Application and Quality Control of Vacuum Freeze Drying in Processing Chinese Herb

Ren Difeng[1], Mao Zhihuai[2], Wang Jianzhong[1]
(1. College of Biology, Beijing Forestry University, Beijing 100083, China;
2. College of Machinery Engineering, China Agricultural University, Beijing 100083, China)

Abstract: The degradation of biochemical active mass especially curative compositions, during the traditional processing of Chinese herb has become an increasingly serious problem while the development and utilization of Chinese herb becomes more comprehensive. Based on the introduction to the principle and the technical points of vacuum freeze drying in Chinese herb processing, the degradation in the drying process of Chinese herb was analyzed through the measurement of catolpol content in *Rehmannia* by means of High Performance Liquid Chromatography. The reaction order, rate constant and the coefficient of the prospective quality control model were determined and verified by experiment. It is indicated that the method of vacuum freeze drying can effectively prevent the degradation during the traditional drying process of Chinese herb, and the quality control model developed in this paper can reflect the effects of moisture content, drying time and temperature on the degradation of curative compositions.

Key words: vacuum freeze drying; Chinese herb; quality control model
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1 Introduction

Abounding in China, Chinese herb is an important kind of medicine to prevent and cure sickness. In recent years, as the causes of diseases vary more complicatedly and the "returning to nature" tide prevails gradually, scholars from many countries have paid their attentions to the research and development of traditional Chinese medicines more seriously than ever. Chinese herb is proved to have more benefits and less side-effects than synthesized medicine in clinic application, such as extracts from *Ginkyo bilobo L.* seeds and leaves for curing amnesia, *Valerian* for curing insomnia, *Urtica* for headache and arthritis, and *Sonchus oleracaus* for tumor[1, 2], etc. However, the degradation of cure and taste properties, loss of biochemical active mass especially curative composition during the traditional drying process of Chinese herb have become more serious while the development of Chinese herb becomes more comprehensive. How to combine traditional herb advantages and advanced technologies, and how to resolve the problems during the processing of Chinese herb in which drying is the most important and weakest procedure, are the foci that badly need our immediate and thorough researches.

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Biography: Ren Difeng, Ph. D., majored in the quality control during the storing and processing of Chinese herb. College of Biology, Beijing Forestry University, P O Box 112, No. 35, Qinghuadonglu Road, Beijing, P. R. China 100083. Email: rendifeng@263.net

2 Advantages of Vacuum Freeze Drying

Drying technology and equipment are key points for the product quality control. Modern drying technologies, in which vacuum freeze drying is especially popular for its unique characteristics and benefits, have been applied in the processing of some valuable herbs including *Rehmannia glutinosa*, *Gastrodia elata Blame*, *Panax Ginseng*, *Cordyceps sinensis*, *and Ganoderma Lucidum*, according to reports[3]. In the vacuum freeze drying process, ice in pre-frozen herbs is directly sublimed to vapor without thawing. The heat is provided for Chinese herb and the vapor is expelled out continuously until the drying product of Chinese herb is obtained finally. The temperature and the drying rate of the material depended on the vacuum in the drying chamber and the heat provided for Chinese herb during the process.

Main advantages of vacuum freeze drying include:

1) To complete freezing of inner moisture in the herb and convert the ice directly into gas, the temperature and pressure should be controlled below the triple point (0.01℃, 610.5 Pa), and vacuum freeze drying has to work at low-temperature and rare-gas condition during its whole process, which avoids common degradation problems of thermo-sensible composition being deteriorated and oxidizable composition being oxidized. In addition, the active mass especially the curative composition in the herb can be preserved easily, the volatility of the fragrant mass is low, and the property and taste of the product

are kept well.

2) Preliminary freeze treatment before vacuum freeze drying helps build steady solid structure for the herb. After the moisture is vaporized, the solid structure keeps unchanged, so the shrinkage of the product is much less than that of the product using other drying technology[4].

3) The moisture in the herb exists as ice crystal state in the solid structure after pretreatment, with the solved inorganic salt in the moisture distributed evenly in the structure. As the moisture being sublimed, the inorganic salt is separated out at its original location, which can avoid the problems of the inorganic salt being separated out on the surface due to the transition of the moisture from the inner to the surface and prevent the surface from being hardened.

4) The herb product of vacuum freeze drying, which does not need to add any pigment and additive, is safe and healthy, because with enzymes being inactivated and the chemical reaction being decreased due to low temperature, the fading and browning phenomenon caused by pigment decomposing and the reaction of enzyme or amino acid will not take place.

5) The product is thoroughly dehydrated, light, and easy to store and transport for long time and distance. Its safety life can be up to 3 to 5 years using vacuum package under normal atmospheric temperature[5].

3 Vacuum Freeze Drying Process of Chinese Herb

Vacuum freeze drying of Chinese herb includes pretreatment, freeze drying (freezing, sublimation drying, resolution drying), packaging and storage processes.

