Effect of Wall Material and Inlet Drying Temperature on Microencapsulation and Oxidative Stability of Pomegranate Seed Oil Using Spray Drying

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Abstract: Pomegranate seed oil is a highly unsaturated fatty acid and liable to be oxidized; hence, oil was encapsulated to protect its bioactive materials and increase shelf life with the most common spray drying technique. Whey protein (WP) alone and in combination with Maltodextrin (MD) in the ratio 1:4 weight was utilized. Feed emulsion, droplet size, encapsulation efficiency (EE), moisture, bulk density, powder morphology, particle size, hygroscopicity, and solubility were also analyzed. The spray drying conditions were applied: inlet temperature 125 to 150℃ and outlet 60 to 67℃, airflow rate 40-42 m³/min, feed rate 5.2 g/m, and pump rate 40%. The shape of particles was spherical and round with dents on their surface. After encapsulation, the oxidative stability was monitored at 60℃ for 15 days (8 h daily). The smaller droplet size of the emulsion was obtained at 35% total solid contents. WP alone showed better EE (90%) and oxidative stability than the combination of WP and MD as wall materials.

Key words: pomegranate seed oil, wall materials, emulsion, encapsulation, spray dryer, oxidative stability

1 Introduction

Pomegranate seed oil (PSO) consists of high polyunsaturated fatty acids, mainly conjugated type, punicic acid (9 cis, 11 trans, 13 cis, 18:3, 65–80%). Due to the high unsaturation, PSO exhibits desirable nutritional and medical properties due to the presence of many bioactive components such as phenols, flavonoids, ellagitannins, and anthocyanidin¹. PSO has many beneficial health impacts because antioxidants reduce diabetes, lower blood pressure, decrease obesity, improve heart problems, ameliorate skin, and alleviate rheumatic arthritis problems, etc.²–⁴. But, PSO is readily oxidized by temperature, light, oxygen, and moisture⁵.

Encapsulation is a well-known technique to protect the oil from spoil and loss of nutrients. Various drying techniques are available, such as spray drying (SD), coacervation, fluid bed coating, spray chilling, and freeze drying. The SD method has been widely used in food and pharma industries because of flexibility in operating, low cost, energy, efficiency, and production on an industrial scale⁶–⁷.

One of the key exciting issues in SD is the choice of wall materials. Encapsulation efficiency (EE) of capsules and stability at storage mainly depends on the nature of wall materials. So, wall materials used in the food industry should have maximum solubility in the water, low viscosity at high quantity, high ability to emulsify and protect core materials from oxidation⁸,⁹. Hence, carbohydrates including maltodextrin (MD), modified and hydrolyzed starches are commonly employed as encapsulation agents for vegetable oils due to better shelf formation. On the other hand, proteins such as whey protein, whey protein isolate and concentrate and skim milk powder is mainly utilised as emulsifying agents are

Abbreviations: PSO; Pomegranate seed oil, PUFA; Polyunsaturated fatty acids, SD; Spray drying, WP; Whey protein, MD; Maltodextrin, DE; Dextrose Equivalent, GA; Gum Arabic, XG; Xanthan Gum, SMP; Skim Milk Powder, GG; Guar Gum, SEM; Scanning electron microscope, EE; Encapsulation Efficiency, PY; Product Yield, PV; Peroxide Value, SO; Surface oil, TO; Total oil

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combined with carbohydrates in the SD process\textsuperscript{9).}

Apart from wall materials, the inlet temperature of SD condition is the most important factor determining EE, physical properties, and oxidative stability of encapsulated materials. Many researchers have investigated the effect of inlet temperature on the physical properties of microcapsules such as EE, size of particles, bulk density, and peroxide value. It has been observed that EE and particle size increased as the temperature varied from 150 to 200°C. The high air temperature causes to enhance the formation of particle crust due to the faster drying rate of droplets resulting in a hard membrane around the particles that inhibits the oozing of oil from droplets. At the same time, moisture contents and bulk density decreased by increasing temperature\textsuperscript{10).} Literature survey showed little work had been done to evaluate the effect of wall materials and inlet temperature on the quality of PSO microencapsulation by SD.

Therefore, the aim of this study was to encapsulate PSO by using WP and MD as wall materials and check the effect of inlet temperature during drying on EE, and oxidative stability to preserve nutritional values of oil.

