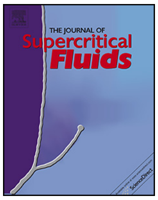
J. of Supercritical Fluids 118 (2016) 194–202

Contents lists available at ScienceDirect

The Journal of Supercritical Fluids

journal homepage: www.elsevier.com/locate/supflu



Oil recovery in rosehip seeds from food plant waste products using supercritical CO_2 extraction

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ARTICLE INFO

Article history:
Received 3 April 2016
Received in revised form 14 August 2016
Accepted 15 August 2016
Available online 16 August 2016

Keywords:
Supercritical CO_2 extraction
Oil recovery from waste
Rosehip seed oil
Fatty acid profiles
Oil solubility
Solubility models

ABSTRACT

Valuable oils in rosehip seeds produced as the solid waste during the process of marmalade production using seed–containing fruits were recovered by supercritical CO_2 extraction method. The influence of the particle size ($125 \leq Dp > 1000\ \mu m$), volumetric flow rate of supercritical solvent (0.75–3.5 mL/min), pressure (20–40 MPa), temperature (40–60 °C) and entrainer concentration (2.5–7.5%vol. ethanol) on the extraction yield in the recovery process was examined. The highest extraction yield determined as 16.5 g oil/100 g dry solid was reached in approximately 150 min by using supercritical CO_2 extraction (30 MPa, 40 °C, 0.75 mL/min, $355 < D_p < 500\ \mu m$) and in the case where 5%vol. ethanol is used as entrainer, it was reached in about 90 min. In similar oil profiles obtained through Soxhlet and supercritical fluid extractions, the ratio of unsaturated fatty acids to saturated fatty acids is about 17. Significant changes were determined in morphological structures of waste seeds compared to unprocessed seeds in marmalade production, by using scanning electron microscope. Apparent solubility values of rosehip oil in supercritical CO_2 did exhibit a significant consistency with Chrastil, del Valle–Aguilera, Adachi–Lu and Sparks solubility models.

1. Introduction

Considering the phytochemical profile and biological potentials, the rosehip fruit has excellent nutrient characteristics. The rosehip fruit, which is one of the richest fruits in nature especially in terms of Vitamin C, contains valuable biological compounds such as tocopherols, phenolics, carotenoids, sugars, organic acids and essential fatty acids [1–3]. Some studies have demonstrated that this fruit exhibits a wide range of bioactivities, such as anti–inflammatory [4–6], antioxidant [7–9], antiproliferative [10,11], anti–obesity and anti–diabetic activity [12]. In this context, the pericarp parts of rosehip fruit are commonly consumed as herbal tea, fruit juice, jelly, jam, marmalade and also used as additive particularly in probiotic beverages, yogurts, soups and baby food today. The rosehip seeds constituting about 30%wt. of the fruit appear as a waste product in the industrial production process of foods mentioned above. The oil content of rosehip seeds varies between 5 and 18%wt. and rosehip seed oil (RHSO) consists of a high amount of unsaturated fatty acids such as linoleic acid (36–55%) in particular and linolenic acid (17–27%) and oleic acid (15–22%) [13,14].

Today, there is a special interest on researches on the recovery of bioactive compounds with high added value from vegetable wastes in food processing processes by using good manufacturing practices (GMP). The fact that some constituents of RHSO exhibit antibacterial, anti–inflammatory, antiseptic and antioxidant activity have a potential importance in the development of versatile products particularly for the cosmetic industry. RHSO is an important natural source involved in the production of skin care and anti–aging products since it contains vitamins (C and E), carotenoids (lycopene and β–carotene) and essential fatty acids (omega 3, 6 and 9) [15–17].

Cold pressing is generally preferred in the production of high–quality RHSO [18]. Oil extraction by cold pressing provides significant advantages in preserving many of the bioactive compounds such as essential fatty acids, phenolics, flavonoids and tocopherol in the oils, but it gives a low oil yield. The oil content of seeds at the end of separation process is between 5 and 15%wt. Cold–pressed oils are considered as healthy oils that are important to human nutrition due to their favorable polyunsaturated fatty acid content, notably α–linolenic acid and linoleic acid [19]. However, the high amounts of polyunsaturated fatty acids in cold–pressed oils are prone to lipid oxidation [19]. For the solution of these bottlenecks, extraction of the oil in rosehip seeds with supercritical CO_2 ($scCO_2$) is an alternative separation process for increasing the yield of the separation and protecting biologi-

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http://dx.doi.org/10.1016/j.supflu.2016.08.011
0896-8446/

cal potentials of valuable biological molecules in the oil. High–tech separation and purification processes using $scCO_2$ in the form of “green solvent” as a separation agent are among alternative processes in the development of industrial processes with GMP used today. In order to increase the yield of oil recovery in the separation process, the physical specifications and transport characteristics of $scCO_2$ may be modified as desired by variation of the pressure and temperature conditions of the extraction. And also the polarity can be modified with a polar/non–polar entrainer addition [20–23]. When the pressure condition of stream leaving the extractor is reduced to atmospheric conditions, the products obtained may be separated in a single stage.

The extraction process of oil from seeds isolated from dried rosehip fruit using subcritical and supercritical fluids (such as CO_2 and propane) have been examined by various researchers [24–31]. Some of these studies were performed to determine the efficiency of oil recovery from the seeds milled in different grinder systems. Furthermore, the effects of operation conditions (such as particle size, pressure, temperature and supercritical solvent flow rate) on the extraction yield were investigated. In addition to the apparent solubility of RHSO in $scCO_2$, the effects of operation conditions on the fatty acid compositions were also examined. However, no detailed study on the recovery of rosehip seed oil from food industry waste by $scCO_2$ extraction processes was found in literature.

The aim of this study is to recover the oil in the rosehip seeds emerging as a waste product in an organic marmalade production process by using a process with GMP. RHSO in waste seeds were separated by $scCO_2$ extraction process. The effects of main process parameters on the extraction yield were investigated. The effects of operation conditions on the initial extraction rate and the apparent solubility of the oil in the solvent under supercritical conditions were also investigated. Furthermore, the compatibility of some semi–empirical solubility models based on pressure and temperature with experimental data were tested. The changes in morphological structures of seeds before and after the separation process were examined using a scanning electron microscope at the microscopic level. Fatty acid profiles of the extracted oil were analyzed by gas chromatography.

