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Supercritical CO_2 Extraction and Infrared Spectrum Analysis of Coix Seed Oil

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This study focuses on the technological conditions of extraction of Coix seed oil by supercritical CO_2 and the infrared spectrum analysis methods of Coix seed oil, and discusses the effects of extraction temperature, extraction pressure, extraction time and CO_2 flow rate on the extraction efficiency. The following optimal technological parameters are obtained from orthogonal test: extraction temperature of 45°C, extraction pressure of 30 MPa, extraction time of 70 min, carbon dioxide flow rate of 30 kg/h. Under these conditions, the extraction rate of Coix seed oil reaches 81.4%. Fourier transform infrared spectroscopy (FTIR) is used to study the infrared spectrum characteristics of Coix seed oil, through which the main components of Coix seed oil can be preliminarily identified, providing a theoretical basis for the deep processing of Coix seed and the quality control of Coix seed oil.

1. Introduction

Coix seed is the mature kernel of Coix lacryma-jobi L. var. mayuen (Roman.) Stapf, a perennial herbal plant of the Graminae family. It is widely distributed in China and can thrive even in wasteland (Hu, 2009). It is a kind of nutritionally balanced grain, with high content of protein and rich content of 8 amino acids that are necessary for human body, such as vitamin B, calcium, iron, etc (Sarrade, 2003). The oil extracted from Coix seed has antipyretic, hemostatic, anti-inflammatory, pus, antiviral, antibacterial, and other pharmacological functions. It can help to improve immunity and resist tumor and stress analgesia (Wei, 2012). It is effective in nourishing hair, preventing hair loss and making hair smooth and soft. It has significant curing effects on facial acne and rough skin. Other than that, it also has the ability to absorb ultraviolet rays, which can be added to cosmetics for sun protection and UV protection effects (Hui, 2005). Therefore, the Coix seed oil has great application value in nutritious food, medicinal and light industry, and it is of great significance to study the extraction of Coix seed oil. Traditionally, there are two kinds of extraction process for Coix seed oil, squeezing extraction and solvent leaching extraction. Supercritical CO_2 extraction is a new extraction and separation technology with rapid development and one of the most advanced extraction methods for plant components, which extracts and separates an active ingredient from a liquid or a solid by using the fluid in a supercritical state as extractant. Compared with the traditional squeezing extraction and solvent leaching extraction, it is characterized by simple operation, high oil yield, and no chemical solvent residue, which can meet the requirements of green food production (Xu, 2015; Zhu, 2014).
The present study uses supercritical CO_2 to extract Coix seed oil, optimizes extraction process parameters, and adopts Fourier transform infrared spectrometer to analyze the infrared spectrum characteristics of Coix seed oil, with a view to providing a theoretical basis for deep processing of Coix seed and quality control of Coix seed oil.

2. Experiment

2.1 Experimental materials

Coix seed available in the market.

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2.2 Reagents and instruments

CO_2 gas (purity: 99.99%); A11 grinding machine (produced by IKA-Works Guangzhou); HAI2l-50-01 supercritical fluid extraction equipment (produced by Jiangsu Nantong Hua'an Supercritical Fluid Extraction Co., Ltd.); NICOLET IS10 Fourier transform infrared spectrometer (produced by Thermo Fisher).

2.3 Experimental methods

2.3.1 Supercritical extraction process

Coix seed → drying → grinding → screening with 40-mesh sieve → weighing → packaging and sealing → supercritical CO_2 extraction → separation I → separation II → Coix seed oil obtained by separating pot → centrifugal removal of impurities → weighing

Weigh 300 g of the dried and ground Coix seed after it is screened by the 40-mesh sieve, and place it into an extraction tank. Place it in an extraction pot. Put on the pressure ring and seal ring and tighten the plug for supercritical CO_2 extraction. After the selected extraction time is reached, the Coix seed oil is discharged from the discharging port of the separation pot. Weigh the Coix seed oil and calculate the extraction rate (Song, 2007).

2.3.2 Calculation of extraction rate

$$Y = \frac{W_2}{W_1 \times C} \times 100\% \quad (1)$$

Where, Y is the extraction rate (%); W_2 is the amount of oil extracted by the supercritical CO_2 fluid (g); W_1 is the weight of the seed (g); and C is the seed oil content (%). The fat content of Coix seed is determined according to the method of cable extraction, which is 6%.