2 Materials and Methods

2.1 Reagents and sample collection

All the chemicals and reagents used in the present study were purchased from E-Merck (Darmstadt, Germany). Wall materials for encapsulations were used, such as maltodextrin (DE 14) and whey protein (WP). In the present study, the waste seeds of pomegranate fruit were collected from fresh juice vendors. The seeds were cleaned from adhering material and stored at room temperature till analysis.

2.2 Oil extraction

Oil was extracted from seeds by the classical Soxhlet extraction method. 5g seeds were placed in a thimble, n-hexane solvent was utilized to extract oil and run the Soxhlet apparatus for 4 h. After that, hexane was evaporated with a Rotavapor@100, Buchi, Switzerland. Then, the extracted oil was placed in an amber glass bottle, purged with nitrogen gas to keep the inert atmosphere, and placed in a deep freezer\textsuperscript{10).}

2.3 Emulsion preparation

First emulsions of wall material WP (35\%) and combination of wall material WP (25\%) and MD (10\%) were dispersed in distilled water, then agitated with a magnetic stirrer (Mtops, model MS300HS, Korea) for 10 min and left overnight for complete hydration. The next day, oil was mixed with wall materials in ratio 1:4 (w/w) and homogenized at 18000 rpm for 6 min using a rotor-stator homogenizer (Ultra-Turrax type, IKA T 25 digital Janke and Kunkel, Germany).

2.4 Droplet size distribution

A Mastersizer 2000 (Malvern, Worcestershire, UK) was used to measure the total droplets and particles size and presented it as Sauter (surface average) diameter \(d_{3,2}\). After 1 h, homogenized samples were analyzed before the droplet, and particles size was calculated at a relative refractive index (1.465) of the dispersed phase (water). When the obscuration index of 15\% was obtained after adding drops of the emulsion and powder into the dispersion liquid, then mean diameter \(d_{3,2}\) and droplets and particles size distribution was measured.

2.5 Spray drying conditions

Finally, emulsions were spray dried on SD (Procept, Belgium) at 125°C and 150°C (inlet temperature) for WP alone and WP and MD combination at the following conditions: outlet temperature 60 to 67°C, airflow rate 40-42 m\(^3\)/min, feed rate 5.2 g/m and pump rate 40%. The SD material was collected in airtight amber glass.

2.5.1 Surface oil

Surface oil is the quantity of the oil that is non-encapsulated and appears on the surface of particles after drying. The surface oil was determined by the method described by Goula and Adamopoulos\textsuperscript{10).} Around 2 g powder was placed in a test tube, added 10 mL hexane and vortex for 5 min. After that, the supernatant was removed and kept in a Petri dish to evaporate hexane to get the surface oil of particles. The amount of oil was calculated by the following formula.

\[
SO = \frac{\text{weight of oil}}{\text{weight of powder}} \times 100
\]

2.5.2 Total oil

The total oil is considered the amount of oil encapsulated inside the particles after drying. The total oil was calculated by the Soxhlet extraction method. Around 5 g powder was placed into a thimble and kept into a Soxhlet extractor for 4 h. Later, hexane was removed from the oil with the help of a rotatory evaporator, and the weight of the oil was determined. The total oil was calculated by the following formula as reported by Goula and Adamopoulos\textsuperscript{30).}

\[
TO = \frac{\text{weight of oil}}{\text{weight of powder}} \times 100
\]

2.5.3 Encapsulation efficiency and product yield

The encapsulation efficiency and product yield of dried powder were calculated by the following formula\textsuperscript{10).}

\[
EE = \frac{OT - OS}{OT} \times 100\%
\]

\[
PY = \frac{\text{weight of oil}}{\text{weight of powder}} \times 100
\]

2.5.4 Surface Morphology

To analyze the structure and the surface morphology of microcapsules of pomegranate oil, a scanning electron mi-
Effect of Wall Material and Inlet Drying Temperature on Microencapsulation and Oxidative Stability

J. Oleo Sci. 71, (1) 31-41 (2022)

Supernatant material weight of powder

2.5.8 Wettability

Nearly 1 g of powder was kept in a pre-weighed Petri dish and stored at 105°C in the oven (Memmert, Schwabach, Germany) for 3 h till a constant weight was achieved. Then the dish was placed in the desiccator. The moisture value of the powder was then measured using the following formula as reported earlier (Goula and Adamopoulos [50]).

