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Extraction Parameters and Analysis of Apricot Kernel Oil

NEZIHE AZCAN* and ELIF DEMIREL

Department of Chemical Engineering, Faculty of Engineering and Architecture, Anadolu University, 26470 Eskisehir, Turkey

*Corresponding author: E-mail: nazcan@anadolu.edu.tr

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Apricot kernel is an alternative raw material for fixed oil, which is used in food, pharmaceutical and cosmetic industries. It can be utilized in place of almond oil because of similarities in fatty acid compositions. Turkey has the largest potential in producing apricot among all other countries in the world. Different varieties [sweet (Hacihaliloglu and Kabaasi) and bitter] of kernel oils (37.9-47.8 %) were obtained by Soxhlet extraction and crude protein contents of the kernels (22.3-26.5 %) were determined by Kjeldahl method. Also, suitable extraction parameters (extraction time, solvent system, solid/solvent ratio) of the oils were investigated. Fatty acid compositions of the kernel oils were determined by GC analysis in methyl esters form and major components were found to be oleic acid (63.3-72.8 %), linoleic acid (21.3-29.0 %), palmitic acid (4.0-5.7 %), stearic acid (1.2-1.5 %) and palmitoleic acid (0.5-0.8 %). Density (0.849-0.936), refractive index (1.4665-1.4700), acid value (0.39-2.06), iodine value (82.2-95.8), saponification value (161.58-178.72) and unsaponifiable matter (1.12-2.87 %) of the oils were determined.

Key Words: Apricot, Kernel oil, Fatty acid, Protein content, Oleic acid, Extraction parameters.

INTRODUCTION

Apricot (*Prunus armeniaca* L.) originally belongs to China has been known since B.C. 3000. Today the Mediterranean countries and the Europe are the main geographical areas for apricot cultivation[1]. Apricot consists of 85 % fruit, 15 % kernel having 70 % of shell and 30 % of pit (internal part of the kernel) which contains 40-50 % oil[2]. Turkey comes first among all other countries in the world in the production of fresh apricot with 200000-400000 tons/year. Malatya region is a well-known place with apricot plantation in Turkey[1]. According to the information obtained from Turkish Statistical Institute (TSI), the exportation data of apricot kernels between 2000 and 2010 is given in Fig. 1. It can clearly be seen that significant amount of apricot kernel is being exported[3].

Apricots are cultivated for the fruit, eaten fresh out of hand or dried, made into conserves or alcoholic beverages[4]. Apricot is treated with sulphur dioxide before getting dried in order to preserve colour or to be protected from disease and detrimental insects. Moreover, enzymatic, non-enzymatic reactions, oxidation reactions are inhibited by sulphur dioxide[1].

The fruit kernels of most types of the apricot are sweet, while the kernels of the wild apricot are bitter[5]. Sweet apricot kernel can directly be consumed as a nut while bitter apricot kernel cannot be used[1] because of the poisonous amygdaline, yielding, 0.06 % HCN. Therefore, the oil cake obtained after

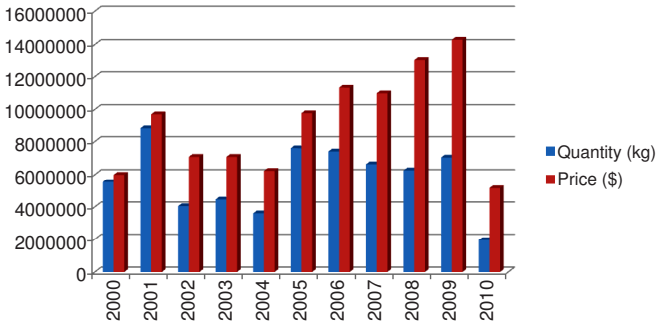

Fig. 1. Amount of exported apricot kernel seeds (Statistical data for 2010 is up to July)

extraction of the seed cannot be used as cattle food. However, its oil can be used for edible purposes since absence of amygdaline in the oil. Sweet variety of apricot kernel, which is called as Chinese almond is used for almond cookies, eaten, salted and blanched, or made into gruel or flour[4]. Products that are manufactured from kernel of the apricot are used in leather, pharmacology, cosmetics and food industries. The major products from them are almond (from the inner part of the kernel) oil, benzaldhyde (increasing aroma), furfural, active carbon, amygdalin and hydrocyanic acid[5].

Apricot kernels can be utilized as a source for oil and protein[2]. Kernels contain 48 % oil[6] and 29 % crude protein[4]. The major fatty acids of the oil are 57.9-68.43 % oleic acid,

22.82-30.4 % linoleic acid, 0.25-0.30 % linolenic acid, 3.9-8.1 % palmitic acid, 1.37-1.7 % stearic acid and 0.98-1.3 % palmitoleic acid[2,6-8]. The physico-chemical characteristics of apricot kernel oil have been studied[2,6,9]. Apricot kernel oil is almost indistinguishable from almond oil in characteristics and composition, classified as minor edible oil[10,11].