2.3.3 Infrared spectrum analysis

Take 2 pieces of KBr window, drop 1 drop of Coix seed oil in the middle of one piece of KBr window, and clamp the sample with another piece of the KBr window. Fix the 2 pieces of KBr windows and place them in a sample cell for measurement. Scan them for infrared spectrum is in the wave number range of 400 ～ 4000 cm^{-1} (Zhang, 2012).

3. Results and Analysis

3.1 Single factor test

3.1.1 Effect of extraction pressure on extraction rate of Coix seed oil

Weigh 300g of ground Coix seed and load it into a 1L extraction tank. The effect of extraction pressure on the extraction rate of Coix seed oil is investigated, with the extraction temperature of 40 °C, extraction time of 60 min, and the extraction pressures of 15, 20, 25, 30, and 35 MPa. The results are as shown in Figure 1.

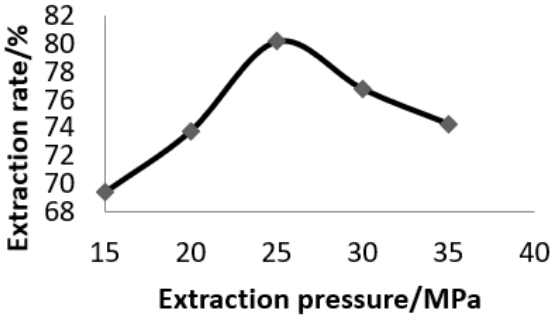

Figure 1: Effects of extraction pressure on yields of Coix seed oil

Extraction pressure is one of the key factors for supercritical CO_2 extraction, and different substances require different suitable extraction pressures. In general, the extraction rate increases with the pressure, but the extraction pressure also affects the selectivity of the product. As can be seen from Figure 1, the extraction rate of Coix seed oil increases with the increase of extraction pressure at the beginning, but when the extraction

pressure exceeds 25MPa, the extraction rate of Coix seed oil gradually decreases. Considering the requirement of extraction rate and pressure to equipment and operation, 25MPa is chosen as the suitable extraction pressure for Coix seed oil.

3.1.2 Effect of extraction temperature on yield of Coix seed oil

Weigh 300g of ground Coix seed and load it into a 1L extraction tank. The effect of extraction temperature on the extraction rate of Coix seed oil is investigated, with extraction time of 60 min, the extraction pressure of 25 MPa, and the extraction temperatures of 30, 35, 40, 45 and 50°C respectively. The results are as shown in Figure 2.

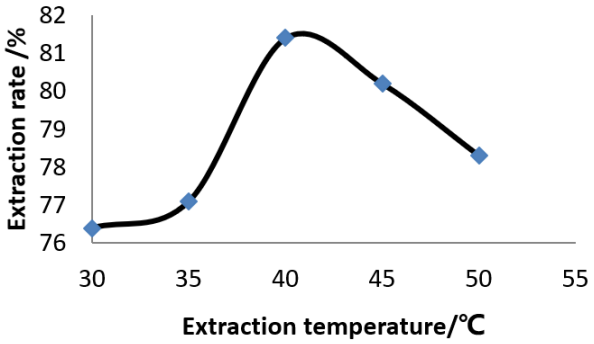

Figure 2: Effects of extraction temperature on yields of Coix seed oil

As can be seen from Figure 2, the extraction temperature also affects the content of Coix seed oil, and the content of Coix seed oil increases with the increase of extraction temperature. When the extraction temperature is 40 °C, the extraction rate of Coix seed oil reaches the maximum. The vapor pressure of the material increases and the volatility of the extracted components increases with the increase of the extraction temperature, which is beneficial to the extraction of the Coix seed oil. However, it is also necessary to prevent the product from deteriorating due to the increase in temperature, so that the extraction temperature should not be set too high. Therefore, it is considered that 40 °C is the suitable temperature for extraction.

3.1.3 Effect of extraction time on yield of Coix seed oil

Weigh 300g of ground Coix seed and load it into a 1L extraction tank. The extraction time curve is obtained, with the extraction temperature of 40°C, the extraction pressure of 25MPa, and the extraction time of 40, 50, 60, 70, 80 and 90 min respectively, as shown in Figure 3.