In the pretreatment process, the herb is cleaned, syncopated, blanched, sulfured and piled for sweating successively to improve the purity, appearance and drying rate of the product. Freeze drying includes three phases freezing, sublimation drying and resolution drying. In the freezing phase, the herb is frozen below the eutectic point (measurable using Differential Scanning Calorimetry or Differential Thermal Analysis method) to convert the moisture into ice. The generation time of the biggest ice crystal decides the form and number of all the ice crystals. The shorter the time, the more the crystals and the less noticeable the phenomenon of the moisture redistributing, so that the decomposition of the tissue and cells will be prevented, which guarantees the product quality and strengthens the later drying effects. Generally, the end time of freezing uses the temperature below eutectic point 5 to 10 Kelvin Centigrade as reference value.

After frozen, the herb is sent to the drying chamber and the sublimation drying begins in certain vacuum and heat condition. When the ice crystals disappear gradually, the micro-porous structure is formed accordingly. If the temperature reaches or exceeds the critical point, the solid base can not maintain the rigidity and will collapse, then the channels through which the vapor passes will be blocked out, the vapor pressure in the channels will rise, and the ice crystals will be thawed, which will finally cause the deterioration and the product quality degradation. To prevent the problems mentioned above, the heat provided for the herb should be equal to what is needed for sublimation. When the ice disappears entirely, the sublimation drying phase will end.

The residual moisture in the resolution drying phase, which is distributed in the structure as vitreous body and bound water state, is evaporated gradually when the temperature rises high enough. To prevent thermo-sensible and curative composition being degraded, the drying process should be finished by stopping heating and breaking vacuum before the temperature rises to the metamorphic temperature point. The equilibrium moisture content is usually used as the end mark. It can be measured by the methods of material heating, temperature difference and pressure equilibrium.

During the enzymatic and biochemical reactions in the drying process, there are some unfavorable changes, including color loss, flavor loss, and degradation of curative and thermo-sensible composition mentioned above. Generally, the quality change of the herb can be shown as the following equation[6,7]

$$-\frac{dQ}{dt} = K_D(T, X)Q^n \tag{1}$$

where Q is biochemical active mass content, %; t is drying time, h; K_D is rate constant, h^{-1}; T is absolute temperature of herb materials, K; X is moisture content of dry base, % (d. b.); n is order of the reaction.

The order of the reaction n can be determined by the experimental values in the condition of constant temperature and moisture content. If it is linear relationship between Q and t, the reaction is called zero order reaction ($n = 0$). If it is linear relationship between $\ln Q$ and t, the reaction is called one order reaction ($n = 1$).

4 Determination of Parameters for the Quality Control Model of a Sample

In the experiment, fresh *Rehmannia* (Bought from Chinese Academy of Medicine Science) was cut into small cubes and put in a tube with plug, then immersed in water bath at 343 K. The content of catolpol, which is the curative composition in *Rehmannia*, was measured by the method of High Performance Liquid Chromatography at different time[8,9]. The results were showed as Fig. 1.

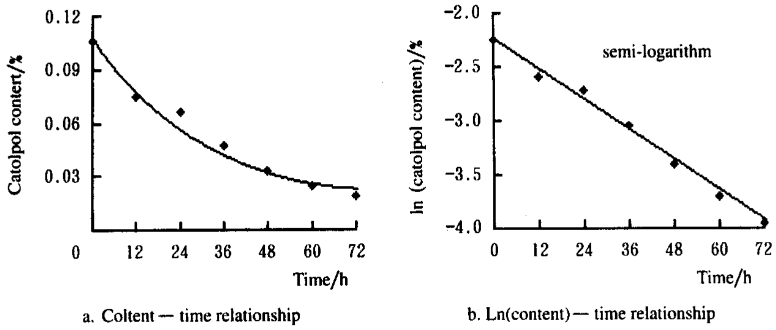

Fig. 1 Changes of catolpol content (343 K water bath)

From above, the change of the catolpol content is complied with one order reaction. The relationship between Q and t can be shown as:

$$Q = Q_0 \exp(-K_D t) \tag{2}$$

where Q_0 is the original catolpol content, %.

The reaction rate constant K_D indicates the degradation extent, and its relationship with the temperature T and moisture content X is complied with the Arrhenius equation in chemical kinetics[7]

$$K_D = K_0 \exp(-\frac{E_D}{RT}) \tag{3}$$

where K_0 is frequency factor, h^{-1}; E_D is activation energy (minimum energy for degradation), kJ/mol; R is ideal gas constant, 8.314×10^{-3} kJ/(mol·K).

As illustrated in this equation, once the temperature T rises, the rate constant K_D rises as well, and the unfavorable reactions will be accelerated, which indicates that vacuum freeze drying can effectively prevent curative and thermo-sensible composition from decomposing for because it is carried out in low temperature condition.

