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Optimization of manufacturing parameters used safflower oil obtained by solvent extraction method for determination of oil properties

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Abstract

In this study crude oil from Remzibey-05 safflower seeds has been breeding in Turkey, was obtained by solvent extraction method. The maximum oil extraction rate of 30% was obtained at the end. Safflower oil has high unsaturated fatty acid content (91.17%) and highest fatty acids found was linoleic (C18:2) 56.82% and oleic (C18:1) acids 33.98%. Physicochemical properties of safflower seed oil were determined with the analysis and measurements. In addition, solvent-type (n-hexane, and dichloromethane diethyl ether), seed, seed-to-solvent ratio: ratio of solvent mixture (1:1, 1:2 and 1:3 (w/w)), stirring rate (200,400 and 600 rpm) and extraction time (1, 2 and 3 hour), the parameters of fat synthesis from solvent extraction method, which determined the effect of experimental design. According to the results of the ANOVA analysis of variance, the parameter that the highest degree of influence the production of safflower oil seed-to-solvent ratio, while the lowest effective parameter was extraction time.

Keywords: Fatty acids, Oil characteristics, Safflower seed, Solvent extraction, Taguchi method

INTRODUCTION

As a member of the family *Compositeae* safflower (*Carthamus tinctorius* L.) is a one year plant. Today, safflower is primarily cultivated for its oil, which is used for food and industrial purposes. As well as using in oil, margarine, mayonnaise and salad oil production, because of its high proportion of linoleic acid is also used in paint and varnish industry. Safflower oil is tocopherol (vitamin E) rich. The amount of the total tocopherol in seed can be up to 400 mg kg^{-1} (Weiss, 2000). After obtaining the remaining portion of the oil, cake contains between 22-24% protein and that makes it a good animal fodder.

Safflower is a minor crop with a world production of about 650,000 tons in 2009 (Weiss, 2000). The world's total plantation area of safflower is 1.121212 ha. India is in the first ranks with area of 700,000 ha and 400,000 tons of production and meets about 70% of world production of safflower. The United States, Mexico, Argentina, Kazakhstan and China were the followers. Approximately 95% of world production of safflower, carried out in these countries. In Turkey, only 165 hectares to 150 tons of seed are produced (Weiss, 2000).

Seed production of safflower is much less in Turkey, so it cannot be processed as a vegetable oil. Safflower can be evaluated as one of the alternative products especially in relatively dry agricultural areas, because of a high tolerance to drought and salinity. Thanks to the drought-resistance the importance of safflower seed is expected to increase due to

breeding problems caused by global warming nowadays. The safflower seed oil content is increased thanks to breeding programs. After turning off edible oil deficit in countries, oil crops which has to be evaluated renewable energy sources and raw materials for the production of oil for biodiesel as the environmentally friendly fuel. Each country should produce oil-seed plants high in fat to ensure continuous production of biodiesel and in accordance with their own local conditions. This is why alternative oil plants as well as the rehabilitation work of existing oil crops are needed to increase oil rates.

In our country, three kinds of safflower seed including Remzibey-05, Yenice and Dinçer are planted. The purpose of this study optimizing the parameters used in solvent extraction of Remzibey-05 such as; the type of solvent (n-hexane, and dichloromethane diethyl ether), seed: ratio of solvent mixture (1:1, 1:2 and 1:3 (w/w)), stirring rate (200, 400 and 600 rpm) and extraction time, and determining the physicochemical properties and fatty acid composition are aimed.

MATERIAL and METHODS

Materials

Safflower seeds (SS) of Remzibey-05 cultivars (*Carthamus tinctorius L.*), were obtained from Agricultural Research Institute in Eskişehir. While determining the physicochemical properties and analysis, as a solvent; n-hexane (Labkim, analytical grade 96%), diethyl ether (purex analytical grade 99.7%) and dichloromethane (HPLC grade 99.5%) was used. Electric mill is used for grinding the seeds, BUCHI rotary vacuum evaporator (Rotavapor R-210), vacuum pump (V-700), HEIDOLPH RZR 2021 mechanical Agitator and NUVE mark NF400 type centrifugation was used in extraction process.

Methods

Remzibey-05 type safflower seeds used in the experiments are dried at 120 ^{o}C for 1 hour. Parametric studies of 100 g of ground safflower seed, extraction with n-hexane, diethyl ether and dichloromethane 1:1, 1:2 and 1:3 (w/w), seed: solvent mixing ratio, 200, 400 and 600 rpm stirring rate 1, 2 and 3 hour oil extraction times were obtained. Milled seeds are taken to rotary evaporator glass flask and mixed with the rates defined for different types of solvent.

At the end of extraction, the mixture filtered after being separated and the remaining portion of the seed-cake mixed with solvent and oil from the evaporator again under vacuum. Then, core centrifuged at centrifugal separator 4200 rpm and 3600 RFC for 45 minute. Particles remaining in suspension in oil are precipitated.

Fatty acid composition and Physicochemical Properties

The density was measured with a densimeter. The color was determined by Lovibond method of AOCS, Cc 13e-92 (AOCS, 1994) using a glass cell with an optical path length of 153 mm with PFX 880 Tintometer.

