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Research of Supercritical CO_2 Fluid Refined Natural Borneol

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Abstract

In this study, with borneol fragments in the crystallized mother liquor of natural borneol used as the raw materials, supercritical carbon dioxide method is adopted for refining to get high purity borneol. The result of the experiment shows that the yield and purity are excellent with an extraction pressure of 11 MPa, an extracting temperature of 40˚C, a carbon dioxide flow rate of 25 $L \cdot h^{-1}$ and an extraction time of 20 minutes. After detected by gas chromatography, the purity of the crystallization products could reach 96%.

Keywords

Natural Borneol, Supercritical Carbon Dioxide, Purification Process

1. Introduction

Borneol (d-Borneol), also known as the D-borneol, plum slices, is commonly called camphane alcohol. Its molecular formula is $C_{10}H_{18}O$ which can be sublimated; it is the white translucent crystal with strong fragrance of pine and smell of camphor and menthol [1]. It has a Melting point of 208˚C (racemic), a boiling point of 212˚C and a flash point of 65.6˚C. It does not dissolve in water, but solubles in alcohol, ether and chloroform. Borneol was widely used in the preparation of rosemary and lavender flavored essence, and also in traditional Chinese medicine and Chinese ink. According to the records in the "Great Dictionary of Chinese Medicine", the Borneol has the medicinal functions such as Tongqiao, eliminating eye screens, improving eyesight, reducing swelling, killing the pain, inducing resuscitation, clearing away heat and toxic materials, diminishing inflame-mation, promoting tissue regeneration, relieving rheumatic pains, expelling phlegm, preventing cancer and curing cancer [2] [3].

Natural Borneol exists in five chemical types of camphor fresh leaves volatile oil (*Cinnamomum camphora* L. *Presl*). The content of volatile oil in the fresh camphor leaves is about 1.2% - 1.9% [4]. It can get the mixture crystalline of borneol and camphor by using steam distillation method, the borneol content is about 84%, camphor content is 14% and others are volatile oil. It cannot reach the requirements of "China Pharmacopoeia" 2010 Edition by using the crude extraction process in natural borneol [5] [6]. It needs to improve the purity of natural borneol by refining. Luo Zhongsheng, *et al*. [7]. used Sublimation method to purify natural borneol, but the molecular weight of natural borneol and camphor are very close, the sublimation temperatures have little difference, the effect was not ideal, and the sublimation temperature was high (about 200˚C) which can be easily charred if operated improperly, therefore, it influenced on the development of natural borneol industry. Nowdays, solvent crystallization was widely used in purifying natural borneol and had ideal effect, the purity of natural borneol could reach 96% which was complied with the pharmacopoeia regulations, but the yield was below 65% [8]. And there were about 35% - 40% borneol fragments cannot be separated from the mother liquor. Even if these borne l fragments were recrystallized and separated, the qualified products could only be improved by 5% - 10%. He Hong cheng, *et al*. got 95% purity and 90% yield by using circulating solvent crystallization [9].

Supercritical CO_2 extraction technology is a new extraction-separation technology which is simple and good separation effect, the product has no solvent residue and is good for heat sensitive material extraction, it's widely used in food industry, medical industry, spices industry [10]-[13] and catalyst [14]. In order to get further recycling of borneol fragments in mother liquor, this topic uses Supercritical CO_2 extraction technology to extract camphor and borneol of borneol fragments, the extraction of these two components could choose the operating conditions of supercritical fluid extraction-temperature and pressure, it provide a new way for separation and purification and application of supercritical.

2. Materials and Methods

2.1. Experimental Apparatus and Reagents

Main experimental instrument: HA121-50-01 supercritical extraction device (Jiangsu Huaan Co., Ltd.); PB403-N electronic balance Mettler-Toledo Group; Clarus 500 GC Miriam (Pekin Elmer); Erlenmeyer flask.

Main experimental reagents: ethanol (Tianjin Damao Chemical Reagent Factory); carbon dioxide gas (purity: 99.9%).

Ingredients: borneol debris (including 65.17% borneol, camphor 34.83%) (Hunan Xin huang borneol factory supplied).

2.2. Experimental Method

2.2.1. Supercritical CO_2 Refined Experimental Methods

Weighed 32 g borneol fragments and put into the extraction vessel, then selected temperature, pressure and flow rate of CO_2, keep the temperature and pressure to extract and separate, after reaching the time, borneol and camphor were respectively removed and preserved from the extraction vessel and the separation Kettle Ⅰ and calculate the yield and detect the purity of the borneol with gas chromatography.