E_D is generally shown as the function of moisture content[10]

$$E_D = a_1 + a_2X \tag{4}$$

According to formula (2), (3) and (4), the model (1) can be shown as

$$Q = Q_0 \exp[-K_0 \exp(-\frac{a_1 + a_2X}{RT}t)] \tag{5}$$

Logarithmically, it can be changed as:

$$\ln(\ln Q_0 - \ln Q) = \ln K_0 - \frac{a_1}{R}\cdot\frac{1}{T} - \frac{a_2}{R}\cdot\frac{X}{T} + \ln t \tag{6}$$

Given $\ln(\ln Q_0 - \ln Q) - \ln t = Y$, $A = \ln K_0$, $B = a_1$, $-1/RT = x_1$, $C = a_2$, $-X/RT = x_2$

Then

$$y = A + Bx_1 + Cx_2 + \ln t \tag{7}$$

Q, X, T and t were obtained by orthogonal experiment in various vacuum freeze drying conditions. The experiment was arranged based on an $L_{25}(5^6)$ orthogonal table with 5 factors including X, T, t and two other relevant parameters, temperature of the heating plate and pressure of the drying chamber, which have direct influences on the drying rate, as the following (Table 1).

Table 1 Levels of the factors

	Temperature of *Rehmannia* T/K	Moisture content X/% (d. b.)	Temperature of the heating plate /K	Pressure in the drying chamber /Pa	Drying time t/h
1	263.5	492.3	273	10	4
2	278.2	386.5	298	15	8
3	293.4	294.1	303	30	12
4	308.1	187.2	328	40	16
5	323.5	57.4	333	50	20

Simulated by the method of 2-Stage Least Square, the coefficient of K_0, a_1 and a_2 in the model can be determined as the following.

Table 2 K_0, a_1 and a_2 values for *Rehmannia* Catolpol

K_0/h	a_1/kJ·mol^{-1}	a_2/kJ·mol^{-1}
9.5906	20.8408	-0.3310

In the purpose of verification, different experiment values were obtained to compare with the model. The results were shown in Fig. 2 (Temperature of *Rehmannia*: 293 K, moisture content: 490.2%

(d. b.), temperature of the heating plate: 333 K, pressure in the drying chamber: 15 Pa).

The experimental values are distributed on both sides of the simulated curve evenly (the standard deviation is 4. 23%), which indicates the performance of the model is good enough to forecast the degradation tendency. As shown in Fig. 2, the decreasing rate of catolpol content is very slow, which numerically indicates low temperature can slow down the degradation.

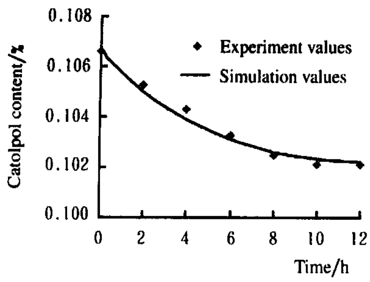

Fig. 2 Comparison between experiment values and simulation values

5 Conclusions

1) Vacuum freeze drying in the drying process of Chinese herb has high benefits for its features to prevent the degradation, to keep the drying quality of the product, and to decrease the loss of curative composition.

2) Curative compositions are degraded exponentially as the drying goes on, and low temperature will accelerate the degradation rate of curative compositions of Chinese herb.

3) The performance of the degradation kinetics model established in the paper is verified good enough to forecast the degradation of curative compositions in Chinese herb during the drying process

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真空冷冻干燥在中药材加工中的应用及质量控制

任迪峰[1], 毛志怀[2], 王建中[1]

(1. 北京林业大学生物学院, 北京 100083; 2. 中国农业大学工学院, 北京 100083)

摘 要: 中草药传统干燥加工过程中所造成的生物活性物质, 特别是药用有效成分损失等问题, 已引起国内外的普遍关注和担忧, 真空冷冻干燥技术以其独有的特点和优势正逐渐成为贵重中草药干燥的首选。文中介绍了中草药真空冷冻干燥的原理和干燥过程中各阶段的工艺流程, 并采用高效液相色谱法, 以药材地黄的有效成分梓醇为检测指标, 考察其在干燥过程中的化学动力学质量降解过程。通过试验确定了反应阶数、速度常数及模型参数, 得出了控制其质量降解的预测模型, 并对预测模型进行了验证。分析结果表明, 所建立的质量降解模型能较好地反映地黄干燥质量随干燥时间、含水率及温度的变化过程, 可用来进行中草药真空冷冻干燥质量降解的模拟。真空冷冻技术应用于中草药干燥能有效地保持中草药药用有效成分, 避免传统干燥方法所造成的有效成分降低等缺陷。

关键词: 真空冷冻干燥; 中草药; 质量控制模型