2. Material and methods

2.1. Materials

As the plant material, seeds of *Rosa canina* L. fruits included in the subspecies of Rosaceae family were used. The seeds were supplied from İlay–Öztemiz Tarım Orman Gıda Ltd. Şti. (Şarkışla, Turkey), which is a company producing organic rosehip marmalade. Fruits containing the seeds were harvested in Şarkışla region in October 2014. Rosehip fruits are used as a whole together with its seeds during the process of marmalade production. In this process, the seeds used together with the fruit are subjected to a heating process under a temperature of 72 °C and a vacuum pressure of 0.05 MPa, and appear as a solid waste product. The *n*–hexane (<0.004% H_2O) and ethanol (<0.01% H_2O) used as the organic solvent in the extraction process was purchased from Merck KGaA (Darmstadt, Germany) and the liquid CO_2 was purchased from HABAŞ Company (İzmir, Turkey).

2.2. Seed pretreatments

After foreign bodies other than the seeds were removed, the seeds were washed with distilled water, and then dried to a constant weight under atmospheric conditions. Dried seeds were ground in a laboratory scale mill (Polymix PX–MFC 90D Model, Kinematica AG, Switzerland) which was equipped with a hammer–grinding attachment and a 1.52 mm sieve. Ground seeds were divided into four fractions with particles sizes of $125 < D_p < 355\,\mu m$, $355 < D_p < 500\,\mu m$, $500 < D_p < 1000\,\mu m$ and $D_p > 1000\,\mu m$ by using a sieve shaker (Vibratory Sieve Shaker AS 200 control, Retsch, Germany). Milling operation and sieve analysis were made in a cold room at 4 °C. The fractionated samples were stored in airtight amber glass bottles at 4 °C in a fridge up to the time of extraction experiments.

2.3. Determination of moisture and volatile component quantity

Moisture and volatile component contents of rosehip seeds were determined according to ISO–659 standard [32] in order to define the extraction yield on dry solid base. Experiments were repeated three times.

2.4. Determination of oil content

Oil content in rosehip seeds was determined according to ISO 659 standard [33]. In the experiments conducted with Soxhlet extraction apparatus, about 10 g of triturated rosehip seed was used together with 250 mL *n*–hexane as the organic solvent in an extraction thimble made of cellulose. The organic solvent in the oil solution obtained as a result of the extraction process was removed in a rotary evaporator (Rotavapor R–114 Model, Büchi Labortechnik AG, Switzerland) working at a temperature of 40 °C *in vacuo*. The mass of the oil obtained at the end of this process was determined gravimetrically. Experiments were repeated three times.

2.5. Supercritical fluid extraction

Extraction of RHSO with $scCO_2$ was performed in an ISCO SFX 220 Model (ISCO Company, USA) supercritical fluid extraction system operated continuously for fluid phase but batch for solid phase (Fig. 1). An extraction column (316–stainless steel) with a volume of 10 mL was loaded with about 3.25 g rosehip seed. There are frits with a pore size of 2 μm at the end parts of the extractor column. Liquid CO_2 was taken from the CO_2 tank was loaded to the extraction unit with a high pressure syringe pump (ISCO 100 DX Model, USA). During the process of pressurization, the cooling fluid at 4 °C was continuously circulated through heat exchangers surrounding the piston heads of syringe pumps by means of a cooled circulator (Haake C25P Phoenix II, Thermo Electron Co., USA). Before being fed to the extractor, the pressurized CO_2 was brought to the desired operating temperature by means of electrical heat exchangers on pipe lines. The extract was brought to atmospheric pressure by passing the flow of extract leaving the extractor through a temperature and flow rate controlled micro valve (restrictor). Thereby, the RHSO isolated from its solvent was accumulated on glass wool inside the product collection unit. The temperature of restrictor was kept around 70 °C depending on the flow rate. In order to determine the change in the amount of extracted oil with the extraction time, the product collection unit was changed at certain operating times (in particular, once in every 5 min during the first 30 min and once in every 10 min during the second 30 min). Extracted oil samples were dried under a nitrogen atmosphere at 40 °C for about 12 h and then, the mass of extracted oil was determined gravimetrically. The second high pressure syringe pump in the system was used to investigate the effect of entrainer concentration. The control unit is able to feed ethanol/CO_2 at a desired volumetric ratio under a constant pressure of fluids in pumps. $scCO_2$ and ethanol at the pump outlet were fed to a micro mixing unit and mixed together therein and the mixture was fed to the extractor. Experiments were repeated 3 times for each condition. The values in figures are arithmetic mean of findings in experiments repeated for each condition.