\[
\text{Moisture content} = \frac{\text{weight of dried powder}}{\text{weight of wet powder}} \times 100 \quad \text{Eq.5}
\]

2.5.9 Hygroscopicity

Nearly 1 g of powder was kept in a 25 mL calibrated measuring cylinder, and the powder height was measured, filled by the volume in the cylinder, and then gently touched to the floor 50 times to cause the powder to settle. The bulk and tapped density measurement was obtained by the same formula dividing the mass of the powder with the volume occupied and expressed in g/mL [50].

\[
\text{Bulk Density} = \frac{\text{weight of powder}}{\text{volume occupied by powder}} \times 100 \quad \text{Eq.6}
\]

2.6 Totox value

The Totox value was calculated by the sum of the peroxide and p-AVs of the oil samples using the following equation as reported by Firestone [22].

\[
\text{Totox value} = 2\text{PV} + p\text{-AV} \quad \text{Eq.9}
\]

2.7 Statistical analysis

Statistical analysis of the data was carried out using Minitab16 USA software. Data were analysed by analysis of variance (ANOVA) followed by the Tukey test (p ≤ 0.05). Results are reported as mean ± (SD) of three replicates (each replicate corresponds to a different batch of emulsion).

3 Results and Discussion

3.1 Emulsion characterization

The stable emulsion is a prerequisite condition for higher encapsulation efficiency and stable microcapsules, leading to smaller particles, better retention of oil, and lower surface oil [13]. The droplet size of different emulsions of various concentrations was measured on Mastersizer. For SD emulsions, the smallest size of the droplet was found at 7 µm of WP, and the highest was 9 µm WP-MD observed in the Sauter mean diameters. In general, small emulsion droplets enclose and embed more efficiently within the microcapsules wall matrix. The resulting emulsion would be
more stable during the SD encapsulation process, which is critical to have optimum efficiency\textsuperscript{9, 14, 15}. Many researchers have reported smaller droplet size causes higher EE\textsuperscript{16, 17}. It is due to envelop droplets effectively in wall material during the drying process\textsuperscript{9, 15}.

### 3.2 Encapsulation Efficiency (EE)

The maximum EE value of 90% was found in WP alone wall material in 35% solid contents at 150°C, and a minimum value of 70% was observed in the MD-WP combination at 125°C, as shown in Table 1. As seen, the temperature had a significant impact on EE at lower temperatures; hence, it caused higher surface oil resulting in lower EE. In comparison, WP alone or in combination with MD produced better EE at a higher temperature. The EE result of SD in this work was almost matched with the PSO values reported by Sahin-Nadeem and Asfın Özen\textsuperscript{18} with starch and WP\textsuperscript{2} materials (75.9 to 87.1%) at 180°C. Bustamante et al.\textsuperscript{19} also reported similar EE trends (68.2% to 92.7%) with bio extraction of pomegranate with starch capsule ratio of 1:3.2 and inlet air temperature of 167.2°C. The values of EE of our study were higher (75% to 90%) than the results of Comunian et al.\textsuperscript{6}, who assessed the effects on the EE of PPO with biopolymers WP:MD, and WP:Capsul\textsuperscript{2} at 150°C inlet temperature and core to coating ratio 1:4. In contrast, Goula and Adamopoulos\textsuperscript{20} reported a higher EE value of PPO (95.6%) by using skimmed milk powder (SMP) at a relatively higher core to coating ratio (1:9) and inlet air temperature (187°C) by SD. Recently, Yekdane and Golii\textsuperscript{21} also reported the same trend of higher microencapsulation efficiency of SPO (93.3 to 96.6%) with 0.08% xanthan gum (XG), 15% PPO, 15% gum Arabic (GA), and 11% juice were used at 170°C inlet temperature. Many studies reported the effect of inlet temperature on the surface morphology of capsules. The high inlet air temperature (150-220°C) causes the quick formation of semi permeable membrane on the droplet surface, resulting in maximum flavor retention and EE. At the same time, some researchers have reported temperature above 190°C does not affect the EE\textsuperscript{9}. Bhandari et al.\textsuperscript{22} has found that increased inlet air temperature caused a decrease in surface oil due to the quicker formation of the hard membrane around particles. Hence, less or no leaching of volatile components occurs on the surface of particles. A similar type of results have also been reported by Réineccius\textsuperscript{23} regarding surface oil content and concluded that particles shelf life increased when dried at high inlet temperature (280°C). On the other hand, inlet temperature below 150°C brought about incomplete drying of microparticles\textsuperscript{24}. In contrast, Aburto et al.\textsuperscript{25}, and Finney et al.\textsuperscript{26} reported no effect of inlet temperature on retention of EE, while Goula and Adamopoulos\textsuperscript{20} reported that EE was dependent chiefly on outlet temperature. The PY of microcapsules of different wall materials with SD at various temperatures was observed in the range of 66 to 77%, as shown in Table 1. The highest PY was obtained (77%) with WP alone as wall material at 150°C, and the lowest PY (66%) was found using WP-MD combination at 125°C. It clearly showed the influence of temperature on PY by increasing temperature leads to higher PY. Sahin-Nadeem and Asfın Özen\textsuperscript{18} also reported 50.6-76.3% PY of PPO using SD at 180°C. These said PY have almost similar values in comparison to our study. In another study, 64-79% of PY has also been reported using flaxseed oil\textsuperscript{27}. On the other hand, Calvo et al.\textsuperscript{28} reported comparatively lower PY 33-52% of the virgin olive oil microcapsules.