2.2.2. Borneol Crystalline Purity Test

Clarus 500 gas chromatograph; DB-5 column (30 m × 250 μm × 0.25); raise the temperature to 80˚C and keep the temperature for 2 min, then raise the temperature to 280˚C in speed of 3˚C min; FDI testing room with temperature of 300˚C; the injection port temperature is 250˚C; injection volume is 1.0 μL. Using area normalization method to quantitative analysis to calculate the purity and yield.

3. Results and Discussion

3.1. Single Factor Experiment

3.1.1. Pressure Selection

Under the processing conditions of extracting temperature is 35˚C, time is 20 min, CO_2 flow rate is 10 $L \cdot h^{-1}$, observed the influence of extracting temperature to the natural borneol separation. The results were shown in Figure 1 shown that when the pressure increased from 5 MPa to 11 MPa, the separating of natural borneol purity rised quickly, increased from 85.33% to 93.24%. But when the presseure increased from 11 MPa to 21 MPa, the purity of the natural borneol didn't increase apparently. The increasing range was small. The reason was that with the pressure increased, the CO_2 fluid density increased, the compressibility was small and the dissolving capacity of camphor was increased, after a certain pressure, CO_2 density reached a certain value, the solubility of borneol was also increased. Then the purity of natural borneol increased gently, the yield decreased. Therefore, additional pressure had no effects. The pressure of extraction kettle was selected by 11 MPa.

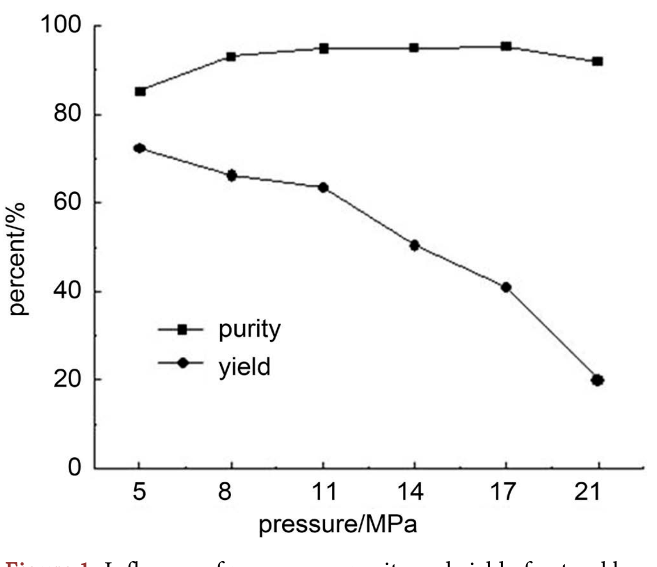

Figure 1. Influence of pressure on purity and yield of natural borneol.

3.1.2. Temperature Selection

Extraction temperature was another important parameter to affect the supercritical extraction efficiency. Selected the extracting pressure of 11 MPa, the extracting time is 20 min and CO_2 flow rate is 10 L·h^{-1}, extracting temperature was in the range of 30˚C - 55˚C. Observed the impact of extraction kettle temperature to the separation of natural borneol. The results were shown in Figure 2 shown that temperature rising have both positive and negative impacts on dissolution of solute. On the one hand, with the increasing of the temperature, the thermal motion of solute molecules accelerated, thereby increased the volatile and the diffusion rate of the components. It was good for borneol fragments to spread to supercritical CO_2 fluid and increased the solubility of the borneol, made the purity of natural borneol increased. On the other hand, with the temperature increasing, the density of CO_2 reduced and the solubility of borneol decreased. so increased the temperature may cause both increasing and decreasing of the purity of natural borneol. The results were shown in Figure 2, under the temperature range of 30˚C - 40˚C, the purity of natural borneol had increasing trend. When the extraction temperature reached 40˚C - 50˚C, the purity of natural borneol had small increse. When the temperature continued to increase, because of the density of CO_2 reduction was the main influence, the solubility declined which was shown a large decline in natural borneol purity. Therefore, the extraction temperature was chosen 40˚C.