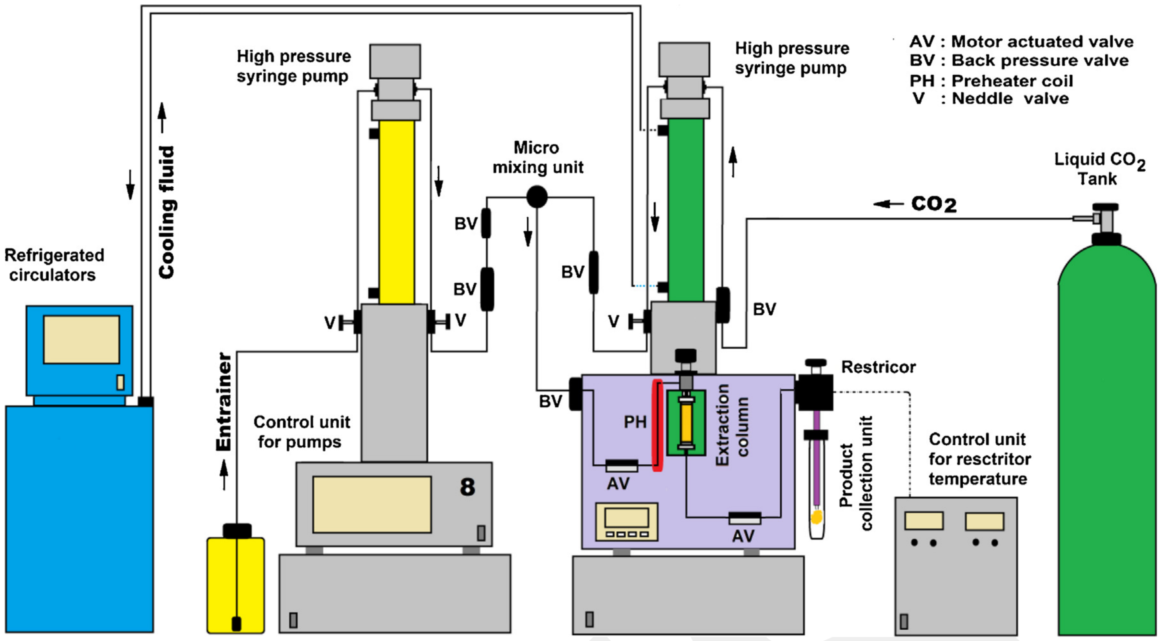

Fig 1. Supercritical fluid extraction system.

2.6. Fatty acid methyl ester analysis

In order to analyze the fatty acids contained in RHSO compositions obtained by supercritical fluid extraction and Soxhlet extraction, first, extracted oils were converted into fatty acid methyl esters (FAMEs) according to IUPAC 2.301 method [34]. Rosehip fatty acid methyl esters were analyzed in a gas chromatography system (Shimadzu GC2010 Model, Japan) equipped with flame ionization detector (FID). Detailed information on the analysis method was provided in our previous works in detail [22,23]. A capillary column containing 100% poly(bicyanopropyl)siloxane (TR–CN100, 60 m × 0.25 mm × 0.20 μm, Teknokroma Co., Spain) was used in the analysis of FAMEs. In order to determine the retention times of FAMEs in the column and identify the fatty acid composition in the RHSO composition, a fatty acid methyl ester standard (Supelco GLC–24 FAME mix) was used. FAME profile of RHSO was determined by chromatogram areas without a correction factor.

2.7. Scanning electron microscope analysis

Morphological changes on the surface of rosehip seeds before and after extraction were examined on a scanning electron microscope (Leo 440, England). Before the analyses, seeds were coated with gold–palladium alloy in a plasm environment by applying a current of 18 mA under a pressure of 4×10^{-4} Pa by means of a coating device (Polaron SC 7620, England).

3. Results and discussion

3.1. Moisture and oil content of the seeds

Due to the polar characteristic of water, the moisture content of oilseeds limits the penetration of the organic solvent used in the solid–liquid extraction processes into porous plant structure and restricts the mass transfer at a molecular level inside the pores by inhibiting the wetting of seed surface by the solvent. Thus, it is preferable to have a low moisture content in plant materials in solid–liquid extraction processes. However, the moisture content in plant materials should be at a level which will protect the flexibility of plant tissue and prevent it from falling apart and will not make the penetration of the solvent used in the separation process difficult. The moisture and volatile contents of rosehip seeds were determined as 6.7 ± 0.3%wt. and 6.5 ± 0.3%wt. respectively for waste rosehip seeds in the food processing process and for original rosehip seeds which were separated from its fruit before food processing process. In order to determine oil recovery rate in separation processes carried out by $scCO_2$ extraction, the initial oil contents of oilseeds are 14.5 ± 0.7%wt. and 13.4 ± 0.3%wt., respectively for waste and original rosehip seeds.

3.2. Supercritical fluid extraction

3.2.1. Effect of particle size on the extraction yield

Pre–treatments, e.g. grinding and classification according to particle size, made before the extraction of RHSO from rosehip seeds which have a very hard outer shell by $scCO_2$ extraction are of quite importance in terms of ensuring the mass transfer efficiency. By this way, the size of particles is reduced, and their surface area is increased, and the ligneous structure composed of lignin and cellulose surrounding the oil is damaged significantly. The effect of particle size ($125 > D_p > 1000\,\mu m$) on the extraction yield during the process of $scCO_2$ extraction of RHSO in waste oilseeds of marmalade production process was examined under the conditions of 30 MPa, 40 °C and 0.75 mL/min. The experimental findings are shown in Fig. 2a. The extraction yield expressed in all graphics is defined as in Eq. (1).

$$\text{Extraction yield} = \frac{g \text{ extracted oil mass}}{100\,g \text{ dry solid}} \tag{1}$$

Considering the initial oil contents, it is seen that the extraction yields achieved at 5 h in separation processes made with particles with a size bigger than 500 μm are about 1/2 fold less than the yields achieved under other conditions. According to Reverchon et al. [28], the reason of this at a microscopic level is that the structures surrounding the oil with a diameter of 30 μm and a length of a few hundred microns cannot be damaged at a significant level in bigger particle fractions and thus no significant increase can be achieved in the extraction yield due to mass transfer limitations inside the pores. del Valle and Uquiche [25] pointed that each fraction classified according to particle size may have differ-