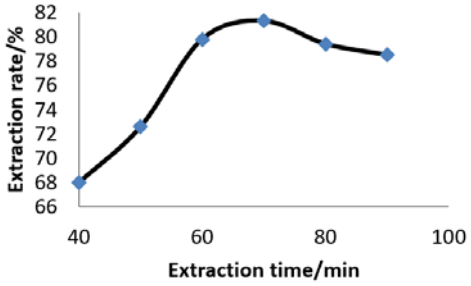

Figure 3: Effects of extraction time on yields of Coix seed oil

As can be seen from Figure 3, different extraction time will also affect the extraction content of Coix seed oil. With the increase of extraction time, the curve shows a rising trend. When the extraction time is 70 min, the content of the Coix seed oil reaches its maximum. The extension of extraction time can help to extract more Coix seed oil. However, when the extraction rate reaches a certain level, the time extension has no obvious effect on the yield of Coix seed oil, or even will lead to a downward trend, thus it is meaningless to continue extraction. Considering extraction rate and efficiency, the optimal extraction time is 70min.

3.1.4 Effect of CO_2 flow rate on yield of Coix seed oil

Weigh 300g of ground Coix seed and load it into a 1L extraction tank. The curve of extraction rate varying with CO_2 flow rate is measured, with the extraction temperature of 40°C, the extraction pressure of 25 MPa, the extraction time of 60 min, and the CO_2 flow rates of 10, 15, 20, 25, 30, 35, and 40 Kg/h, respectively. The results are as shown in Figure 4.

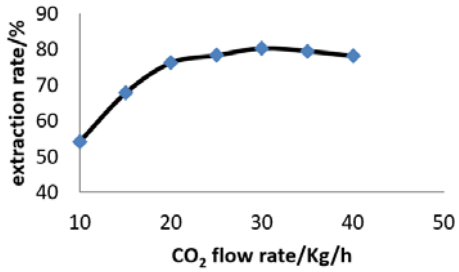

Figure 4: Effects of CO2 flow rate on yields of Coix seed oil

CO_2 flow rate is an important factor affecting supercritical extraction. When the CO_2 flow rate is high, which means there is a large mass ratio between the extractant and the material, it is beneficial to the diffusion of the extracted substance into extractant, leading to an increase of the extraction rate. As can be seen from the Figure, when the flow rates are 10 kg/h and 15 kg/h, the extraction rate is very low. This is because when the flow rate is very low, the extraction speed is very slow, thus the components in the material cannot be fully extracted out within a fixed time. With the increase of the flow rate, the extraction rate is obviously increased. Because the speed of the supercritical fluid passing through the bed is increasing as the CO_2 flow rate increases, which means that the content of the solvent increases within the same time, the contact with the material is enhanced, and the mass transfer coefficient and the mass transfer area increase correspondingly, thus the mass transfer efficiency is improved and the extraction rate raised. When the flow rate reaches 35Kg/h, the extraction rate has a downward trend because the flow rate is too fast, the CO_2 residence time in the extraction tank becomes short, and thus the contact with material is not sufficient. Based on the above factors, CO_2 flow rates of 25 Kg/h, 30 Kg/h, and 35 Kg/h can be selected as the factors of orthogonal test.

3.2 Orthogonal test

In the process of supercritical CO_2 extraction of Coix seed oil, it is necessary to consider not only the yield of Coix seed oil, but also the extraction rate, energy consumption and other comprehensive factors. After the exploration of single factor test, orthogonal test is adopted, with the extraction rate of Coix seed oil as the evaluation standard and the factors such as extraction pressure, extraction temperature, extraction time, CO_2 flow rate and so on, which affect the extraction rate of Coix seed oil as variables.

In order to determine the influence of each factor in the extraction process, with the extraction time, the extraction pressure and the extraction temperature selected as the investigation factors according to the single factor test result, and 3 levels of content of Coix seed oil extracted by supercritical CO_2 taken as the indexes, $L_9(3^4)$ orthogonal test is carried out in order to determine the optimal extraction conditions of supercritical CO_2 extraction of Coix seed oil. The design of the orthogonal test factors and their respective levels are shown in the following table.

Table 1: Factors and levels of orthogonal test

Levels	Factors			
	Extraction pressure (MPa) A	Extraction temperature (°C) B	Extraction time (min) C	CO_2 flow rate (Kg/h) D
1	20	35	60	25
2	25	40	70	30
3	30	45	80	35

Orthogonal test is performed according to the factors and levels designed in table 1. And then the content of Coix seed oil extracted by supercritical fluid is weighed with electronic balance, and the calculated results are shown in Table 2.