3.1.3. Extracting Time Selection

The extracting pressure was 11MPa, extracting kettle temperature was 40˚C and CO_2 flow rate was 10 L·h^{-1}, the reacting time was from 5 to 30 min, the impacts of reacting time on the separation of natural borneol are examined. The results were shown in Figure 3 shown that the purity of natural borneol was gradually increased with the

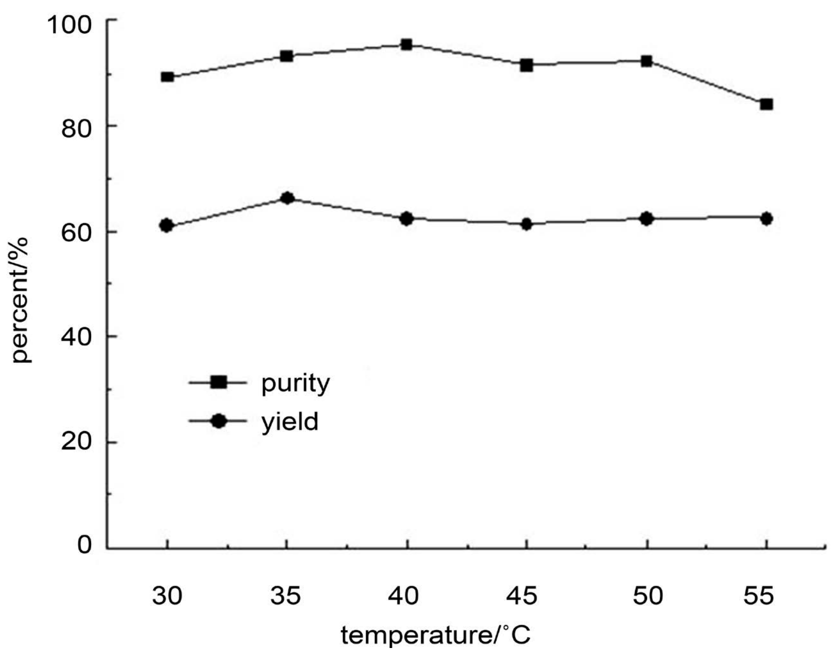

Figure 2. Influence of temperature on purity and yield of natural borneol.

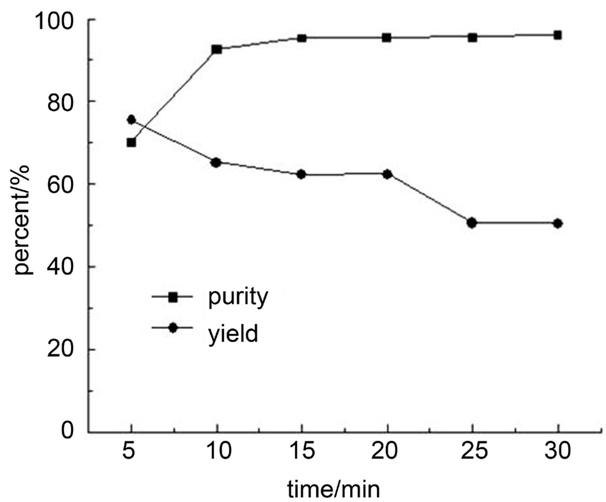

Figure 3. Time on the natural purity and yield borneol.

reaction time increaing, but the range of increasing gradually slow. According to the purity of natural borneol in unit time, it can be seen that in less than 20min, with the reaction time increasing, the borneol yield increased significantly. When the reacting was 20 min, the purity of natural borneol was 95.35%, the yield was 62.39%, After 25 min, the purity of natural borneol basically had no increase, but the yield declines rapidly. So 20 min for the extraction time was considered appropriate.

3.1.4. CO_2 Flow Rate Selection

The experiment was taken under the condition of an extracting pressure of 11 MPa, an extracting kettle temperature of 40˚C and an extracting time of 20 min. And the CO_2 flow rate was set from 10 $L \cdot h^{-1}$ to 35 $L \cdot h^{-1}$. The impacts of CO_2 flow rate on the separation of natural borneol were shown in **Figure 4**. From **Figure 4**, with the increase of CO_2 flow rate, the purity of natural borneol gradually increased. When the CO_2 flow rate reached 25 $L \cdot h^{-1}$, the purity of natural borneol almost reached the maximum. Therefore, the CO_2 flow rate could be 25 $L \cdot h^{-1}$.

3.2. Verification Experiment of the Optimization of Process

In order to further test the optimized process of Supercritical CO_2 fluid refined natural borneol. according to the experiments of 2.2.1 and taken 3 parallel tests under these conditions: extracting pressure was 11 MPa, extracting temperature was 35˚C, CO_2 flow rate was 10 $L \cdot h^{-1}$ and extracting time was 20 min. The results of three experiments were shown below. The yields were respectively 62.3%, 62.91%, 63.26% and the average value was 62.85%. The purities were respectively 98.07%, 97.53%, 98.14% and the average value was 97.71%.