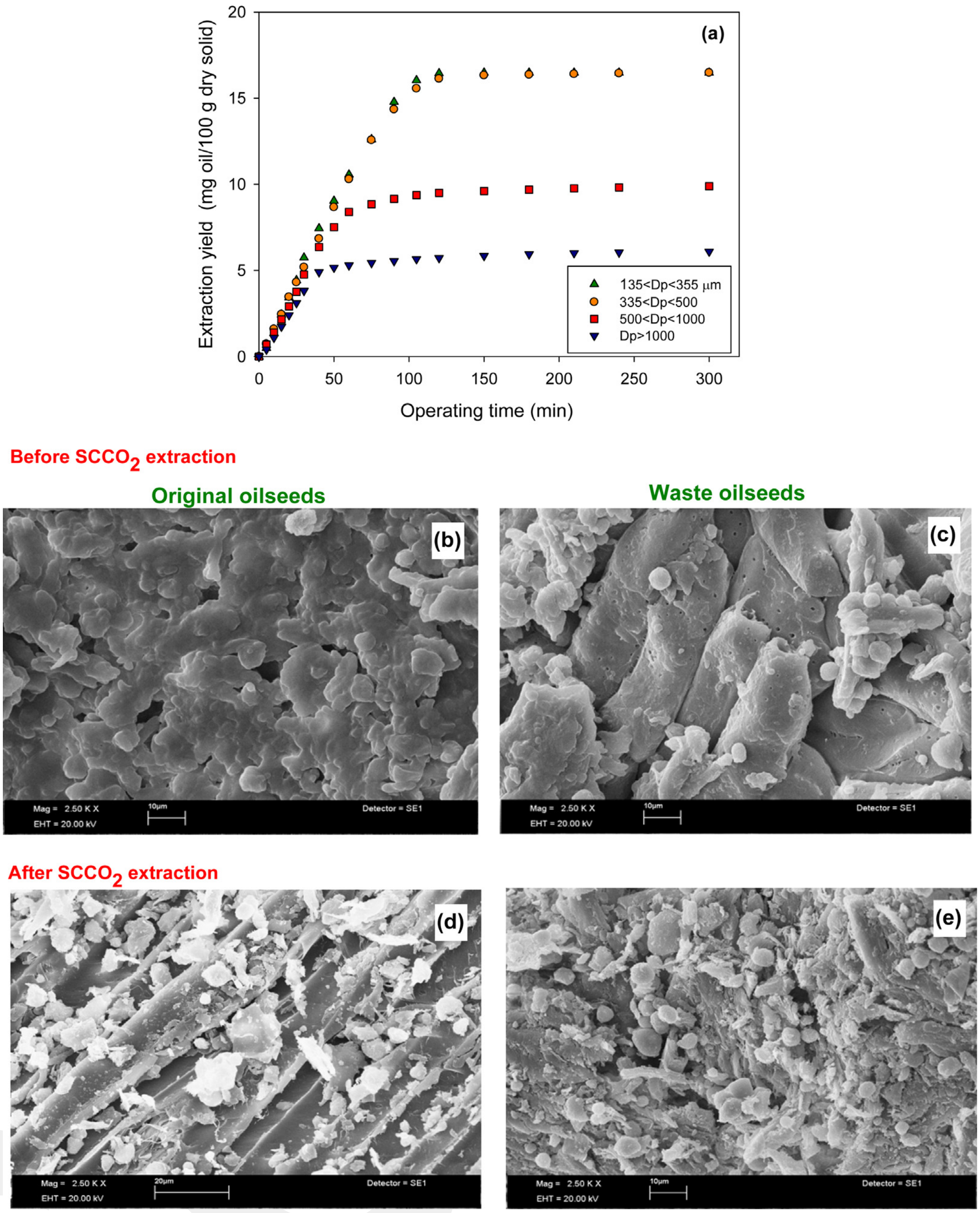

Fig. 2. Effects of pre-treatments on rosehip seeds on the extraction yield and seed morphology.
(a) Effect of particle size on the extraction yield.
(b) Original oilseeds.
(c) Waste oilseeds.
(d) Original oilseeds extracted with $scCO_2$.
(e) Waste oilseeds extracted with $scCO_2$.

ent oil content. They also reported that particularly the fractions having a bigger particle size distribution consist of testae which have low oil content. In this study, no significant mass transfer limitation has been observed inside the pores in separation processes made with particles with a size distribution of $125 < Dp < 355$ μm and $355 < Dp < 500$ μm. Therefore, almost all of the initial oil content of seeds can be extracted at the end of an extraction period of about 2 h.

Compared to morphological structures of original rosehip seeds shown in Fig. 2b, significant differences are explicitly seen in the morphological structures of waste rosehip seeds shown in Fig. 2c. It seen that the oil in original seeds is distributed homogenously on the inert solid whereas the oil in waste seeds is accumulated because of the damage on the ligneous structure composed of lignin and cellulose. Scanning electron microscope analyses of the oil–free original and waste seeds obtained at the end of the $scCO_2$ extraction operation under the conditions of 30 MPa and 40 °C for 5 h are shown in Fig. 2d and e, respectively. The surface morphology of the oil–free original seed shows similarities with the morphologic structure of seeds isolated from their dried rosehip fruits as used in the works of Reverchon et al. [28] and del Valle and Uquiche [25]. As emphasized by the researchers, RHSO is distributed inside these micro porous structures. However, it is explicitly seen on Fig. 2e that a structural deformation occurs on the seeds as a result of the exposure of oilseeds to a heating process at 72 °C *in vacuo* during the production of rosehip marmalade. In the extraction process car-

