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Process Optimization for Extraction of Millet Small Bran Oil by Aqueous Ethanol

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Abstract. Millet small bran is a kind of byproduct of the millet processing. It is a cost-effective resource for healthy nutritious oil, which contains 23% oil, with 72% essential fatty acid, tocopherol, phytosterol and oryzanol. In recent years, aqueous enzymatic extraction of millet bran oil has been researched widely. However, this method has the disadvantages of high production costs, low extraction efficiency and great loss of nutrition. In order to reduce the production cost and improve nutritive value of the products, the ethanol extraction method was developed and response surface method (RSM) was used to optimize extraction conditions. The research investigated the influence of extraction temperature, extraction time, solid-liquid ratio and ethanol concentration. The result showed that extraction time, solid-liquid ratio and ethanol concentration made the most contribution to enhancing free oil yield. According to the principle of box–behnken design, response surface analysis of 3 factors and 3 levels was used to optimize the extraction process. The optimal conditions of this aqueous extraction method were: extraction time (120min), solid-liquid ratio (1:5) and ethanol concentration (30%). Under the optimal conditions, the oil yield reached 89.216%. Through determining the quality indices such as acidity, peroxide value and water content of millet small bran oil extracted by aqueous ethanol solution, it could be concluded that the quality of extracted oil was superior to the national standard of crude millet bran oil and similar to the first grade pressed bran oil under the national standard. The contents of tocopherol and phospholipid in millet small bran oil were 131.32mg/100g and 1.12g/100g, respectively. Aqueous ethanol extraction method is not only an efficient and suitable method of extracting millet small bran oil, but also preserve the nutrients like phospholipid and tocopherol to the greatest extent. Hence, it can be concluded that aqueous ethanol technology has a good applying prospect in oil production industry.

1. Introduction

Millet is an annual gramineous plant. And its English name is foxtail millet. It originated in the Yellow River basin of China and Shanxi is one of the main producing regions. China is a country with largest output of millet in the world. It produces about 4.5 million tons of millet and discards 30 thousand tons of the small bran of millet with high nutrition and high added value every year. If it is exploited, it will not only make effective use of agricultural waste resources, but also be of great significance in driving farmers to become rich and improving people's living standards.

Millet small bran is a by-product of millet being processing into refined millet after shelling, rich in fat, bran wax, amino acids, phospholipids, glycolipid, multivitamins, polysaccharides and other nutrients [1], the fat content reached 21%, the unsaturated fatty acids content was over 90%, linoleic acid, linolenic acid, arachidonic acid and other essential fatty acids were 72% in the millet small oil [2], the oil also contains vitamin E、phytosterol、group B vitamins and other active ingredients.

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At present, the common production methods of edible oil are press, solvent leaching and pre-press leaching [3]. The oil yield of pressing method is low and there are some problems such as toxic solvent residue in leaching method. A new green extraction process is urgently needed to improve the quality of oil. In recent years, some researchers have carried out researches about supercritical extraction method and water-enzymatic method. The high equipment cost of supercritical extraction method is difficult to be popularized, and the use of enzyme in large doses by water-enzymatic method and long enzymatic hydrolysis time are the same, which greatly limits the application in vegetable oil industry [4]. Ethanol aqueous extraction is the latest stage in the development of water-enzymatic method, the addition of ethanol can make the oil-water emulsification system unstable, which is beneficial to demulsification or reduce the formation of emulsion, and increase the yield of clear oil [5].

In this study, the ethanol aqueous solution extraction method was used to extract millet bran oil from millet small bran. The Box-Behnken test design and response surface analysis method were used to determine the extraction optimum temperature, ethanol concentration, solid-liquid ratio and extraction time of extraction of millet small bran oil. This method is not only green safe and environmentally friendly, but also has low extraction cost and high extraction efficiency [6]. It provides the theoretical basis and technical reference for the high value utilization of millet small bran and the extraction of green safe edible oil.

2. Materials and methods

2.1 Materials and reagents

Millet small bran is the origin of Linfen, Shanxi Province, the variety is jingu No.1 and provided by Yao shen millet processing factory, Linfen Province. After the millet was shelled, the millet bran was obtained in the process of milling.

Petroleum ether (boiling range: 30~60 ºC), concentrated sulfuric acid, potassium permanganate, potassium thiocyanate, ferrous sulfate, ammonium oxalate, zinc sulfate, coomassie brilliant blue, all above are analytical pure reagents of the chemical reagent co., Ltd of Chinese medicine group.

2.2 Main instruments and equipment

FZ102 micro plant grinding machine (Tianjin taisite instrument co., ltd), LYS electro-heated thermostatic water bath (Beijing yong guang ming medical instrument co., ltd), PHS-3C precision acidity meter (Shanghai leici instrument factory), WFJ7200 ultraviolet visible. Spectrophotometer (Shanghai unico instrument co., Ltd).