### 3.3 Morphology of freeze dried microcapsules

#### 3.3.1 Surface characterization

The SEM analysis was carried out to understand the morphology of powder (shape and surface). SD particles showed a smooth surface with dents and wrinkle, spherical, regular shape, fine particles tending agglomeration, and occupying places between larger particles, as shown in Fig. 1. Many researchers have reported that inlet drying temperature significantly affects particles shape and structure in the SD process. Toro Sierra et al.\textsuperscript{29} have observed spherical and smooth particles at high inlet temperature 190°C using WP in the SD process. The indented surfaces of particles were formed in SD due to particles contraction at high inlet temperature. Quick evaporation and elevated

| Wall materials    | SO      | TO      | EE      | PY      |
|-------------------|---------|---------|---------|---------|
| WP25%-MD10% (125°C) | 7.4 ± 1.0c | 58.0 ± 0.6c | 82.0 ± 0.7c | 68.0 ± 0.9c |
| WP25%-MD10% (150°C) | 6.5 ± 1.0d | 64.0 ± 0.8a | 90.0 ± 0.7a | 77.0 ± 0.8a |
| WP35% (125°C)     | 9.1 ± 0.4a | 45.0 ± 0.8d | 75.0 ± 0.8d | 66.0 ± 0.5d |
| WP35% (150°C)     | 7.9 ± 0.3b | 61.0 ± 0.6b | 88.0 ± 0.5b | 72.0 ± 1.0b |

a–d Different letters indicate significant difference in SO, TO, EE and PY among different wall materials at p < 0.05. Abbreviation of SO, TO, EE and PY stand for surface oil, total oil, encapsulation efficiency and product yield.
Effect of Wall Material and Inlet Drying Temperature on Microencapsulation and Oxidative Stability

J. Oleo Sci. 71, (1) 31-41 (2022)

pressure were the leading cause of the shrinkage inside the particles\(^{30}\). The same observations were reported for astaxanthin and lycopene encapsulated with starch\(^{31, 32}\). Goula and Adamopoulos\(^{10}\) have also reported smooth, spherical, and excellent PSO particles with SMP at a high temperature 187°C. Since spherical shapes with extensive dented, smooth surfaces and irregular agglomeration inclination of PSO encapsulated with starch capsule were also reported in the SD process\(^{33}\). Comunian \textit{et al.}\(^{34}\) has also observed round particles of PSO with different wall materials such as WPI, GA, MD and Capsule\(^{®}\) modified starch (smoother surface with Pickering of WPI gel, but pores with WPI due to alteration in WPI structure during gel formation). Removal of water during atomization in SD caused shrinkage alone in GA, or mixing WPI:MD and WPI: GA particles.