Evaluation of the crude apricot kernel oil added to different types of biscuits and cake revealed that it has excellent properties and is comparable with corn oil at the same level. It did not affect the flavour, colour and texture of these products[12].

There have been reports[2,5] giving crude protein content, oil yield and composition of sweet and bitter types of apricot kernel but no data have been reported yet on Hacihaliloglu and Kabaasi varieties and effect of SO_2 either on oil yield or composition.

In this study, oil and crude protein content and fatty acid compositions of different varieties of apricot kernels were investigated and the quality of the oils was determined to show that they can be used in food industry. The extraction parameters (extraction time, solvent system, solid/solvent ratio) of the oil were also determined.

EXPERIMENTAL

Oil contents of apricot kernels were determined by Soxhlet extraction (250 mL capacity) and moisture contents were determined by volumetric method using moisture determination apparatus. Total nitrogen was determined by the standard Kjeldahl method[13] using an apparatus (Gerhardt Turbotherm TT 6/4, Gerhardt Vapodest 40, Gerhardt Laboratory Instruments, Bonn, Germany). Buchi rotary evaporator system (Buchi R-114, water bath B-480, vacuum controller B-721, Switzerland) was used for the evaporation of the solvents from the miscella. Refractive index of the oil samples was determined using Abbe Refractometer.

The fatty acid composition of the oils were analyzed on their methyl esters (prepared by the 14 % BF3-methanol) using a gas chromatograph (Agilent Technologies, 6890N).

Apricot kernel samples (treated and untreated with sulphur) which are sweet (locally known as Hacihaliloglu and Kabaasi varieties) and bitter types were supplied from Malatya region in Turkey. The kernel samples are named as sweet-I (Hacihaliloglu untreated with sulphur), sweet-I* (Hacihaliloglu treated with sulphur), sweet-II* (Kabaasi treated with sulphur), bitter (untreated with sulphur) and bitter* (treated with sulphur). All chemicals were of analytical grade and those were purchased from Merck or Aldrich.

Moisture determination: Approximately 10 g of crushed kernel seeds and 150 mL xylene, saturated with water were added into a flask (250 mL). The mixture was refluxed until constant water level in the graduated part of the apparatus[14].

Soxhlet extraction: 30 g of crushed material was placed into cartridge. Kernel oils were extracted by *n*-hexane for 8 h using 250 mL capacity Soxhlet apparatus. The solvent was then evaporated at 40 ºC under reduced pressure using a rotary evaporator. Oil yields were calculated on dry material bases.

Protein determination: The total protein content was determined by Kjeldahl method. 1 g of kernel seed sample was placed in the Kjeldahl tube. 10 mL of sulphuric acid, 1.5 g copper(II) sulphate, 3 g potassium sulphate and 3 drops of hydrogen peroxide were added. Another tube was used for blank. Then, samples were digested at 410 ºC for 50 min. The digested materials were distilled using NaOH (40 %, v/v), boric acid (10 %, v/v) solutions and distilled water. The distillate was titrated with 0.1 N HCl by using methylene red as an indicator. Crude protein content was calculated through nitrogen amount[13].

In order to find out suitable solvent for kernel oil extraction, several solvent systems [hexane, petroleum ether, acetone, chloroform-methanol (2:1, v/v) and ethanol] were used. Fractions were collected every 2 h during extraction time (8 h) in order to determine suitable extraction time. Different solid/solvent ratios [0.08, 0.15, 0.23, 0.30 and 0.38 (w/w)] were applied for extracting the kernel oils.

Physico-chemical characteristics: Physico-chemical characteristics (density, refractive index, acid value, iodine value, saponification value and unsaponifiable matter) of the oils were determined according to the standard methods.

Density: Densities of the materials were determined using capillary tube[14].

Refractive index: Refractive index of oils was determined by refractometer at 25 ºC[15].

Acid value: 10 g oil was weighed into an Erlenmeyer and dissolved in 150 mL of the solvent. After adding 0.5 mL phenolphthalein, the mixture was titrated with 0.1 N potassium hydroxide by shaking to the end of the indicator and the acid value was calculated[15].

Iodine value: 1 mL of oil was weighed in a ground-necked bottle and 15 mL of carbon tetrachloride was added to dissolve the oil. After adding 25 mL of the reagent (glacial acidic acid) the stopper was inserted in the bottle, shaked gently and kept in a dark place for 1 h. Then 20 mL of the potassium iodide solution and 100 mL distilled water were added and the solution was titrated with the aqueous thiosulphate solution using starch solution as indicator continuing the titration until the blue colour just disappeared after vigorous shaking[15].