2.3 Experiment methods

2.3.1 Extraction process of millet small bran oil. Technological process: millet small bran→ dry → pulverizing → weighing → alcohol aqueous solution extraction→ separation → clear oil. Clear oil rate (%) = (the quality of upper layer of clear oil / the quality of total oil in 10g raw materials)×100%

2.3.2 Methods for determination of components. Fat content: (GB/T5512-2008); phospholipid content: colorimetr [7]; total ash content: burning of high temperature method (GB5505-1985); calcium content: potassium permanganate titration; iron content: colorimetric method of thiocyanate; zinc content: dithizone colorimetric method.

2.3.3 Experimental design. Effects of extraction temperature; solid-liquid ratio; ethanol concentration and extraction time on the yield of clear oil were studied respectively by single factor experiment at PH7.0 of ethanol solution with 10g millet small bran power weighed accurately. Based on the results of single factors test, three main factors affecting the yield of oil were determined. According to the design principle of center combination test of box-behnken in design-expert 8.0 statistical software, three main factors affecting extraction (ethanol concentration, solid-liquid ratio and extraction time)

were taken as independent variables, and the yield of oil was taken as the response value. Three factors and three levels of response surface analysis test were carried out to optimize the extraction process parameters [8]. The statistical analysis software SPSS Statistics 17.0 was used to analyze the date and T test for single factor analysis.

3. Result and analysis

3.1 Main components and contents of millet small bran

The main nutritive components of millet and millet small bran were compared and analyzed in the experiment. The contents of total ash, calcium, iron and zinc in small bran of millet are obviously higher than those in millet. The content of crude fat reaches 23.20%, the content of phospholipid is very high (4.83%), millet small bran oil is a kind of high nutritional value millet processing by-product and is very suitable for developing and extracting high quality healthy edible oil.

3.2 Single factor experiment on extraction of millet small bran oil

3.2.1 Effect of improving extraction temperature on the yield of millet small bran oil. First of all, the clear oil yield was analyzed respectively when the extraction temperature was 20 ºC、40 ºC、60 ºC、80 ºC, the clear oil yield increased significantly with the increased of extraction temperature (fig. 1a). The highest yield was obtained at 60 ºC and the yield of clear oil was 66.08%. When the extraction temperature is 80 ºC, the oil yield is 59.35%, which is 6.37% lower than that at 60 ºC. This may be because the rise of temperature accelerates the volatilization of ethanol and decrease of ethanol concentration in extract, which leads to the reduction of the extraction rate of clear oil [9]. Therefore, the optimum extraction temperature is 70 ºC determined by single factor test.

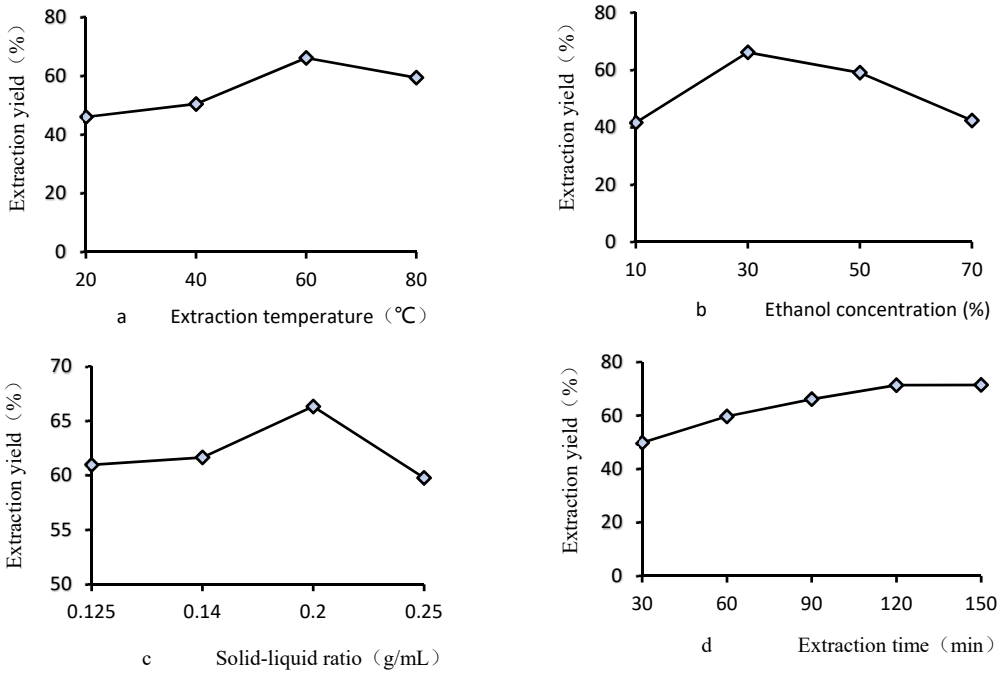

Fig. 1. The effect of extracting temperature (a), ethanol concentration (b), solid–liquid ratio (c) and extracting time (d) on the yield of millet small bran oil