3.4 Size of spray dried microcapsules

The particle size of powders was determined by the Mastersizer and observed in the range of 14 to 19 μm. The size of particles depends on the drying process, wall material, and ratio of core to wall materials. For WP microparticles, smaller size of 14 μm was obtained at a higher temperature of 150°C and a larger size of 16 μm at a lower temperature of 125°C. Similar results were also observed with WP and MD combination. The smaller size of particle 17 μm was found at a higher temperature and larger particle size 19 μm at a lower temperature.

Usually, smaller particles depend on the atomized droplets size, which decreases feed solids concentration and increases core to wall material ratio, thus reducing powder particle size in the SD process\(^{9}\). Removal of moisture is also an essential factor for determining particle size that is achieved at high inlet drying temperature up to 180°C. Above this temperature shows an increase in particle size due to the increased drying rate, resulting in capsules formation and doesn’t let the particles shrink\(^{5, 35}\). In contrast, a higher drying airflow rate causes increased particle size because of the short stay time of particles in the drying chamber resulting in less moisture removal and bigger particles\(^{30}\).

Our results agreed with Goula and Adamopoulos\(^{10}\), who reported the same particle sizes during encapsulation of PSO with SMP\(^{5.8–18.7 \, \mu m}\). In contrast, a minimum particle size of 4.6 μm of PSO with modified corn starch at 167°C was reported by Bustamante \textit{et al.}\(^{33}\). It was explained that powder particle size depends on the SD process parameters and feed properties (the viscosity, solid content, size, and stability).

Recently, Yekdane and Goli\(^{20}\) have also reported lower particle size (4.4 to 6.3 μm) at 170°C of PSO combined with GA and XG. On the other hand, Comunian \textit{et al.}\(^{34}\) reported a little higher particle size 9.9–22.6 μm at 150°C. Different wall materials and their combination influenced the particle size; such as WPI:MD treatment presented the most significant particle size (22.6 μm); one hypothesis for this was that because MD did not possess emulsifying property (the structure was not stable enough to obtain smaller particles, so they agglomerated). Moreover, there was no significant difference reported between GA and WPI:Capsule treatments.

3.5 Physical characteristics of microcapsules/encapsulated material

3.5.1 Moisture content

Water activity parameters and moisture levels determine the stability and reliability of the food powder. Moisture content below 5% is a sign of improved stability in powder.
The moisture value of WP alone as a wall material was showed 3 to 3.5% at 150 and 125°C, respectively. A similar trend was also observed in a combination of WP and MD wall materials ranging from 3.6 to 4.3% at temperatures 150 and 125°C, respectively.

The product’s moisture content is generally controlled by the temperature and humidity of the exhaust air of the drying chamber. As lower inlet temperature could not cause to evaporate water from particles in the drying process, it increases moisture in particles. An increase in inlet air temperature up to values around 180°C led to decreased moisture content. This may be due to the faster crust formation, which makes water diffusion difficult inside the particle. Frascareli et al. also observed a similar trend of encapsulated coffee oil when the inlet air temperature increased above 175°C. Increased residence times lead to a greater degree of moisture removal. As a result, an increase in drying air flow rate, decreasing the products residence time in the drying chamber, led to higher moisture contents.

The current moisture content results matched with the study reported by Sahin-Nadeem and Afşin Özen, who observed moisture values of PSO encapsulated particles at 180°C (2.3 to 3.5%). Similarly, Comunian et al. also reported a comparable moisture value of PSO particles (3.8 to 4.8%) at 150°C with the SD method.

3.5.2 Bulk and tapped density

The bulk and tapped densities are vital for the food industry’s manufacturing, packaging, handling, transport, and marketing aid. Thus, storing the larger powder in a small container is useful than lower density powders. A variety of particle sizes affects bulk density when a large number of smaller particles fill the smaller gap than larger particles. A large number of smaller particles increase density. Besides, particles that are circular or irregular are less dense than flat ones.

The bulk density of SD powders of different wall materials was found at 0.21 to 0.23 g/mL. Since lower bulk density was obtained by 0.21 g/mL of WP and 0.22 g/mL of WP-MD at 125°C, a higher value was recorded between 0.22 and 0.23 g/mL, WP and WP-MD, at higher temperature 150°C, respectively. The tapped density in SD encapsulated powder was produced in the range of 0.26 to 0.30 g/mL. Lower tapped density was obtained at 125°C, and higher value was recorded at higher temperature 150°C, respectively, as shown in Table 2.