Saponification value: 0.005 g of oil was weighed into a round-bottomed flask and 25 mL of ethanolic potassium hydroxide solution and some boiling chips were added. A reflux condenser was fitted and the solution boiled with occasional shaking for 1 h. 0.5 mL phenolphthalein was added to the hot solution and the solution was titrated with the hydrochloric acid solution until the colour of the indicator changed[15].

Unsaponifiable matter: 1 g of oil was hydrolyzed with a 1 N solution of potassium hydroxide in 95 % ethanol (6 mL) for 1 h. The solution was cooled, water (12 mL) was added and the solution was extracted thoroughly with diethyl ether (3 × 10 mL). The extract was washed several times with water, dried over anhydrous sodium sulfate and the non-saponifiable materials were recovered on removal of the solvent in a rotary evaporator. The water washings were added to the aqueous layer, which is acidified with 6 N HCl and extracted with hexane (3 × 10 mL). The free acids were recovered after washing the extract with water, drying it over anhydrous sodium sulfate and removing the solvent in the usual way[16].

Fatty acid composition determination

Methylation of fatty acids: For the preparation of fatty acid methyl esters, the AOAC method[13] was modified as follows. Two hundred mg of the oil sample was weighted accurately into 50 mL flask and 5 mL of 0.5 N methanolic solution of sodium hydroxide were added for the saponification. Reflux condenser was attached to the flask and heated in water bath for 10 min. 5 mL of 14 % (v/v) boron trifluoride-methanol was added through condenser and continued heating for 2 min. 5 mL *n*-heptane was added through condenser then 2 min later flask was removed from the water bath and the solution allowed to standing at room temperature. After the mixture was transferred into 25 mL graduated flask, 5 mL saturated NaCl solution was added and then it was rotated several times, when heptane layer was totally separated from the water layer 1 mL of upper phase (*n*-heptane solution) was transferred into a test tube and dried with anhydrous Na_2SO_4. The fatty acid methyl esters were recovered after the solvent was removed using nitrogen gas[13].

GC analysis: The fatty acid compositions were determined by GC analysis using fatty acid methyl ester standards. Relative percentage amounts of the compounds were calculated by GC-FID. An Agilent/DB-23 FSC column (60 m × 0.25 mm I.D., 0.15 μm film thickness) was used with helium as carrier gas (2.3 mL/min). The split ratio was adjusted to 100:1 and the injection volume was 1 μL. The injection temperature was 250 ºC and oven temperature was kept at 50 ºC for 1 min and programmed to 175 ºC at a rate of 25 ºC/min then increased to 230 ºC with rate of 4 ºC/min and kept 5 min at this temperature.

RESULTS AND DISCUSSION

The moisture contents of the grounded apricot kernels were found in between 5 and 8 %. Oil and crude protein contents of different varieties of apricot kernels are given in Table-1.

TABLE-1
OIL CONTENTS OF DIFFERENT VARIESTIES OF APRICOT KERNELS (HEXANE-EXTRACTED)

Ground apricot kernels	Oil yield (%)	Crude protein content (%)
Sweet-I	37.9	26.5
Sweet-I*	47.8	26.0
Sweet-II*	42.6	22.3
Bitter	39.5	22.6
Bitter *	45.7	22.7

*Treated with sulphur.

According to Table-1, kernels treated with sulphur have more oil (42.6-47.8 %) than kernels untreated with sulphur (37.9-39.5 %). There is no significant difference in protein contents based on sulphured and unsulphured kernel but in oil yields. It is obvious that sulphurization has no effect on protein content of kernels. Kernel extraction of sweet-I* gave the highest oil yield (47.8%). Therefore sweet-I* was used in further experiments in order to determine extraction parameters.

Extraction yields of sweet-I* kernel with different solvent systems are given in Table-2.

TABLE-2
EXTRACTION YIELDS WITH DIFFERENT TYPES OF SOLVENTS

Solvent	Extraction yield (%) (extraction time: 8 h)
Hexane	47.8
Petroleum ether	39.2
Acetone	46.0
Chloroform:methanol (2:1, v/v)	54.6
Ethanol	30.3

Highest oil yield (54.6 %) was obtained using chloroform-methanol solvent system since extract consist of other lipid components such as waxes, hydrocarbons, chlorophylls and carotenoids. Therefore hexane is considered to be the best solvent due to its selectivity towards oil (Table-2).

In order to determine suitable extraction time, oil fractions were collected in 2 hours intervals and yields were plotted against time (Fig. 2).

