lower quality level. The produced powders via FMD had significantly higher

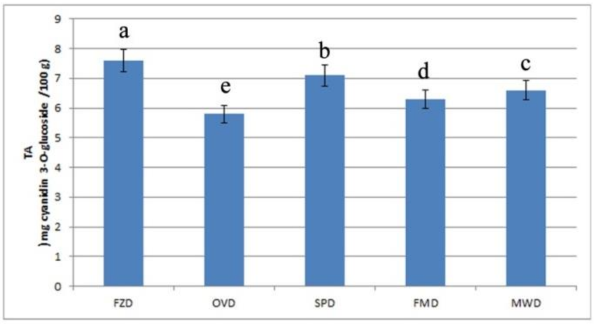

Figure 2. Effect of different drying method on total anthocyanin (TA) of apple powder.

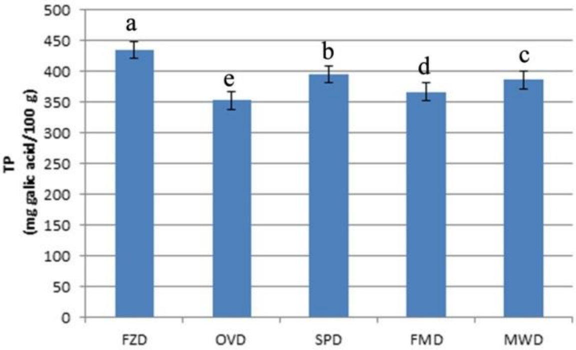

Figure 3. Effect of different drying method on total phenolic compounds (TP) of apple powder.

amount of bioactive components than those produced with OVD ($p < 0.05$) mainly due to the profound decrease in process time as a result of foam structure of apple juice.

F. Total phenolic

Polyphenol compounds are known by their heat sensivity, especially those are unbound and in high moisture systems (Yan and Kerr, 2013). The total phenolic (TP) of apple powders produced with different drying method were within 353 galic acid equivalent (GAE)/g ds (for the dried sample using OVD) to 435 mg GAE/g ds (for the dried sample using FZD) (Fig. 3). Changes in TP content of samples as a function of drying technique had a same trend with TA. That way, the highest and lowest amount of TP were observed in powders of FZD and OVD, respectively, revealed that drying method has a meaningful impact on TP, like other bioactive components of apple. These finding are in agreement with those obtained by Wolfe and Liu (2003) for apple peel drying, who claimed the highest values of TP obtained after FZD, without significant difference in comparison with fresh apple. Francini *et al*. (2017) observed a decrease in TPC of apple after drying that is in agreement with our finding. A general trend on the TPC heat dependence based on increasing degradation in parallel to temperature increment has been reported by several researchers worked on drying of different fruits (Alfaro *et al*., 2014; Sultana *et al*., 2012; Izli *et al*., 2018).

G. Glass transition measurement

Differential scanning calorimetry (DSC) was utilized to detect the glass transition temperature (Tg) of apple powder samples. In general, fruits and fruit products reflect a specify thermal manner when expose to a certain heat flow, due to the inclusion of sugars and biopolymers, known as glass transition temperatures, at which the physical properties of components were changed from glass to rubber state (Bhandari and Howes, 1999). On the other hand, some of the food materials have more than one glass transition temperatures (Vega-Gálvez *et al*., 2012). Apple (*Golden Delicious*) contains sugars of fructose, glucose, and sucrose, pectin and proteins that play significant role in its Tg. As shown in Table 4, the glass transition temperatures of apple powders (1^{st} and 2^{nd}) were measured to be in the range of - 7.8 to - 20.5 °C and 38.1 to 79.6 °C, respectively. This trend is ascribed to the presence of high molecular weight biopolymers and the incongruousness of apple matrix as a complex food system (Matveev *et al*., 2000). Several researches have been reported this trend as multiple glass transition temperatures for dried apple (Vega-Gálvez *et al*., 2012), dried banana (Katekawa and Silva, 2007) and rice kernels (Perdon *et al*., 2000). It seemed that the statistically difference between glass transition temperatures of powders produced from apple slice and those produced from apple juice was not as a result of difference in drying method and could attribute to the presence of whey protein and xantan gum as foaming agents in FMD and maltodexterin as carrier for SPD. Similar results were reported by Raharitsifa and Ratti (2009) on foam mat freeze drying of apple juice. On the one hand, glass transition temperatures are a function of dissolved solids, on the other; aw play a significant role in variation of glass transition temperatures (Fongin *et al*., 2017; Santhalakshmy *et al*., 2015; Moraga, 2011; Tylewicz *et al*., 2016). Adding maltodextrin and foaming agents not only change the concentration of total dissolved solids, but also impress the water activity of final product, and both mechanisms, cause to glass transition temperatures of final products to be increased followed by increasing the storage stability towards inhibiting of such problems like caking (Bhandari and Howes, 1999).

H. Microstructure

Field emission scanning electron micrograph (FESEM) of apple powders produced via different drying methods are showing Fig. 4 Crushing the dried apple slices produced via approaches of FZD, OVD and MWD, and also those dried with FMD into powder form produced irregularly shaped particles while maintaining its total structures.