Our findings matched with the results of Comunian et al., who found bulk density in the range of 0.21–0.29 g/mL in PSO with different wall materials alone and combination by SD method. The same trend was also reported by Fernandes et al. for rosemary essential oil encapsulated with GA (0.25–0.36 g/mL). In our results, the bulk density of SD particles increased as the temperature reached 150°C as compared to 125°C due to the impact of inlet air temperature on average particle size. On the other hand, above 180°C temperature led to a decrease in bulk density due to faster evaporation rate resulting in dried product to more porous and scrambled structure (hallow caused by puffing and inflation ballooning of particles). Goula et al. observed bulk density increased as temperature increased up to 180°C. In contrast, Aghbashlo et al. noticed decreased bulk density as temperature increased from 150 to 180°C during encapsulation of fish oil.

3.5.3 Solubility

The capacity of powders to form a suspension in water is known as solubility. The powder must demonstrate better solubility for food products, so it is essential for food items. In the SD process, particle solubility with different wall materials was found in the range of 84 to 91%, as shown in Table 1. WP alone or in combination with MD particles obtained at 150°C showed higher solubility (91% and 89%). In comparison, lower solubility (86% and 84%) was observed for WP alone and in combination with MD particles at 125°C. Lower solubility in WP alone and in combination with MD at 125°C was due to higher surface oil that prevented its solubility. The higher water solubility indicated that PSO microcapsules could be applied in food products. Sahin-Nadeem and Afşin Özen found higher solubility (97%) of PSO microcapsules of different wall materials by the SD method. Similar results were also reported by Comunian et al., who obtained PSO solubility powder from 88.16 to 91.90%. In contrast, lower solubility (41.85 to 47.72%) of rosemary oil particles by SD was reported by Fernandes et al. The lower solubility of particles might

### Table 2: Physical parameters of different wall materials of microencapsulation spray dried

| Wall material | Moisture (%) | Bulk Density (g/mL) | Tapped Density (g/mL) | Wettability (s) | Solubility (%) | Hygroscopicity (g water/100 g) |
|---------------|--------------|---------------------|-----------------------|----------------|----------------|-------------------------------|
| WP25%-MD10% (125°C) | 4.3 ± 0.4a | 0.22 ± 0.0b | 0.29 ± 0.0b | 40.0 ± 0.5a | 84.0 ± 0.7d | 17.8 ± 0.6a |
| WP25%-MD10% (150°C) | 3.6 ± 0.3b | 0.23 ± 0.0a | 0.30 ± 0.0a | 37.0 ± 0.4b | 89.0 ± 0.8b | 15.7 ± 0.7d |
| WP35% (125°C) | 3.5 ± 0.2b | 0.21 ± 0.0c | 0.26 ± 0.0d | 35.0 ± 0.2c | 86.0 ± 0.4c | 17.2 ± 0.4b |
| WP35% (150°C) | 3.0 ± 0.3c | 0.22 ± 0.0b | 0.27 ± 0.0c | 31.0 ± 0.3d | 91.0 ± 0.5a | 16.3 ± 0.8c |

a–d Different letters indicate a significant difference in physical properties of spray dried capsules among different wall materials at p < 0.05.
be due to the hydrophobic nature of oil.

3.5.4 Wettability

Wettability is an important physical property (presented in seconds) of powder to absorb water since it helps mix two molecular phases directly. In the SD method, the wettability was found in the range of 31 to 40 s with various encapsulated powders, as shown in Table 2. It has been reported that the properties of wall material significantly affect wettability. The shortest time of wettability 31 s was recorded with WP alone at 150°C, suggesting the WP had more ability to dissolve in water. In contrast, the longer time of wettability 40 s was obtained with WP-MD particle obtained at 125°C in the SD process.

3.5.5 Hygroscopicity

Hygroscopicity is a crucial factor in the encapsulated powder consistency and specifies the food product storage capacity. The absorption of water enhances the oxidation of fat and lipids resulting in the flowability of powder (detrimental to foodstuffs).