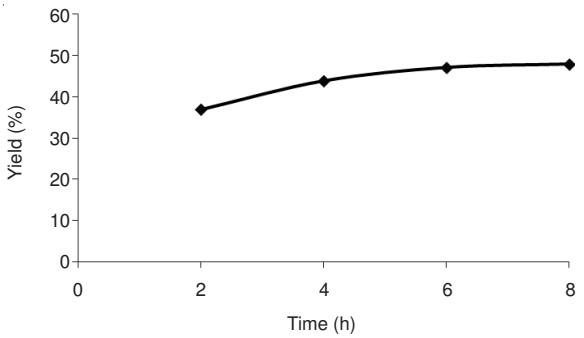

Fig. 2. Variation of oil yield with time

It can be seen in Fig. 2 that 91.5 % of total oil was extracted in 4 h time. According to the found result, suitable extraction time is 4 h depending on oil yield. Besides, after 6 h oil yield remained almost constant.

Yields were plotted against solid/solvent ratio in Fig. 3.

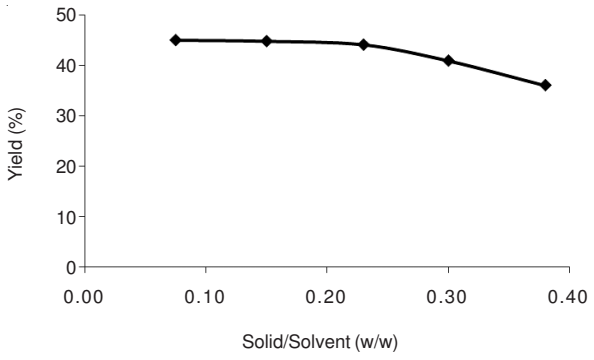

Fig. 3. Variation of oil yield depending on the solid/solvent ratio

According to Fig. 3, suitable solid/solvent ratio is 0.23 (w/w) depending on the cost of solvent and energy needed to evaporate the solvent from the extract solution. Using further amounts of solvent will not compensate the amount of oil obtained.

The physico-chemical properties are in good agreement with reported data[2,5,6,9,17] (Table-3).

TABLE-3
PHYSICO-CHEMICAL CHARACTERISTICS OF OILS

Varieties	Density	Refractive index	Saponification value	Iodine value	Acid value	Unsaponifiable matter (%)
Sweet-I*	0.849	1.4665	161.58	87.7	2.06	1.12
Sweer-II*	0.936	1.4700	178.72	95.8	1.98	2.17
Bitter*	0.855	1.4678	168.05	82.2	0.39	2.87

*Treated with sulphur.

TABLE-4
FATTY ACID COMPOSITIONS OF KERNEL OILS

Kernel oil	Fatty acids								
	16:0	16:1	18:0	18:1	18:2	$\Sigma_{sat.}$	$\Sigma_{unsat.}$	Σ	18:1/18:2
Sweet-I	5.2	0.7	1.4	69.7	23.0	7.3	92.7	100	3.0
Sweet-I*	5.3	0.6	1.5	71.3	21.3	7.4	92.6	100	3.3
Sweet-II*	5.7	0.8	1.2	63.3	29.0	7.7	92.3	100	2.2
Bitter	4.0	0.5	1.3	72.8	21.4	5.8	94.2	100	3.4
Bitter *	4.6	0.5	1.3	69.5	24.1	6.4	93.6	100	2.9

*Treated with sulphur.

Kernel oils were analyzed by GC and the relative percen-tage of characterized fatty acid components appear in Table-4. Table-4 indicates that apricot kernel oils mainly consist of oleic acid (63.3-72.8 %), linoleic acid (21.3-29.0 %), palmitic acid (4.0-5.7 %), stearic acid (1.2-1.5 %) and palmitoleic acid (0.5-0.8 %). While bitter kernel oil has the highest oleic acid content (72.8 %), sweet-II* has the lowest (63.3 %). There is no significant difference between fatty acid compositions and percentages of total unsaturated fatty acids (92.3-94.2 %) of studied materials. Kernel seed oils show similarities in fatty acid compositions with some edible oils which are olive oil, corn oil and hazelnut oil[10,11].

Stability of oil increases with the ratio of oleic acid to linoleic acid. Bitter kernel oil is the most stable one with the value of 3.4 (oleic acid/linoleic acid)[18].

Bitter kernel oil can be utilized as an edible oil source because it has high oil content (39.5-45.7 %) with 69.5-72.8 % oleic acid. Although it contains 22.7 % crude protein, extraction meal cannot be used as cattle food because of amygdalin but as fertilizer[4].

There is no big difference between different varieties of sweet kernel oils either in oil content or in oil compositions. Since extraction meal is free of amygdalin and rich of protein (22.3-26.5 %), it can be used as cattle food. Besides, kernels can be consumed as a nut. Amount of apricot kernel is *ca.* 7000 tons in 2009 based on the data supplied from TSI (Institute of Turkish Standards). 3150 tons of kernel oil can be produced commercially considering apricot kernels consist of about 45 % of oil. Therefore apricot kernel can be utilized for edible oil production in order to partly cover demand of edible oil.

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