The pH value was measured with a digital pH meter (Hanna pH211). Dry matter was determined by oven drying at 105 ^{o}C to the constant weight (AOAC, 1990). FFA content, peroxide value (POV) and iodine value (IV) were determined using AOCS methods, Ca 5a-40 (AOCS, 1989), Cd 8-53 (AOCS, 1997) and Cd 1-25 (AOCS, 1993), respectively. The degree of unsaturation (DU) was determined as described by Porzucek and Raznikiewicz (1990)

using the following equation with computed values obtained from GLC after comparison with reference standards:

$$DU = \frac{1\times(\%wt\ MUFA)+2\times(\%wt\ DUFA)+3\times(\%wt\ PUFA)}{100}$$

where: MUFA – represents monounsaturated fatty acid; DUFA – diunsaturated fatty acid and PUFA – polyunsaturated fatty acid.

The refractive index was determined using an Abbe refractometer (WYA Abbe refractometer, Ningbo Yuda Import & Export Co. Ltd, China) at 20 ^{o}C(AOAC, 1990). Fatty acid methyl esters (FAMEs) were prepared from the oil samples according to a laboratory protocol described previously (Yu et al., 2002; Lutterodt et al., 2011). Individual fatty acid methyl esters were identified by comparing their retention times with those of FAME standards. Area under each fatty acid peak relative to the total area of all fatty acid peaks was used to quantify the fatty acids identified. Results are reported as g fatty acid 100 g^{-1} total fatty acids (Lutterodt et al., 2011). All samples were analyzed in duplicate.

Taguchi Design

The Taguchi optimization method was used for the process optimization of solvent extraction of safflower seeds. Taguchi method was employed to reduce the number of experiments and improve the performance characteristics. This method uses special orthogonal arrays to study all the design parameters using a minimum number of experiments. Orthogonal array means that parameters can be evaluated independently of one another; the effect of one parameter does not interfere with the estimation of the influence of another parameter (Ross, 1989). In Taguchi method, the signal-to-noise (S/N) ratio is used to measure the quality characteristics deviating from the desired value. In the present study, three levels are defined for each of the parameters and a L9 orthogonal array scheme was adapted, which required nine experiments instead of 27 individual experiments to complete the process. After that the results were converted into S/N ratio data. In order to more systematically perform an analysis of the relative importance of each parameter, an analysis of variance (ANOVA) was used to optimize the results obtained using Taguchi method.The four selected parameters, at three levels L9 experimentally studied are shown in Table 1.

Table 1. Design experiments for the production of safflower seed oil

Parameters	**Levels**		
	1	**2**	**3**
Seed-to-solvent ratio (A)	1:1	1:2	1:3
Solvent type (B)	n-hexane	Diethyl ether	Dichloromethane
Stirring rate (rpm) (C)	200	400	600
Extraction time (h) (D)	1	2	3

Table 2 is indicate the levels of the parameters. Values represent the average of three analyses.

Table 2. The result of orthogonal test L9

Experiment no	Solvent type	Seeds-to-solvent ratio	Extraction time (h)	Stirring rate	Oil extraction w/w
1	1	1	1	1	18
2	1	2	2	2	24
3	1	3	3	3	30
4	2	1	2	3	27
5	2	2	3	1	21
6	2	3	1	2	28
7	3	1	3	2	14
8	3	2	1	3	16
9	3	3	2	1	25

RESULTS and DISCUSSION

Fatty Acid Composition

Fatty acid composition of safflower seed oil Remzibey-05 is given in Table 3. Content of fatty acids is composed mainly linoleic acid of 56.82%, 33.98% oleic and 5.84% and palmitic acid.

Total saturated fatty acid content was 8.83% and total unsaturated fatty acid content was 91.17%. Mono unsaturated fatty acids were 34.29% and poly unsaturated fatty acids were 56.88%.

Table 3. Fatty acid compositions of safflower seed oil

Fatty acids (%)		Safflower seed oil
Palmitic	(C16:0)	5.84
Margaric	(C17:0)	0.03
Stearic	(C18:0)	2.22
Arachidic	(C20:0)	0.36
Behenic	(C22:0)	0.28
Lignoceric	(C24:0)	0.01
Palmitoleic	(C16:1)	0.09
Oleic	(C18:1)	33.98
Linoleic	(C18:2)	56.82
Linolenic	(C18:3)	0.06
Gadoleic	(C20:1)	0.19
Erucic	(C22:1)	0.01

Physicochemical Properties

Density of safflower oil was 0.819 g mL^{-1}. Free fatty acid content was about 0.28 g $100mL^{-1}$ in terms of oleic acid. Refractive index value of oil was 1.468. Iodine value of safflower oil was 117.87 and higher values are indicators of higher unsaturated fatty acid amounts and obtained data are confirmed with fatty acid compositions further.

Peroxide value of safflower oil was 2.45 meg kg^{-1}, saponification value of samples were 178.33 mgKOH g^{-1}. unsaponifiable matter content was about 1.24 on the other hand pH value of samples were 5.18 (Table 4).

