Differences in Color and Volatile Components of Oyster Shells During Different Calcination Temperatures

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Abstract. The objective of this study is to explore the differences in volatile components during the calcination process of oyster shells and provide quality monitoring basis for calcined oysters. The volatile components of calcined products from oyster shell at different temperatures were extracted using headspace solid-phase microextraction method, and their volatile components were qualitatively and quantitatively analyzed by GC-MS to determine the common characteristic fingerprint peaks of the calcined products. The results showed that 155 chemical substances were detected from raw oyster shell and its five calcined products, with a total of 11 components. The products with the most abundant volatile substances were those calcined at 500℃. Compared to raw oysters, the effective substances produced by calcination at 300℃ were better, and as the temperature increases, more odor was generated from combustion.

Keywords: oyster shell, volatile component, calcination, fingerprint patterns.

1. Introduction

The main inorganic substance in oyster shells is calcium carbonate, accounting for 80% to 95%, while the organic substances are mainly proteins and polysaccharides, as well as 17 free amino acids such as glutamic acid and glycine. As an economic crop, 60% of oysters are made up of oyster shells, which are wasted in large quantities. Oyster shells have functions in the medical field, such as lowering blood pressure, antioxidation, treating bone diseases, and resisting gastric ulcers. In the field of agriculture, the problem of soil acidification can be solved [1].

Oysters are included in the Chinese Pharmacopoeia. Oysters are commonly used traditional Chinese medicine, with a salty taste and a slightly cold nature. They belong to the liver, gallbladder, and kidney meridians. Oyster shells have the effects of promoting sleep, calming the liver and latent yang, softening and dispersing nodules. Calcined oyster shells are astringent, used for self-sweating, night sweating, nocturnal emission, and acid reflux in the stomach. ZHAO Yu-ying et al. [2] used infrared, elemental analysis, and Kjeldahl nitrogen determination methods to detect calcined oyster shells. Which indicate that the carbonate peak intensity of calcined oyster shells is stronger, and the calcined oyster shells are more helpful in treating stomach diseases caused by excessive stomach acid, but the nitrogen content of calcined oyster shells is lower. The oyster shell is calcined at high temperature. As the temperature increases, the interaction between calcium salts in the oyster shell and organic matter decomposition products such as proteins will produce new substances [3]. The oyster shell is most suitable for calcination at 300℃, which is conducive to the formation of pore structure on the surface of the oyster shell, ensuring a larger specific surface area and higher calcium carbonate content, and facilitating the evaporation of decoction and medicinal effects [4]. The peak value of oyster shells is relatively weak around 220℃ and 445℃, which is caused by the thermal decomposition of organic matter in the oyster shell powder and the transformation from aragonite to calcite crystals. At 647-785℃, there is a strong endothermic peak, which is due to the decomposition of calcium carbonate in calcite to produce calcium oxide and carbon dioxide. Use the silver diethyldithiocarbamate (DDC Ag) method to detect the differences in arsenic content in oyster shells from six different production areas before and after calcination. The arsenic content in calcined oyster shells is lower than that in raw oyster shells, with a calcination time of 50 minutes being the most suitable. Excessive temperature can lead to the loss of effective ingredients [5].

In the Chinese Pharmacopoeia and most research reports, the quality control standard and active ingredient of oysters are calcium carbonate. The Chinese Pharmacopoeia stipulates that the method for calcining oysters is to "take clean medicinal materials, smash them into small pieces, place them on a smokeless stove or in a suitable container, calcine them until they are crispy or red, take them out, let them cool, and crush them. Salt medicinal materials containing crystal water do not require calcination, but they need to evaporate the crystal water completely or form a honeycomb like solid block.". But there is no clear quality control standard. Fingerprint, as an effective means of evaluating the quality of traditional Chinese medicine, can comprehensively reflect the relative relationships of chemical components and complex multi-component systems contained in traditional Chinese medicine. It can comprehensively reflect and effectively control the quality of traditional Chinese medicine, and has certain advantages in the evaluation of traditional Chinese medicine quality. For example, Yan Dan [6] established a fingerprint map of sand scalded pangolin processing. Currently, there is a lack of fingerprint studies on oysters and their processed products.

This experiment used a colorimeter to measure the appearance changes of oyster shells before and after calcination, and used headspace solid-phase microextraction gas chromatography-mass spectrometry technology to extract the volatile components of oyster shells calcined at different temperatures, exploring the differences in their volatile components. The objective of this study is to provide a basis for rational evaluation and control of the quality of calcined oysters.