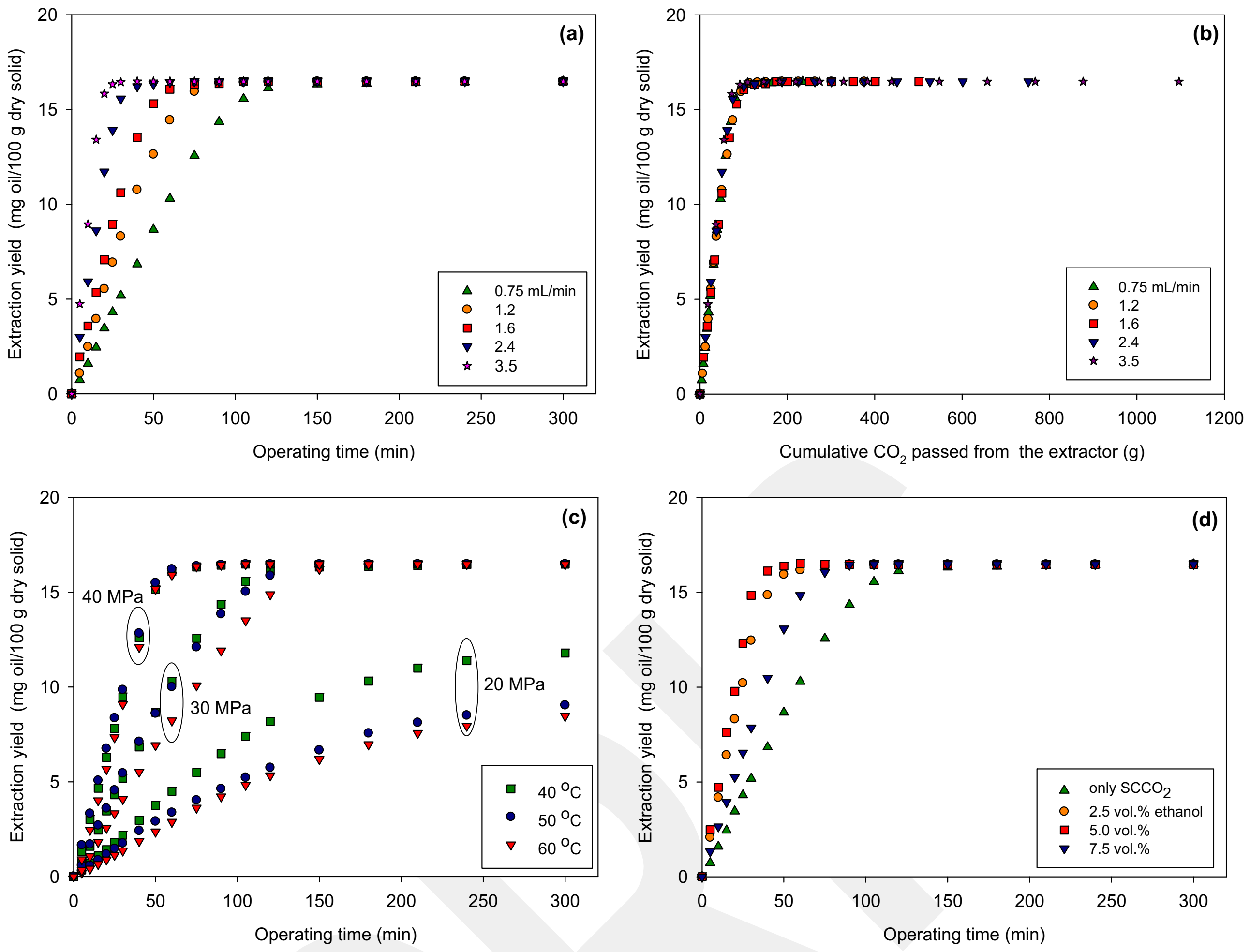

Fig. 3. Effect of operation conditions on the extraction yield.
(a) Effect of $scCO_2$ flow rate with the operating time on the extraction yield.
(b) Effect of $scCO_2$ flow rate with the amount of solvent passing through the column on the extraction yield.
(c) Effect of the extraction pressure and temperature on the extraction yield.
(d) Effect of the entrainer concentration on the extraction yield.

ried out with $scCO_2$ under 30 MPa and 40 °C for 5 h, the extraction yield identified as 15.6 g oil/100 g dry solid for original seeds is less than the extraction yield of heat–treated rosehip seeds identified as 16.5 g oil/100 g dry solid. Machmudah et al. [31] emphasized that the amount of oil, therefore the extraction yield may increase as a result of the structural deformation of seeds at 80 °C during the $scCO_2$ extraction of RHSO.

3.3. *Effect of operation conditions on the extraction yield*

As shown in Fig. 3a and b, the effect of the volumetric flow rate of supercritical solvent (0.75–3.5 mL/min) on the extraction yield during the $scCO_2$ extraction of RHSO from waste oilseeds of the food processing process was examined under the conditions of 30 MPa, 40 °C and $355 < D_p < 500$ μm. As the highest extraction yield determined as 16.5 g oil/100 g dry solid could be achieved for all flow rate conditions examined, the flow rate of supercritical solvent has no effect on the extraction yield. However, as seen in Fig. 3a, significant increases are achieved in the extraction rate in the first periods of the separation process as the flow rate of the supercritical solvent increases. When the flow rate was increased from 0.75 to 3.5 mL/min, the optimal operating time decreased by approximately 5–fold and fell down to 30 min from 150 min. In this study, when the extraction yields achieved with different volumetric flow rates was arranged according to the amount of supercritical solvent passing through the filled column as shown in Fig. 3b. it was seen that the extraction process was controlled in terms of solubility. These results were also explained by some researchers [26–28,31] that the equilibrium solubility of RHSO controls at least the first part of extraction process.

The effect of the extraction pressure (20–40 MPa) and temperature (40–60 °C) on the extraction yield was examined under the conditions of 0.75 mL/min and $355 < Dp < 500$ μm. The obtained experimental findings are shown in Fig. 3c. Although the operating temperature has a significant effect on the extraction yield at a constant pressure of 20 MPa, but there is no such effect under a pressure of 30 MPa or more. At a constant pressure of 20 MPa, when the temperature was increased from 40 to 60 °C, the recovery of oil in the seed improved at a ratio of 2/3–1/2 at 5 h. This is caused by the low solvating power of $scCO_2$ under a pressure of 20 MPa and a temperature between 40 and 60 °C. Therefore, it is necessary to increase the operating time in order to fully recover the oil in the seeds. Similarly Illes et al. [26] also found that small amount of RHSO can be recovered by $scCO_2$ at the lowest operating pressure (10 MPa) and low $scCO_2$ density (less than 600 g/L). At 30 and 40 MPa, for all operating temperatures examined, the oil can be fully extracted in shorter operating time such as 150 and 90 min, respectively. The extraction rate increases as the operating pressure

Table 1
Effect of process parameters on initial extraction rate and apparent solubility.