At 75% relative humidity (room temperature), the water adsorption of microcapsules of PSO was varied from 15.7 to 17.8 g water/100 g. The higher hygroscopicity 17.2 and 17.8 g water/100 g of particles possessed with WP and WP-MD combination at 125°C, and a lower value of 15.7 g water/100 g were observed with WP-MD particles produced at 150°C in the SD process (Table 2). As milk protein can absorb moisture from the surrounding, it had a higher value of hygroscopicity than other capsules (wall materials). As Goula and Adamopoulos suggested, the hygroscopicity of encapsulated oil with SD increased as solid feed concentration. The airflow rate increased while increasing the inlet temperature caused a decrease in moisture that led to a higher glass transition temperature (Tg) and resulted in increased hygroscopicity of powders.

Goula and Adamopoulos reported a lower value of hygroscopicity (7.6 to 10.8 g water/100 g) with the higher Tg of PSO encapsulated with SMP that partially matched with our results. Since higher hygroscopicity value (14.0 and 23.2 g water/100 g) was found for encapsulated PSO powders when inulin combined with MD, it was also observed that when a high quantity of oil is mixed with a low wall materials ratio, it decreased the hygroscopicity of powder due to the hydrophobic nature of oil. On the other hand, Comunian et al. observed lower values (2.6 to 3.6 g water/100 g) of hygroscopicity of PSO powder in the presence of pomegranate juice with different wall materials.

3.6 Storage oxidation of encapsulated oil

Oil oxidation is caused by air, temperature, and light, and oil consistency and nutritional values are impaired. By encapsulating oil with various wall materials, oxidation is prevented. The lower oxidation level during storage means that the oil is of higher quality. Therefore, during storage at 60°C for 15 days, the oxidative stability of bulk and encapsulated oil of various wall materials from SD processes were tested using PV, p-AV, and Totox values.

3.6.1 Peroxide values

The peroxide value uses to verify the efficiency of encapsulated and bulk oil during processing and storage. The quality, taste, and nutritional value of fat and oil products is a significant measurement scale. Usually, as storage continues, PV of bulk and encapsulated oil increases, and value increases to a greater degree at elevated temperatures or for a longer time.

PV of SD particles was almost similar on 1st day of all oil, as shown in Fig. 2. But bulk oil was oxidized rapidly, and its value increased as storage proceeds and reached a maximum PV 14.8 meqO2/kg on the 15th day of the storage. Since particles of WP had the highest encapsulation efficiency (90%) provided the lowest lipid oxidation 1.91 meqO2/kg oil on the first day and increased up to 4.5, 6.1, and 9.9 meqO2/kg on 5th, 10th, and 15th day, respectively. On the other hand, the highest PV (1.95 meqO2/kg oil) was obtained for WP-MD powder (125°C), which had lower encapsulation efficiency of 75.6%. From the first day, the PV increased to 6.1, 7.9, and 12.5 on 5th, 10th, and 15th day, respectively.

Oil oxidation is impacted by independent variables such as inlet drying temperature, oil amount, and solid content. Usually, higher oil and lower solid content cause higher oxidation linked to lower EE, resulting in less protection of oil against oxidation. The higher surface oil is present on the surface of particles causing contact with oxygen and more prone to oxidation, unlike encapsulated oil. Particles were produced at a higher temperature, 150°C caused better EE and oxidation resistance. It was also supported by Goula et al. that higher temperature caused enhanced oxidation-reduction due to increasing EE. While in contrast, Aghbashlo et al. found a higher PV of fish oil encapsulated at a higher temperature of 180°C.

Yekdane and Gol separated the oxidative stability of PSO at 60°C for 30 days and found higher PV 16.8 meqO2/kg of encapsulated oil and 19.0 meqO2/kg of unencapsulated oil from our results. The higher PV may be due to the higher storage time. Similarly, Sahin-Nadeem and Afşin Özen reported a relatively higher PV 17.01 meqO2/kg of encapsulated PSO on the 5th day of storage in a similar condition. On the other hand, Sun-Waterhouse et al. observed lower PV 13.9 meqO2/kg of encapsulated olive oil at a lower temperature 37°C for 30 days of storage. The lower PV might be due to the low temperature and high amount of oleic acid in olive oil. The results displayed that the current encapsulation process has defended oil against oxidation during 15 days of storage at 60°C. Since the lower value of PV was found in the encapsulated oils than in bulk oil, results implied that the oil encapsulation using a combination of different wall materials such WP alone, MD, and WP combinations could delay the oxidation process of
3.6.2 \textit{p}-Anisidine value

\textit{p}-AV is used to calculate secondary oxidation products, such as aldehydes, ketones, and other substances. Generally, it is a belief that less than 20 \textit{p}-AV value is suitable for oil quality. The \textit{p}-AV of bulk oil was much higher in the current study than encapsulated oil for 15 days of storage.