2. Materials and Methods

2.1. Materials

Oyster shell, produced in Guangdong, purchased from Guangdong Huiqun Traditional Chinese Medicine Decoction Co., Ltd.

2.2. Calcined oyster shells

Six portions of 100g oyster shells were placed in a box type electric furnace (SX2 type, Shanghai Pudong Rongfeng Scientific Instrument Co., Ltd., China). Calcinate at 0 ℃, 100 ℃, 200 ℃, 300 ℃, 400℃, and 500℃ for 1 hour, and set aside.

2.3. Color difference analysis of calcined oyster shells

The NS810 colorimeter (Shenzhen Sanenchi Technology Co., Ltd., China) was used to determine the L * value, a * value, and b * value of calcined oyster shells.

2.4. Volatile components extraction of calcined oyster shells

3.0 g oyster shell powder was placed in a 10 mL sample bottle, placed in a headspace sampler at 60°C and equilibrated for 10 minutes, then inserted into a 50/30 container μ M DVB/CAR/PDMS, manual sampler with StableFlex fiber head. After 50 minutes of headspace extraction, remove the extraction head and immediately insert it into the gas chromatograph inlet (temperature 250 ℃). Heat analyzes for 5 minutes before injection.

2.5. Volatile components identification of calcined oyster shells

The GCMS-QP 2010 Ultra gas chromatography-mass spectrometry (Shimadzu Institute, Japan) was used for the identification of volatile components.

The detection conditions of the gas chromatography-mass spectrometer were as follows: chromatographic conditions: Carrier gas: helium (purity 99.99%); Column flow rate: 0.92mL/min; Injection port temperature: 250.0℃, non-split injection; Program heating: initial temperature of 60℃, maintained for 5 minutes; Subsequently, heat up to 180 ℃ at a rate of 5℃/min-1 for 5 minutes, and then heat up to 260℃ at a rate of 6℃/min-1 for 10 minutes. Mass spectrometry conditions: Ionization method was EI. Ion source temperature was 230℃. Quality scanning range were 40-450m/z.

According to the HS-SPME-GC-MS method and programmed heating conditions, flavor enrichment and analysis were carried out on oyster shells calcined at different temperatures, and total ion flow chromatograms of raw oysters and 5 calcined oyster shell samples were obtained. To establish a common pattern of fingerprint spectra, the original fingerprint data was imported into Origin software, with time as the x-axis and peak intensity as the y-axis, to automatically match the control fingerprint spectra of raw oysters and 5 types of calcined oyster shell samples. By using the total ion flow diagrams of raw oysters and 5 types of calcined oyster shells samples, automatic integration was performed using data analysis software to remove peaks with peak areas less than 0.1 and similarity less than 80. The retention time and corresponding retention peak areas of each calcined oyster shell were obtained.

3. Conclusion

3.1. The effect of calcination temperature on the color difference of oyster shells

The color of traditional Chinese medicine is closely related to its medicinal properties, active ingredient content, and efficacy. The traditional empirical identification method is an effective method for evaluating the quality of traditional Chinese medicine, and color is one of the important indicators for quality evaluation [7-8].

As the calcination temperature increases, the L value, a value, and b value of oyster shells all show a trend of first increasing and then decreasing. When the temperature was 200℃, the L value was maximum and the color was brightest, while the color was darkest at 500℃; When the temperature was 0℃ and 100℃, the value of a was negative, indicating that the color of the oyster shell was close to green. The value of a gradually increases from negative to positive, indicating that the color of the oyster shell was gradually changing from green to red; At a temperature of 300℃, the b value was highest and yellow was most prominent. As the calcination temperature increases, E * ab generally shows a trend of first increasing and then decreasing, with a range of 0.43-11.81. The difference in E * ab between raw oysters and calcination temperature was the largest at 500℃. Like E * ab at 100℃, with a difference of 0.43.

Table 1. Color difference analysis of oyster shell samples calcined at six different temperatures

	L	a	b	E*ab
S_0	79.04	-0.46	3.73	79.13
S_1	79.49	-0.57	3.25	79.56
S_2	79.60	2.36	10.74	80.36
S_3	69.10	2.98	11.56	70.12
S_4	69.81	2.49	7.52	70.26
S_5	66.87	2.61	7.28	67.32

According to Fig.1, as the calcination temperature increases, the color of oyster shells changes from white to yellow, and then from yellow to gray. The sample calcined at 200 ℃ was the brightest and appears yellow. The color of the product calcined at 500 ℃ was the darkest, appearing gray.