D_p (μm)	Q (mL/min)	P (MPa)	T (°C)	C_{EtOH} (%vol.)	ρ kg/m^3	S (g/L)	R_{Ext} (g/kg h)
$125 < D_p < 355$	0.75	30	40		918	5.9	116.8
$355 < D_p < 500$						5.3	104.5
$500 < D_p < 1000$						4.9	96.1
$D_p > 1000$						3.9	76.4
	0.75	30	40		918	5.3	104.5
	1.2		40			5.3	166.2
	1.6		40			5.2	204.6
	2.4		40			5.2	292.3
	3.5		40			5.3	412.1
$355 < D_p < 500$	0.75	20	40		847	2.2	44.3
		30			918	5.3	104.5
		40			962	9.9	191.2
		20	50		791	1.6	35.8
		30			879	5.1	109.9
		40			927	9.7	194.2
		20	60		729	1.2	28.1
		30			836	4.2	85.9
		40			893	9.0	187.3
		30	40	2.5	922	11.7	229.9
				5.0	926	13.3	258.7
				7.5	929	8.1	156.9

increases during the first periods of the separation process at a constant operating temperature. The density of scCO$_2$ increases with increasing operating pressure at a constant operating temperature. Therefore, the solubility of the oil also increases. Our experimental results at 40 MPa showed a negligible effect of the operating temperature increase on the initial extraction rate; i.e. the experimental point at different operating temperature practically overlap as shown in Fig. 3c. Indeed, the experiments performed at 40 MPa and over give extraction rates at different temperature that could be in agreement with the previous studies [27–29]. However, different findings as stated by Machmudah et al. [31] have also been reported in the literature. They reported that the extraction yield decreases with increasing temperature at 15 and 30 MPa, but increases with increasing temperature at 45 MPa. Therefore their high extraction yields (13–16%wt.) were reached at the conditions of between 30 and 45 MPa of pressure at 40–80 °C.

The effect of the entrainer concentration (C_{EtOH} = 2.5–7.5%vol.) on the extraction yield was examined under the conditions of 30 MPa, 40 °C, 0.75 mL/min and 355 < Dp < 500 μm, and the obtained experimental findings are shown in Fig. 3d. Ethanol with a GRAS (Generally Recognized as Safe) characteristic was fed to the extraction media together with scCO$_2$ at predetermined concentrations. The highest extraction yield determined as 16.5 g oil/100 g dry solid could be reached in all entrainer concentrations. However, the optimum operating time required for the separation process decreases at first and then increases as the entrainer concentration increases. When compared to the separation process carried out with scCO$_2$, the operating time decreases by 1/3 and falls down to 90 min if ethanol is used at a concentration of 2.5 and 5%vol.

3.4. *Effect of operation conditions on extraction rate and apparent solubility*

The effects of the operation conditions on the extraction yield are shown in Figs. 2 and 3. During the initial period of any extraction curve, the solute's accessibility results in a maximal extraction rate that is constant. Hence, the slope of the extraction curve, the mass of extract versus the mass of CO$_2$, can be used to determine the solved content of RHSO in CO$_2$. This value corresponds to apparent solubility (S) if extraction process is in equilibrium. The initial extraction rate (R_{Ext}, g RHSO kg/dry solid/h) were obtained from the slope of the first linear extraction period of the extraction curves as given in these figures except for Fig. 3b. However, the solved content of RHSO in CO$_2$ or S (g RHSO/kg CO$_2$) was also obtained from the data which were plotted as the mass of RHSO extracted versus the mass of CO$_2$ utilized. The effect of operation conditions on R_{Ext} and S are shown in Table 1. The density of supercritical fluid (r), based on pressure (P), temperature (T) and entrainer concentration (C_{EtOH}), were calculated by using a package program (SF–Solver^{TM} Software for Supercritical Fluid Analysis, ISCO Inc., USA).

As expected, R_{Ext} decreased with increasing D_p since the mass transfer resistance increases in inner parts which are not damaged due to the hard structure of the seed. However, the internal mass transfer limitation oilseed was partially dominant in the oil recovery performed with original seed due to differences in morphology between the seeds (Fig. 2b–e5). For original seed, The values of R_{Ext} and S at 30 MPa, 40 °C, 0.75 mL/min aafor 355 < Dp < 500 μm was determined as 92.5 g/kg/h and 4.8 g/L, respectively. As shown in Fig. 3a, R_{Ext} values increased as expected when Q was increased, but S values remained at a close value around 5.3 ± 0.05 g/L. However, R_{Ext} increased about 4–fold when Q was increased from 0.75 to 3.5 mL/min. Both R_{Ext} and S improved when the extraction pressure was increased at a constant temperature, but these values decreased when the extraction temperature was increased at a constant pressure. The change in the scCO$_2$ density with temperature and pressure conditions is also similar. The value of S varied from 1.2 to 9.9 g/L during the scCO$_2$ extraction of RHSO in waste seeds under the conditions of 40–60 °C and 20–40 MPa. Our experimental findings are among the S values reported by some researchers [26–28,31]. Machmudah et al. [31] reported that the S values varied from 0.4 to 4.4 g/kg at the conditions of 50–80 °C and 20–45 MPa. These results was lower than that obtained by Illes et al. [26] at the condition of r > 900 kg/m^3. The authors reported that it might be caused the lower CO$_2$ flow rate was applied, which was mainly due to the better recovery of extracted oil at the lower CO$_2$ flow rate (2–4 mL/min) in the collection vessel. Moreover, they stated that in practice differences can occur due to a difference in matrix structure as well as the possible oil losses in the system at higher CO$_2$ flow rates. Their results are 2–3 fold higher when compared with our experimental findings. As it is explicitly seen in Table 1, in the extraction process at the temperature range of 40–60 °C, S values varied between 1.2–2.2 g/L at 20 MPa. Increase in the S values has an average of 3–fold at 30 MPa and varied between 4.2–5.3 g/L. R values also increased at same ratio in parallel to such increased in S values. Thereby, the oil in seeds can be fully extracted in about 150 min. Optimal operating time set for the separation process fell

Table 2
Solubility models and its coefficients.