As shown in Fig. 4A. and as expected, due to the nature of foam mat drying towards producing stable foam, the obtained apple powders have porous structure and the observable cavities in the micrograph, are due to the stable bubbles produced via WPC action during foming process (Kumalaingsih and Wijana, 2013; Hamzeh *et al*., 2019). Salehi *et al*. (2017) and Raharitsifa and Ratti (2009) reported similar results on foam mat drying of cantaloupe (*Cucumis melo*) and foam mat freeze drying of apple juice, respectively.

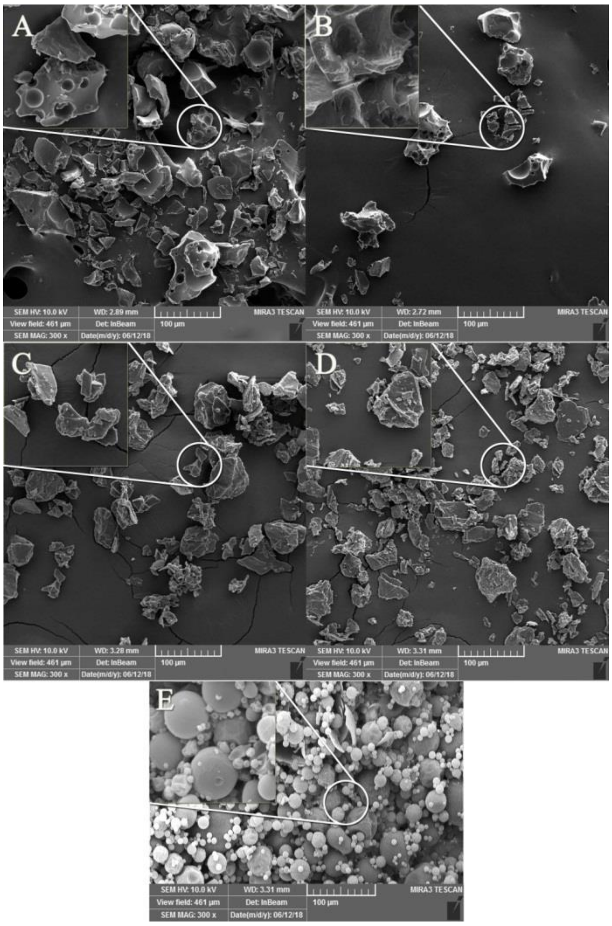

Figure 4. Field emission scanning electron microscopy (FESEM) of apple powders dried using: (A) FMD, (B) FZD, (C) MWD, (D) OVN and (E) SPD.

As shown in Fig. 4B, the freeze dried powders could describe through their high porosity and the presence of plant cell structure. Converting the water of fresh apple to ice followed by removing of ice in forms of vapor under high vacuum caused to keep the integrity of plant tissue and obtain the lowest level of shrinkage and structural collaps (Ratti, 2001). Similar results reported by several studies (Parnikov *et al*., 2016; Tylewicz *et al*., 2016; Caparino, 2012; Moraga *et al*., 2011; Azarpazhooh and Ramaswamy, 2011; Garcia *et al*., 2018).

The micrograph of microwave drying apple powders (Fig. 4C) showed a layered-like structure was smooth in surface and flaky with relatively alike thickness. The porosity of these structures is distinguishable as distance between layers makes them to have higher volume than oven dried powders. Similar results obtained by Ando *et al*. (2019) and Huang *et al*. (2012) working on microwave-vacuum drying and microwave drying of apple, respectively.

The microstructure of oven dried powders (Fig. 4D) are similar to those produced via microwave drying approach with more rigidity. These powders are smooth in surface and have more compact (low volume) structure resulted in the highest bulk density and lowest porosity. This trend maybe comes from the applying high temperature in long time resulted in high level of shrinkage and collapse (Jakubczyk *et al*., 2010; Lewicki and Wiczkowska, 2006).

As it is clear from Fig. 3E, the spray dried powders have a smooth and spherical shape with a particle size varied from 7.9 to 34.5 µm. Lack of the fragmented particles comes from the appropriateness of drying process towards carrier selection and operating conditions (Rajabi *et al*., 2015). In accordance with results of present study, Caparino *et al*. (2012) revealed that spray drying of mango juice resulted in spherical and oval microparticels were smooth in surface, having high porosity than conventional drying methods. Also, Rajabi *et al*. (2015) demonstrated the same morphological feature for the spray dried saffron extract powder using maltodextrin (40% w/w) as carrier.

IV. CONCLUSIONS

The present study works on the assessment of the influence of different drying method on physicochemical and microstructural properties of apple fruit. FZD was a better method for apple slice drying than OVD and MWD towards retaining highest values of TP, TA and Vc in the final powder. On the other hand, SPD provided an appropriate condition for apple juice drying in order to produce powder with higher level of bioactive components than FMD. Addition of foaming agents and carrier respectively in FMD and SPD resulted in increasing glass transition temperatures than those produced from apple slice, which could increase the storage stability of apple powder. FESEM analysis showed the porous structure for foam mat and freeze dried sample resulted in decreasing bulk density while a dense structure appeared for oven dried powder followed by bulk density increasing. It can be concluded that based on the results both nutritional quality (highest amount of Vc, TP and TA) and physicochemical properties (density, porosity, color), the FZD produced powder with highest quality from apple slice while SPD is the most appropriate method for apple juice drying.

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