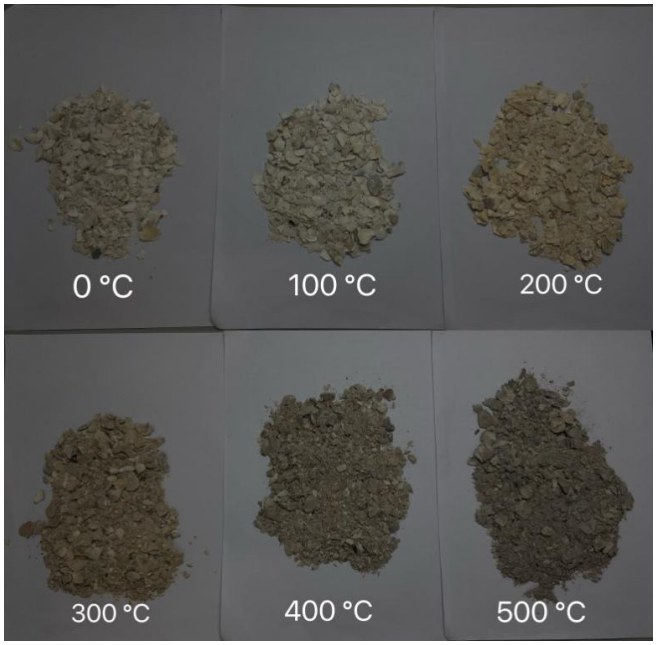

Figure 1. Pictures of oyster shell samples calcined at six different temperatures

3.2. The effect of calcination temperature on the volatile components of oyster shells

From Fig.2, the peak was most concentrated within 15-45 minutes, and the components with the highest volatile odor content in all samples appear at 40 minutes, 31 minutes, 29 minutes, 30 minutes, 28 minutes, and 31 minutes, respectively. The proportion of peak area shows a trend of first increasing and then decreasing, with the highest value being 300 ℃, the highest content being 300℃, and the lowest at 500℃. Compared with raw oysters, except for 500 ℃, all others have increased.

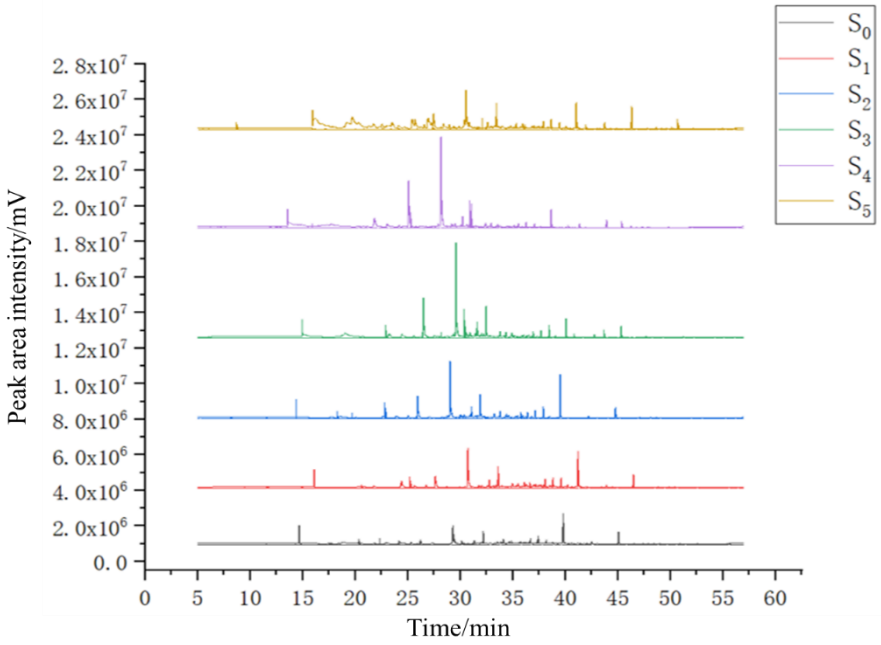

Figure 2. Fingerprint patterns of oyster shell samples calcined at six different temperatures

All samples contain complex and diverse volatile components, consisting of 155 chemical components. Among them, 11 substances were common to all samples, 9 substances were present in 80% to 100% of the samples, 42 substances were present in 20% to 80% of the samples, and the remaining 93 substances were only present in one sample. It contains 18 types of alcohols, 72 types of alkanes, 8 types of aldehydes, 8 types of olefins, 10 types of esters, 24 types of aromatic hydrocarbons, 1 type of quinone, 1 type of sulfide, 1 type of phenol, 6 types of heterocyclic

compounds, and 1 type of aromatic amine. The main volatile substances were alkanes, but they do not play a decisive role in their flavor components.