3.2.2 Effect of ethanol concentration on the field of millet small bran oil. The oil yield of the system with 10%, 30%, 50% and 70% ethanol concentration was studied (fig. 1b). When the ethanol

concentration in the range of 10~30%, with the increase of ethanol concentration, the oil yield increased accordingly. When the ethanol concentration is 30%, the yield of clear oil reaches the maximum value of 67.11%; when the ethanol concentration is over 30%, the yield of clear oil began to decrease. Therefore, the best ethanol concentration is determined to be 30% by single factor test.

3.2.3 Effect of the solid-liquid ratio on the yield of millet small bran oil. The oil yield was studied when the solid-liquid ratio was 1:4, 1:5, 1:7 and 1:8. It can be seen from the figure 1c that when the solid-liquid ratio is 1:5(0.2g/mL), the oil yield reaches the maximum value of 66.32%.When the ratio of solid-liquid is increasing to 0.2g/ mL, the powder and ethanol aqueous solution are in full contact, thus it will cause the waste of ethanol extract [10]. Therefore, the optimum ratio of solid-liquid is 0.2g/mL.

3.2.4 Effect of extraction time on the yield of millet small bran oil. It is shown that the effect of extraction time on the oil yield of millet small bran in the fig. 1d. With the prolongation of extraction time, the oil yield increases gradually. When the extraction time ranged from 30 to 150min, the oil yield increased rapidly from 49.82% to 71.32%. When the extraction time ranged from 120min to 150min, the oil yield did not increase. It can be inferred that the oil in millet small bran powder has been fully extracted at 120 min [11]. Therefore, the optimal extraction time is 120min.

3.3 Optimization of extraction process parameters by response surface method

3.3.1 Response surface design and test results. The single factor test determined that the extraction time, ethanol concentration and the solid-liquid ratio were the three main influencing factors. According to the design principle of center combination test of Box-Behnken in Design-Expert 7.0, the response surface analysis test of three factors and three levels was carried out with the ethanol concentration(A), extraction time(B), and solid-liquid ratio(C) as an independent variable(X_1, X_2, X_3) and the yield of clear oil as the response value. The coding of factors and levels of response surface are shown in table 1 and design program and results of response surface are shown in table 2.

Table 1. Coding of factors and levels of response surfaces

Independent variables	Factor level		
	-1	0	1
Ethanol concentration (%)	10	30	50
Extraction time (h)	1.5	2	2.5
Solid-liquid ratio (%)	0.15	0.20	0.25

Table 2. Design program and results of response surfaces

No.	X_1	X_2	X_3	Y （%）
1	-1	0	1	77.65
2	1	-1	0	68.78
3	0	0	0	90.96
4	1	0	-1	82.14
5	0	1	-1	65.67
6	-1	1	0	68.00
7	0	0	0	89.98
8	1	0	1	60.93
9	0	0	0	88.73
10	-1	0	-1	66.39
11	1	1	0	71.76
12	0	0	0	87.96
13	0	0	0	88.45

14	0	1	1	63.91
15	0	-1	-1	69.27

3.3.2 The establishment of regression equation and analysis of variance. Quadratic regression analysis based on box-behnken test design and ANOVA analysis method, the regression equation of each factors variables and response value oil yield(Y) is: $Y = 89.22 + 0.83X_1 + 0.41X_2 - 2.24X_3 - 0.02X_1X_2 - 8.12X_1X_3 + 1.12\ X_2X_3 - 7.27X_1^2 - 13.58X_2^2 - 10.17X_3^2$. The regression equation shows that the quadratic coefficient of extraction time is 13.58, while the other two quadratic coefficients are 7.27 and 10.17 respectively. The result of analysis of variance is shown (table 3) that the regression equation is significant and the test of mismatch not significant, which indicates that the model is ideal.

Table 3. Variance analysis of DH experiment

Soure	Sum of squares	df	Mean square	F value	α
Model	1904.16	9	211.57	58.54	<0.0001
X_1	5.49	1	5.49	1.52	0.2574
X_2	1.37	1	1.37	0.38	0.5577
X_3	40.23	1	40.23	11.13	0.0125
X_1X_2	0.016	1	0.016	0.043	0.9838
X_1X_3	263.58	1	263.58	72.92	<0.0001
X_2X_3	5	1	5	1.38	0.2782
X_1^2	222.57	1	222.57	61.58	0.0001
X_2^2	775.98	1	775.98	214.69	<0.0001
X_3^2	435.32	1	435.32	120.44	<0.0001
Residual	25.3	7	3.61		
Lack of fit	19.27	3	6.42	4.27	0.0975
Pure error	6.03	4	1.51		
Cor total	1929.46	16			