3.3. Product Test

According to test method in 2.2.2, the results of the products were shown in **Figure 5** and **Figure 6**. **Figure 5** was the GC chromatogram of raw material borneol fragment;

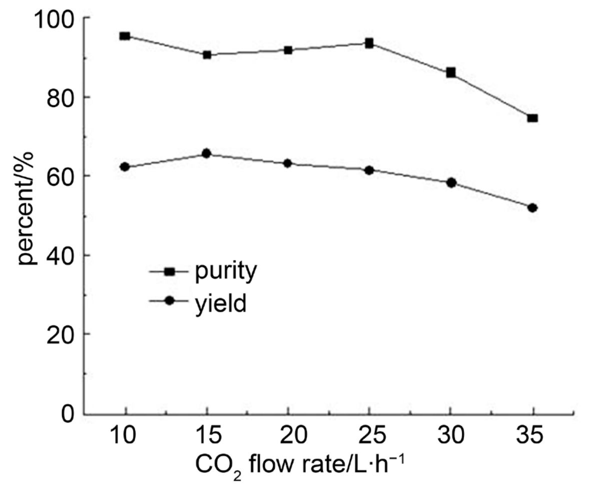

Figure 4. Influence of CO_2 flow rate on purity and yield of natural borneol.

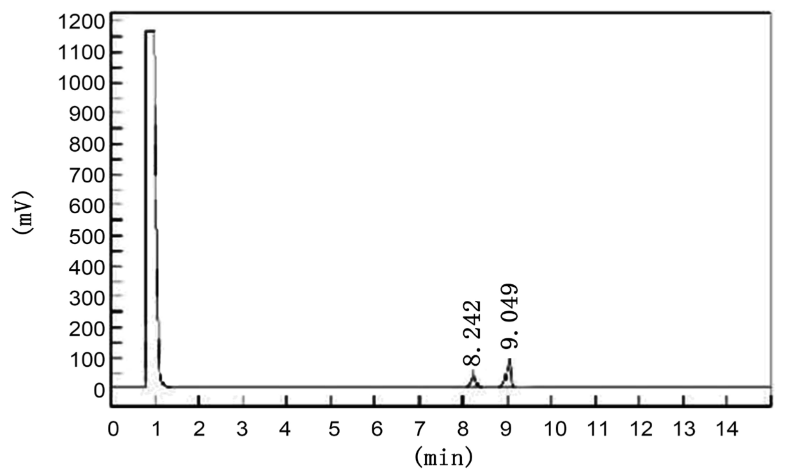

Figure 5. Chromatogram of Gas in raw material of borneol fragments.

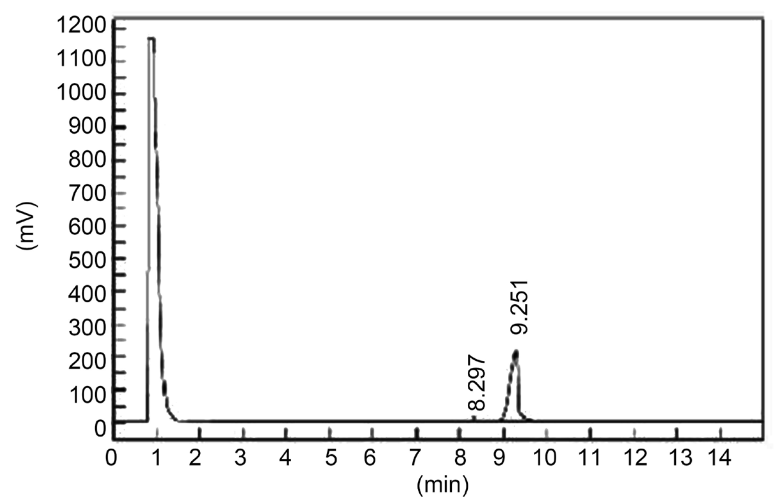

Figure 6. Chromatogram of gas in products of natural borneol by supercritical carbon dioxide purification.

Figure 6 was the GC chromatogram of supercritical CO_2 method refined natural borneol product. In Figure 5 the purity of borneol fragments was 65.17% and in Figure 6 the purity of the product was 98.14%.

4. Conclusions

1) The appropriate process parameters to refine natural borneol by using supercritical CO_2 separation method are: the pressure is 11 MPa, the temperature is 40˚C, CO_2 flow rate is 25 $L \cdot h^{-1}$, time is 20 min. The purity and yield of natural borneol were respectively 96.66% and 61.47%.

2) Using supercritical CO_2 separation to refine natural borneol has these advantages: simple operation, high efficiency, good reproducibility, high security, no organic solvent residue, no chemical changed, high yield and it could recovery by-products from camphor. And it could also be used for the purification of the crude products.

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