Solubility models	Model coefficients						
	α1	α2	α3	β1	β2	β3	r^2
Chrastil model [35] $\boldsymbol{S}=\rho^{\alpha_1}{}_{\boldsymbol{e}}\left(\beta_1+\frac{\beta_2}{T}\right)$	9.657			−50.56	-4.241×10^3		0.990
del Valle-Aguilera model [36] $\boldsymbol{S}=\rho^{\alpha_1}{}_{\boldsymbol{e}}\left(\beta_1+\frac{\beta_2}{T}+\frac{\beta_3}{T^2}\right)$	9.658			−4.4.03	-8.464×10^3	6.812×10^5	0.990
Adachi-Lu model [37] $\boldsymbol{S}=\rho^{\alpha_1+\alpha_2\rho+\alpha_3\rho^2}\boldsymbol{e}\left(\beta_1+\frac{\beta_2}{T}\right)$	−23.52	8.067×10^3	-1.870×10^{-5}	1.36.3	-4.325×10^3		0.999
Sparks model [38] $\boldsymbol{S}=\rho^{\alpha_1+\alpha_2\rho}\boldsymbol{e}\left(\beta_1+\frac{\beta_2}{T}\right)$	−6.413	2.480×10^3		43.86	-4.342×10^3		0.999

to 60 min at 40 MPa. Increase in the S values at 40 MPa has an average of 5.8–fold and varied between varied between 6.2–9.7 g/L. Compared to the process of $scCO_2$ extraction of RHSO, increase in the values of R_{Ext} and S varied between 1.5–2.5 fold depending on C_{EtOH} when ethanol was used as the entrainer. Although there was no significant difference between the density of $scCO_2$ and the densities of $scCO_2$ + ethanol mixtures, R_{Ext} increased about 2.5–fold when ethanol was used in the concentration of 5%vol.

3.5. *Solubility models*

In this study, four semi–empirical density–based correlations were applied to correlate the measured solubility data. Although these models are not suitable for pseudo ternary systems, the wide applicability of these and similar models promoted as the reference equation for vegetable oil solubility estimation in process design, kinetics and equilibrium calculations. It was revealed that these models are useful to correlate oil solubility for a wide variety of oilseeds [22,23,28,29,39]. One of the first density–based models was proposed by Chrastil [35]. Chrastil model is based upon the theory that at equilibrium a solvato complex is formed between associating solute and solvent molecules. Chrastil's theory led to the development of a model that relates the solubility of the solute and the density of the pure solvent. In the model, S is the solubility of RHSO in g/L, ρ is the density of $scCO_2$ in kg/m^3, α_1 is an association number, β_1 is a function of the association number and molecular weights of RHSO and $scCO_2$, β_2 is a function of the enthalpy of solvation and enthalpy of vaporization, and T is temperature in K. In studying the solubility behavior of vegetable oil in $scCO_2$, del Vella and Aguilera [36] proposed the following modification to Chrastil's model in order to recompense for the change in the vaporization enthalpy with temperature. The association number given in Chrastil model and del Valle–Aguilera model equations weres assumed to be constant, and independence of $scCO_2$ density or temperature. Adachi and Lu [37] modified Chrastil's models to better model the solubility of triglycerides. As given in Adachi and Lu model, the association number was changed to a second–order polynomial of $scCO_2$ density. Additionally, the association number to a linear function of the density of $scCO_2$ was expressed by Sparks et al. [38]. Authors formed Sparks model with the simplification of the Adachi–Lu model. α_1, $\alpha_{2,}$ $\alpha_{3,}$ β_1,β_2 and β_3 given in all solubility models can also be defined as model constants. In order to find all the constants in semi–empirical equations specified for solubility values of RHSO in $SCCO_2$, all the models were linearized and nonlinear regression was determined by using statistic XL (version 6.0) software program (c/o Digital River Inc., MN, USA), and also the model coefficients calculated were reported in Table 2. It is seen that the experimental findings and results of models are strongly consistent. Compared to the findings of Chrastil and del Valle–Aguilera model, it is seen that Adachi–Lu model and Sparks model are strongly consistent with each other.

3.6. *Effect of extraction processes on fatty acid composition*

As indicated in Table 3, the fatty acid profiles of RHSO obtained by Soxhlet extraction with *n*–hexane and $scCO_2$ extraction with entrainer or without contained palmitic (2.3–2.5%), stearic (1.9–2.5%), oleic (20.5–20.7%), linoleic (47.0–48.5%), linolenic (19.9–21.9%) and arachidonic acid (1.0–1.1%) for waste oilseeds, and also palmitic (3.7–3.8%), stearic (2.1–2.4%), oleic (19.9–20.5%), linoleic (48.5–49.2%), linolenic (20.5–22.0%) and arachidonic acid (0.8%) for original oilseeds. Also according to Table 3, by analyzing the composition of unsaturated fatty acids from the samples, it was possible to verify that the fatty acid profile is consistent for RHSO and in accordance with some researchers [24,26,27,30,31] with the major components oleic, linoleic and linolenic acids being approximately 80% of the extracted RHSO. The percentage distribution of the fatty acid components determined for the waste and original oilseeds in this work had some similarities and differences from those of other studies. The reason was explained by Yılmaz et al. [40] as these similarities and differences could be attributed to difference climate, soil, ecological conditions and also genetic factor by different researchers. For example, del Vella et al. [24] reported that linoleic acid (43.9%) was the most abound followed by linolenic acid (35.1%) and oleic acid (14.2%) of fatty acid composition which was obtained with the $scCO_2$ extraction (40 °C, 30 MPa, 21 g CO_2/min) of RHSO in the seeds of Rosa *aff. rubiginosa*. However, Eggers et al. [27] reported for the similar plant origin that linolenic acid (40.8%) was the most abound followed by linoleic acid (37.5%) and oleic acid (9.2%) of fatty acid composition which was obtained with the $scCO_2$ extraction at 30 MPa, 60 °C, 6 kg CO_2/h. The findings of these two researchers are very different from each other. The experimental findings of Machmudah et al. [31] are in agreement with Illes et al. [26]. Both researchers are reported that linoleic acid was the most abound (52–55%) followed by linolenic acid which accounted for 23–24% of total fatty acid profiles. A comprehensive study concerning the effects of temperature (40–80 °C), pressure (15–45 MPa) and CO_2 flow rate (2–4 mL/min) on fatty acids percentage of total fatty acid species in the extracted was investigated by Machumudah et al. [31]. The rosehip seeds separated from the dried fruit was used as an oilseed material. They reported that the fatty acids composition was influenced by the extraction conditions. The aforesaid studies emphasized that there are no significant changes in fatty acid profiles of the obtained oils from rosehip seeds by Soxhlet, cold press and $scCO_2$ extraction methods. However, Illes et al. [26] reported that $scCO_2$ extraction is more than efficient in extracting such precious micronutrients when compared to Soxhlet extraction with *n*–hexane. Szentmihalyi et al. [30] showed that the biologically active substances of rosehip seeds can be extracted in favorable yields by supercritical CO_2 and propane, and also $scCO_2$ extraction results in an oil less rich carotene as compared to Soxhlet, microwave and ultrasound extractions with *n*–hexane. The effect of entrainer contribution in the $scCO_2$ extrac-