Table 4. Physicochemical properties of safflower seed oil

Parameters	Safflower seed oil
Density at 15 ^{0}C (kg m^{-3})	819
Kinematic viscosity at 40 ^{0}C (mm^2 s^{-1})	16.5
Free fatty acid (% FFA as oleic acid)	0.28
Acid value (mgKOH g^{-1})	0.56
Iodine value	117.87
Peroxide value (meg kg^{-1})	2.45
Refractive index (25 ^{0}C)	1.468
Saponification value (mg KOH g^{-1} oil)	178.33
Unsaponifiable matter (% g g^{-1} oil)	1.24
Colour (5.25")	4R-20Y
Molecular weight (g mol^{-1})	876.30
Percentage oil content in seed (%)	30±0.4
Physical state at room temperature	Liquid
Iron (mg kg^{-1})	1.49
pH	5.18

Optimization of Parameters

The main principle of Taguchi method of experiment, the minimum number of individual and mutual effects of the factors obtained from the research community. Taguchi method is used to test the effectiveness of changes in the S/N ratio was determined by measuring the state of the factors, and safflower oil, is aimed to obtain the maximum amount of oil is better than the largest calculations were performed according to the criteria (Mandal et al., 2008).

Four variables (solvent type, seed-to-solvent ratio, stirring rate and extraction time) at three levels were used to design the experiment in MINITAB 14

Safflower oil solvent extraction method is used to obtain the highest degree of importance to the control parameters, respectively, were as follows: A (seed-to-solvent ratio)> B (solvent type)> C (stirring rate)> D (extraction time). Safflower oil production from the control parameters and their impact on the different levels of the S/N ratio, shown in Figure 1.

Who obtained the maximum amount of safflower oil is the best set of experimental conditions, takes place 90% confidence interval $A_3B_2C_2D_3$. In other words, seed-to-solvent ratio of parameter 3 level (1:3), solvent-type parameter 2 level (diethyl ether), stirring rate, the parameter 2 level (400 rpm) and extraction time of parameter 3 level (3 h) experiments performed and resulted the maximum oil extraction. In these circumstances, at the confirmation test (confirmation experiment) 30 g of safflower seed oil was obtained 100 g seed.

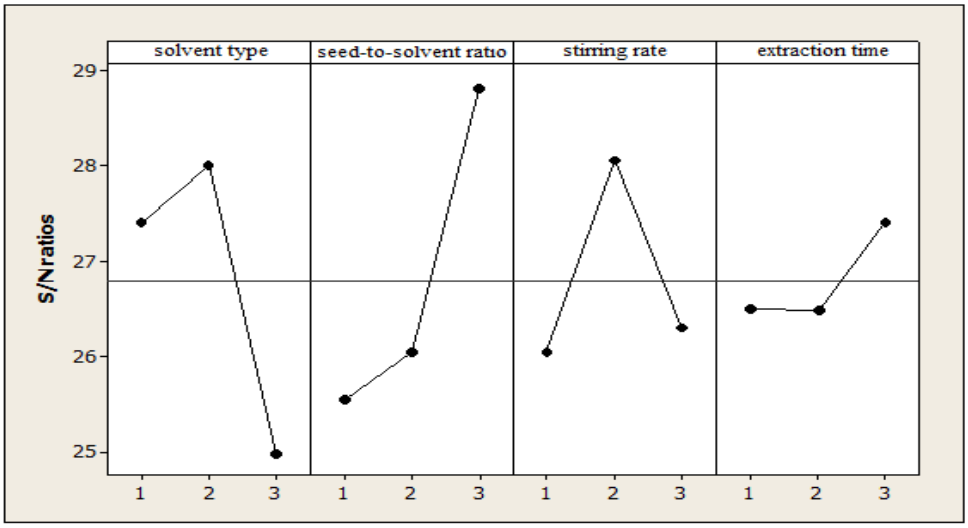

Figure 1. The effects of each parameter at different levels on the yield of safflower oil.

According to the results of the ANOVA analysis of variance, seed-to-solvent ratio of 90% confidence level (confidence interval) is effective. The P value was found to be 0.084. Safflower seed oil production, the percentage of impact of seed-to-solvent ratio, parameter was 35.32%, the percentage of solvent-type parameter effect was 32.72%, stirring rate 21.88% and the percentage of impact parameter, extraction time parameter influence was found to be 10.07%.

In this study, the most influential factors were seed-to-solvent ratio and solvent-type and degrees of impact parameters close to each other. As seen in Figure 1 solvent-type parameter is very little difference between levels 1 and 2, instead of diethyl ether using n-hexane solvent does not alter the result.

CONCLUSION

Safflower oil, edible oil from an examination of its physical and chemical properties due to the human diet, after the oil portion taken off, the remaining pulp was used in animal nutrition. Taguchi experimental design, the minimum number of experiments done by applying the solvent extraction method and the ANOVA analysis of variance with the least amount of safflower oil production will be provided more effective control parameters and the degree of importance of each parameter were determined. Specified conditions to be achieved for production to maximize the amount of fat while the lowest degree of impact parameter is defined as a shortened extraction time will be possible to save time.

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