One of three factors was fixed at zero level, and the other two factors and oil yield(Y) were used as the three dimensional response surface diagrams and contour map (fig. 2). With the increase of each factor value, the value of Y increased to some extent, when the value of each factor continues to increase; there is a downward trend of Y. The relationship between three factors and Y is parabolic relation, which accords with the quadratic regression equation mentioned above. Mathematical analysis based on response surface shows that the optimum extraction conditions are as follows: ethanol concentration is 30, extraction time is 2.0h and solid-liquid ratio is 0.2 (1:5). The maximum value of oil yield predicted by regression model is 89.216% and the error from the measured value is 0.85%.

3.4 Quality index of millet small bran oil extracted by ethanol aqueous solution

The content of the water and volatile of the oil is 0.063%, the acid value of the oil is 0.25mg/g and peroxide value of oil is 5.6mmol/kg, which is much smaller than the national standard of crude millet bran oil and is similar to the standard of the first grade pressed finished product of millet bran oil. The content of phospholipid is 1.12g/100g; the content of vitamin E is 131.32mg/100g. The above indexes indicate that the small bran oil of millet is of good quality by ethanol aqueous solution extraction and all indexes meet the requirements of national standards. Hence, it can be concluded that aqueous ethanol technology has a good applying prospect in extracting millet small bran oil.

4. Conclusion

- By using the central combination design test and response surface analysis, it is shown that the order of influence of three factors on oil yield is as follow: extraction time＞solid-liquid ratio ＞ethanol concentration. The regression equation process of the extraction process of small

bran millet is as follows: $Y = 89.22+0.83X_1+0.41X_2-2.24X_3-0.02X_1X_2-8.12X_1X_3+1.12X_2X_3-7.27X_1^2-13.58X_2^2-10.17X_3^2$;

- The optimal extraction conditions of optimization for RSM are as follows: ethanol concentration is 30%, extraction time is 120min and ratio of material to liquid is 0.2(1:5). Under the optimal conditions, the oil yield reached 89.216%. It is shown that RSM can be used for regression analysis and parameter optimization of the extraction process of millet small bran oil;
- The small bran oil extracted by ethanol aqueous solution has good quality, the content of water and volatile is 0.063, the content of acid value is 0.25mg/g and the content of peroxide value is 5.6mmol/kg. The oil has high nutritive value and the content of phospholipid is 1.12g/100g, the content of vitamin E is 131.32mg/100g.

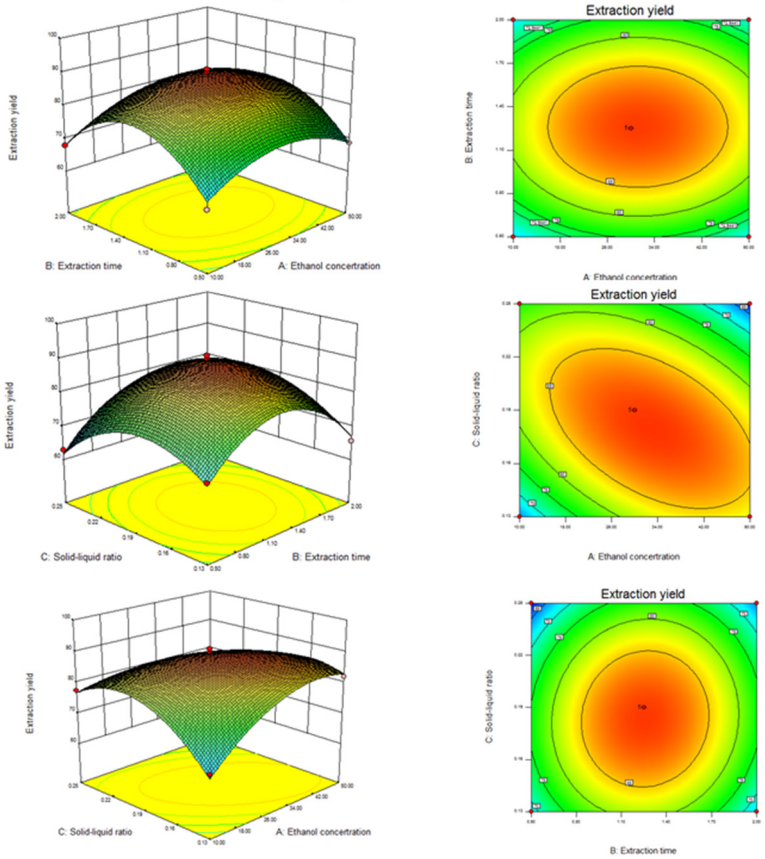

Fig. 2 Response surfaces and contour lines of millet small bran oil yield

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