Table 2: Results of L9 (34) orthogonal test

NO	Factors				Extraction rate (%)
	A	B	C	D	
1	1	1	1	1	65.55
2	1	2	2	2	81.88
3	1	3	3	3	67.89
4	2	1	2	3	62.72
5	2	2	3	1	68.78
6	2	3	1	2	80.21
7	3	1	3	2	81.86
8	3	2	1	3	70.38
9	3	3	2	1	81.17
K_1	215.32	210.13	216.14	215.50	
K_2	211.71	221.04	225.77	243.95	
K_3	233.41	229.27	218.53	200.99	
k_1	71.77	70.04	72.05	71.83	
k_2	70.57	73.68	75.26	81.32	
k_3	77.80	76.42	72.84	67.00	
R	7.23	6.38	3.21	14.32	

According to R value analysis results of orthogonal test, in the scope of this experiment, with the extraction rate of Coix seed oil as the evaluation index, the degree of influence of each factor on extraction effect is D (CO_2 flow rate) >A (extraction pressure) >B (extraction temperature) >C (extraction time), and the optimal condition is A3B3C2D2, which means the case when extraction pressure is 30MPa, extraction temperature is 45°C, CO_2 flow rate is 30kg/h, and extraction time is 70min. Under these conditions, the content of Coix seed oil is the highest, and the extraction rate is the largest.

3.3 Verification experiment

The best extraction process parameters determined by the single factor test and the orthogonal test are verified through the following experiment. The experimental conditions are: extraction temperature is 45°C, extraction pressure is 30 MPa, extraction time is 70 min, and CO_2 flow rate is 30 kg/h. The experiment is repeated 5 times. The average extraction rate of Coix seed oil obtained is 81.4%.

3.4 Infrared spectrum analysis

According to the infrared spectrum analysis conditions stipulated in 2.3.3, infrared spectrum scanning of the Coix seed oil extracted under the optimum technological conditions is carried out. The results are shown in the following Figure 5.

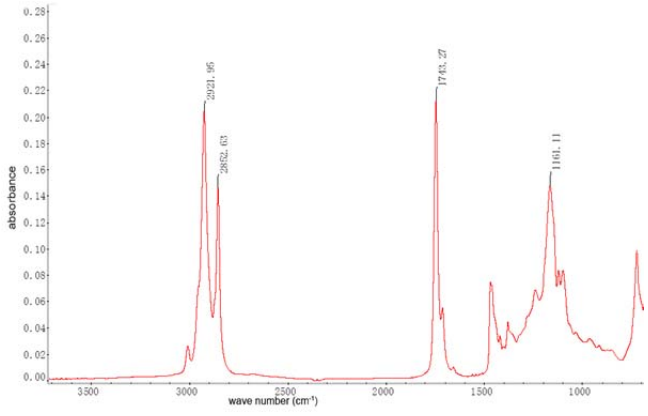

Figure 5: FTIR spectra of Coix seed oil

As can be seen from the Figure, the infrared spectrum can reflect the overall information of the components in the Coix seed oil. In the wave number range of 400cm^{-1}-4000cm^{-1}, there appear 9 obvious absorption peaks in the infrared absorption spectrum of the Coix seed oil, including the C-H stretching peaks near 3010cm-1 and C-H stretching vibration peak near 2921cm-1 and 2852 2852cm^{-1}, the C=O stretching vibration peak at

1743cm^{-1}, C-H bending vibration peak near 1465cm^{-1} and 1370cm^{-1}, C-O stretching vibration peaks in triglycerides at 1240cm^{-1}, 1161cm^{-1}, and 1100cm^{-l}, and vibration peak of carbon chain skeleton at 730cm^{-1} (Zhang, 2013; Liu, 2016). The near infrared spectrum of Coix seed oil is plotted to provide theoretical basis for the detection and quality identification of Coix seed oil.

4. Results and Discussions

(1) The extraction of Coix seed oil with supercritical carbon dioxide is studied in this paper. The optimal extraction process parameters determined by the orthogonal test are as follows: the extraction temperature is 45°C, extraction pressure is 30 MPa, extraction time is 70 min, and CO_2 flow rate is 30 kg/h. The average extraction rate of Coix seed oil obtained is 81.4% under these conditions. Compared with other extraction methods reported in the previous studies, the extraction rate of the present study is higher and has obvious advantages.

(2) The Fourier transform infrared spectrometer is used to study the infrared spectrum characteristics of Coix seed oil. In the wave number range of 400cm-1-4000cm-1, there appear 9 obvious absorption peaks in the infrared absorption spectrum of the Coix seed oil. The comprehensive information of the samples displayed in the infrared spectrum of the Coix seed oil can provide a theoretical basis for the detection and quality identification of the Coix seed oil.

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