Table 3
Oil profiles of rosehip seed oil extracted with different extraction methods and under different operating conditions.

	Fatty acids					
	Palmitic (C16:0)	Stearic (C18:0)	Oleic (C18:1)	Linoleic (C18:2)	Linolenic (C18:3n3)	Arachidonic (C20:0)
Waste oilseeds						
Soxhlet extraction	2.5	1,9	20.7	47.0	21.9	1.0
SFE (only CO_2) 40 °C, 30 MPa, 0.045 L/h	2.4	2.1	20.5	48.3	20.4	1.0
SFE (with 5%vol. ethanol) 40 °C, 30 MPa, 0.045 L/h	2.3	2.5	20.7	48.5	19.9	1.1
Original oilseeds						
Soxhlet extraction	3.8	2.1	19.5	48.5	22.0	0.8
SFE (only CO_2) 40 °C, 30 MPa, 0.045 L/h	3.7	2.2	19.5	49.0	21.2	0.8
SFE (with 5%vol. ethanol) 40 °C, 30 MPa, 0.045 L/h	3.7	2.4	19.9	49.2	20.5	0.8

tion of RHSO has not been carried out so far. Ethanol may enhance the extraction of polar compounds in original or waste oilseeds of the rosehip because of their lower solubility in $scCO_2$. Temelli [41] emphasized that an important aspect in oil extraction is the use of entrainers to increase solvent loading and to recover polar components as CO_2 is selective for non–polar compounds. Because specialty oils as RHSO are receiving growing interest due to their high concentrations of bioactive components which have various health benefits. Therefore, ethanol addition would be advantageous in an extraction process if the selectivity can be improved due to specific intermolecular interactions between the co–solvent and specific components of a mixture [42,43]. In this study, the percentage of linoleic acid in the extracted oils from the original and waste oilseeds did not change significantly with the contribution of 5%vol. ethanol into $scCO_2$ at the conditions of 40 °C, 30 MPa and 0.045 L/h. The percentage of oleic acid increased when using 5%vol. ethanol, but the percentage of linolenic acid decreased. These tendencies for both original and waste oilseeds are similar. As shown in Table 3, the extraction with supercritical fluids of RHSO in both original and waste oilseeds resulted in favorable fatty acid compositions. Linoleic acid content in RHSO obtained by Soxhlet extraction is higher than the supercritical fluids. In contrast, oleic and linolenic is lower than.

4. Conclusions

It is determined by scanning electron microscope analyses that the ligneous structure composed of lignin and cellulose on rose hip seeds which are the waste product of a food processing operation is damaged significantly compared to rosehip seeds directly isolated from dried rosehip fruits. Additionally, since this damage is increased more due to the milling process, it became possible to omit the mass transfer resistances inside the pores for particles with a size smaller than 500 μm. In the studies made to increase the mass transfer rate of the oil from the solid phase to supercritical phase during the process of extraction of RHSO with supercritical CO_2, the solubility of RHSO in CO_2 constitutes the step which limits the speed in the separation process. Since the fatty acids contained in the seeds used in these studies are different, no cross–over effect has been observed at around 30 MPa as stated in Ref. [26]. A similar results with us was reported that Machmudah et al. [27]. They explained that although the flow rate should not have such an effect on the oil solubility, in practice differences can occur due to a difference in matrix structure as well as the possible oil losses in the Illes's extraction process at higher CO_2 flow rate (1–1.5 L/min). Because they collected the better oil recovery of extracted oil at the lower CO_2 flow rate (2–4 mL/min) in the collection vessel. The cross–over phenomenon is due to the competing effects of reduction in the $scCO_2$ density and enhancement in the fatty acids volatility, which accompany the temperature rise. This phenomenon is traditionally observed in the high compressibility region of supercritical solvents. The density of $scCO_2$ is increased with decreasing temperature at a constant pressure, and hence the oil solubility increases with the density effects. However, the $scCO_2$ density alone does not give the complete explanation of solubility enhancement. Another factor, the volatility of oils is also responsible for contributing to the oil solubility behaviors. As a matter of fact, the crossover phenomenon is explained by the relative influence of the density effect and the volatility effect. The extraction yield was determined as 16.5 g oil/100 g dry solid in the separation process made with Soxhlet extraction. This specified yield can be reached at 150 min during the supercritical CO_2 extraction made under the conditions of 30 MPa, 40 °C, 0.75 mL/min and at 90 min in the cases where 5%vol. ethanol is used as the entrainer. No significant change is determined in the profile of fatty acids in the specified extraction processes. As a result of nonlinear regression analyses, it is seen that the apparent solubility values of rose hip seed oil in supercritical CO_2 show a strong consistency ($r^2 \geq 0.990$) with Chrastil, del Valle–Aguilera, Adachi–Lu and Sparks solubility models.

Acknowledgements

The present work supported by Republic of Turkey Prime Ministry State Planning Organization (DPT/SPO) (Project code: 2011K120250). We would like to thank Mr. Şükrü Öztemiz (İlay–Öztemiz Tarım Orman Gıda Ltd. Şti., Sivas, Turkey) for providing of the rosehip seeds.

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