The relative content of alcohol substances ranks second, among which five substances can emit fragrance, including 2-ethylhexyl alcohol, dodecanol, 1-tetradecanol, undecanol, and 7-methylenechamomile 6-ol. 2-ethylhexanol was only detected at temperatures below 100℃ and above 400 ℃, and can exhibit a sweet taste and a faint floral aroma. Dodecanol was only detected at temperatures of 0℃ and 400℃, and has a weak and persistent oily odor with irritancy. 1-Tetradecanol shows a decreasing trend at temperatures ranging from 100℃ to 300℃. Elemental alcohol only exists at 300℃, with a faint sweet wax odor and a rose like floral fragrance. 7-Methylenechamomile 6-ol can only be detected at 500℃, with weak woody aroma and creamy aroma, and strong persistence.

Esters are formed by the interaction between free fatty acids and alcohols produced by fat oxidation, and have a fruity aroma. Among them, ethyl palmitate was present in each sample and contributes to its characteristic aroma, with weak waxy, fruity, and creamy aromas. Diisobutyl phthalate and dibutyl phthalate provide aromatic odors for multiple samples.

There was a higher content of nonanal in aldehydes, with the highest content at 100℃. It is found that at low threshold concentrations, aldehydes have additive effects, such as hexanal, octanal, and nonanal, which are the main fishy substances in aquatic products. Octal, on the other hand, exists at 100℃ and 400℃, with a waxy aroma and a fruity jasmine scent.

Aromatic and heterocyclic substances exist in high-temperature calcined samples. Naphthalene only exists at 500℃ and has a strong tar flavor. Ethylbenzene and m-xylene exist at 500 ℃ and have an aromatic odor. Quinoline is a heterocyclic substance that can emit a strong odor at room temperature. Phenol was detected in samples above 300 ℃ and showed an upward trend, providing it with a foul and burning odor.

Among the 11 common substances, 6 substances have the highest content in raw oysters, and the content generally shows a gradually decreasing trend with the increase of calcination temperature. They were tetradecane, n-pentadecane, 3-methylpentadecane, undecyl cyclopentane, n-heptadecane, and ethyl palmitate, respectively.

Thirteen volatile components were not detected after calcination, such as 2-ethyl-2-methyl-13decanol, 4,8-dimethyl-13decane, 1-iododecane, n-triacontane, N-octadecane, 3,9-dimethylundecane, 3,3-diethyl-13decane, 2, 4-dimethyldocosane, pentadecene, 2-ethylhexyl pentafluoro octane, triadecyl vinyl carbonate, and hexyltetradecyl sulfite β- Methylnaphthalene. New volatile components have also been generated, and the reason for this result may be that the thermal effect during the calcination process causes some volatile components to degrade or transform into new substances.

4. Discussion

Comparing the calcined oyster shells, the data shows that there were differences in the color, chemical composition, and content of the calcined oyster shells at different temperatures. As the temperature increases, the color gradually changes from bright white to dull black.

A total of 155 chemical substances were produced from raw oysters and five temperature calcinations, including alcohols, alkanes, aldehydes, olefins, esters, aromatic hydrocarbons, quinones, sulfides, phenols, heterocycles, and aromatic amines, with alkanes being the most abundant. There were five types of alcohol substances that can emit a fragrance, presenting a sweet and light floral, oily, and sweet wax scent. Esters have a faint aroma of wax, fruit, and cream. Aldehydes have a waxy aroma and a fruity jasmine scent. Aromatic and heterocyclic substances have a strong tar flavor.

There was a total of 11 components in the six samples. Oyster shells were calcined at 500℃ and have the most abundant volatile components. Heterocyclic and ester compounds can only be detected at high temperatures, which contribute to their flavor components. Compared to raw oysters, the effective substances produced by calcination at 300℃ were better, and as the temperature increases, more odor was generated from combustion.

Based on the dynamic changes in the peak area ratio and color difference values of common substances in the fingerprint spectrum during the calcination process of oyster shells, it was preliminarily determined that the calcination temperature should be controlled at around 300 ℃ to avoid a decrease in effective ingredient content caused by high temperature.

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