After the 15\textsuperscript{th} day at storage condition, each type of oil eventually had a higher \textit{p}-AV. It was seen lowered \textit{p}-AV of encapsulation oil than bulk oil. An elevated \textit{p}-AV indicated an increased level of secondary oxidation products in oil. As far as \textit{p}-AV of SD microparticles is concerned, its value has risen from day one in all types of oils, but the higher value was found 24.6 of bulk oil and 2\textsuperscript{nd} higher value 21.9 of WP-MD at 125\textdegree C encapsulated oil. Particles of WP had higher EE, so a lower \textit{p}-AV value of 17.6 was observed, as shown in Fig. 3.

In contrast to our results, Sahin-Nadeem and Afşin Özen\cite{11} reported relatively low \textit{p}-AV (5.60 meqO$_2$/kg oil) of PSO on five days of oxidation at 60\textdegree C.

3.6.3 Totox values

A Totox value offers a full degree of oil oxidation. The 30 Totox value is considered the acceptable quality of the oil. When storage continued for 15 days at 60\textdegree C temperature, the Totox value also raised and, the oil quality lowered, as shown in Fig. 4. The Totox value of bulk oil was exceeded to 30 after the 10\textsuperscript{th} day, while encapsulated oils surpassed the same value on the 15\textsuperscript{th} day. Such Totox values are not suitable for the quality of oil, as Firestone reported\cite{12}. Although encapsulated oil showed a lower value of Totox as

![Fig. 2 SEM images of Spray Dried microcapsules. a) WP-MD at 125\textdegree C, b) WP-MD at 125\textdegree C, c) WP at 125\textdegree C, d) WP at 150\textdegree C.](image)

![Fig. 3 Peroxide values of different wall materials of Spray Dried microcapsules during storage at 60\textdegree C. A significant difference in PV was observed during storage using different wall materials at \( p < 0.05 \).](image)
compared to bulk oil. The oil could be spoiled due to oxidation at higher temperatures, whether encapsulated or not, because of the presence of a higher proportion of unsaturated fatty acids in PSO. Thus, Totox value also showed more significant increment over time in all powders of SD, but the maximum value was found 39.4 in bulk oil, and 34.4 in oil of WP-MD 125°C, and the minimum value was observed 27.4 in oil of WP that had higher EE as shown in Fig. 5.

All these results showed oxidation of PSO at higher temperature storage spoiled the quality of the oil. Another critical factor in preventing oxidation was EE. In this study, the higher the EE better is the protection of oil against oxidation, and it depends on the inlet temperature that should be optimum.

As high EE in the SD process was obtained, less oil appeared on the surface of particles resulting in better protection against oxidation. The SD particle structure also played an important role in protection against oxidation as smooth and spherical particles of SD provided higher resistance against oxidation. Hence, viewing these results could suggest that the SD process for encapsulating oil enhanced the oil shelf life by providing better protection against oxidation.

4 Conclusion

Encapsulation of PSO was carried out efficiently with MD and WP as wall materials. Effect of temperature on the EE, physical properties of microcapsules, and oxidative stability was evaluated. The wall materials and temperature highly influenced the EE. The higher solid content (35%) and coating ratio (1:4) had produced better EE. The highest EE (90%) of particles produced at 150°C showed better stability during storage in protecting the active material when WP alone or combined with MD. Results of the study indicated that lipid oxidation was higher for the particles having lower EE during storage of 15 days. Encapsulated pomegranate oil is the best source of conjugated linolenic acid, which positively impacts human health and could be used in many products. However, there is a further need to explore the effect of drying temperature on oxidative stability and the use of natural protein to enhance the beneficial impact of microcapsules on human beings.
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