RELEASE KINETICS OF CARDAMOM OIL FROM MICROCAPSULES PREPARED BY SPRAY AND FREEZE DRYING

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ABSTRACT

The stability of encapsulated cardamom oil, which was prepared by spray and freeze drying, was studied in view of the release characteristics. HiCap 100 was used as the wall material. The powders were stored under the conditions of 45, 60 and 75% relative humidity at 25 and 50 °C. The rate of release of cardamom oil was analyzed using Avrami's equation. The results showed that spray drying was a better method to encapsulate 1,8-cineole as an indicator for the release of cardamom oil, than freeze drying. In constant temperature, the release of 1,8-cineole increased with increasing relative humidity. However, when comparing the different temperature, the release of 1,8-cineole at 50 °C was higher than that observed at and 25 °C.

Keywords: cardamom oil, HiCap100, release, Relative humidity.

1. INTRODUCTION

Flavor plays an important role in consumer satisfaction and influences further consumption of foods. Flavor stability in different foods has been of increasing interest because of its relationship with the quality and acceptability of foods, but it is difficult to control. Manufacturing and storage processes, packaging materials and ingredients in foods often cause modifications in overall flavor by reducing aroma compound intensity or producing off-flavor components (Lubbers, Landy and Voilley 1998). To limit aroma degradation or loss during processing and storage, it is beneficial to encapsulate volatile ingredients prior to use in foods. The release characteristics of encapsulated flavors from the powder are quite important for estimating the storage period, as well as the controlled release applications in food (Reineccius 1995; Whorton and Reineccius 1995). The advantages of controlled release are: the active ingredients are released at controlled rates over prolonged periods of time; loss of ingredients during processing and cooking can be avoided or reduced; reactive or incompatible components can be separated (Dziezak 1988; Brannon-Peppas 1993). Soottitantawat, Bigeard, Yoshii, Furuta, Ohkawara and Linko (2004) investigated the release characteristics and oxidation stability of encapsulated d-limonene, which gum arabic, soybean water-soluble polysaccharide, or modified starch, blended with maltodextrin were used as the wall materials. The powders were stored under the conditions of 23-96% relative humidity at 50 °C. They have reported the release rate and the oxidation rate increased with increasing water activity, but around the glass transition temperature, the rates decreased sharply to increase again at a further increase of water activity. However, in the same manner for the shelf life of encapsulated flavor. Pena et al. (2009) have recently reported that Vanillin release from capsules was encountered to increase when increasing the stirring rate or when increasing the temperature of the release medium. Cardamom oil has a highly chemically reactive volatile compounds and unstable in the presence of air, moisture and high temperature, which has been used as a flavor. This major compounds are 1,8-cineole, a-terpinyl acetate and limonine comprising two-third of the total volatiles (Prabhakaran Nair 2006). Krishnan, Bhosale, and Singhal (2005) used binary and ternary blends of gum arabic, maltodextrin, and modified starch as wall materials. They showed that the presence of gum Arabic in blend increased the protective effect of wall on core material and proposed a simple mathematical model for estimating the flavor retention. Controlled release of flavors from capsule matrices seemed to be a useful application.

In this study the encapsulation of emulsified cardamom oil by spray and freeze drying was carried out with modified starch such as HiCap 100 as wall material. The release kinetics of encapsulated powders was investigated using different method of drying and storage conditions (relative humidity and temperature).

2. MATERIALS AND METHODS

2.1. Materials

Cardamom oil and Tween 80 (GA) were purchased from Sigma-Aldrich Co., Ltd. (Germany). Modified starch (HiCap 100) were obtained from National starch (UK). The HiCap 100 was derived from waxy maize base, were modified with *n*-octenyl succinic anhydride (OSA) for use in the flavor encapsulation process. Other organic chemicals used were of analytical grade. Deionized water was used for the preparation of all solutions.

2.2. Preparation of spray and freeze dried powder

Wall material of HiCap 100 was added into deionized water to obtain 30% w/w mixture and allowed to hydrate overnight. After that, cardamom oil was added to solution at a mass ratio of 0.05 to wall material. The mixture was homogenized by using a rotor/stator type homogenizer (Ultra-Turrax T25, IKA, Germany) at rotational speed of 20,000 rpm for 1 min, followed by use of a 20 kHz ultrasonic processor (Vibracel 750 W, Sonics, USA) programmed to continuously insonify samples for 5 minutes at its maximum output power. The cardamom oil emulsion was fed through Büchi 190 Mini Spray Dryer (Büchi Labortechnik AG, Flawil, Switzerland), equipped with a centrifugal atomizer. The operating conditions of the spray dryer were air inlet temperature of 180 ± 10 °C, air outlet temperature of 90 ± 10 °C, feed rate of 10 ml/min, and air flow rate of 110 kg/h. For freeze drying of emulsions, they were introduced into large Petri dishes and frozen at -25 ºC for 24 h followed by drying in a freeze dryer (Chrisa, Germany) under reduced pressure. The freeze dried mass was pulverized into a fine powder by using a pestle and mortar. Finished powder was stored in a hermetically sealed bottle at a desiccator of constant temperature and humidity to evaluate the release rate of the flavor encapsulated in powder.

2.3. The stability of encapsulated cardamom oil

Approximately one tenth of a gram of the encapsulated powder was weighed and spread in a thin layer glass plate, and placed in a desiccator. The relative humidity (RH) inside the desiccator was constant of 45, 60 and 75 RH at 25 and 50 °C. Constant RH was created using saturated salt solutions of magnesium nitrate for 45% RH, strontium chloride for 60% RH, and sodium chloride for 75% (Rockland 1960). The desiccator was sealed and held in an air bath to keep the temperature as above to reach equilibrium. Sample plates were placed in a desiccator to study the release and oxidation kinetics for 25 days. At fixed time intervals, the bottles were removed from the desiccator to residual amount of 1, 8-cineole in the powder was measured by the solvent extraction method described below. The retention of 1, 8-cineole in the releasing experiment was expressed as the ratio to the initial one. Avrami's equation, also called Weibull distribution function, which was successfully applied to the release time-courses of the encapsulated flavors (Soottitantawat et al., 2004; Yoshii et al., 2001) was also employed in this work.

2.4. Extraction of cardamom oil from the Powder

0.1 gram of powder was dispersed in 4 ml of water in a glass bottle, and then 2 ml of hexane was added, followed by forceful mixing with a vortex mixer for 1 min. To extract encapsulated cardamom oil into the organic solvent, the mixture was heated in a heating block with intermittent shaking at 45 °C for 20 min. Then, after cooling down, the extracted mixture was then centrifuged at 4000 rev/min for 20 min to separate the organic phase from water. The organic phase solution left from above was dispersed in hexane; volume made to 10 ml in a standard volumetric flask and used to estimate 1,8-cineole by taking absorbance at 270 (Krishnan et al. 2005). This wavelength was found to correspond to the maximum absorbance of 1,8-cineole over the spectrum of wavelengths from 200 to 600 nm. A standard curve was obtained by measuring absorbance of 1, 8-cineole mixed in hexane at various concentrations (w/w). A blank sample of hexane was used in the spectrophotometer to prevent the effect of absorbance by hexane. All of the samples were analyzed in duplicate and the data were presented as an average.

2.5. Statistical analysis

All experiments were carried out based on fully factorial design and the results represent the mean of at least two replicates. General Linear Model of MINITAB (Version 14, 2004) was used for performing analysis of variance (ANOVA) to determine the difference between treatments at the significance level of $P<0.05$. Duncan's multiple range test was employed to investigate the significant difference between treatments means at the probability levels of $P< 0.05$ and $P< 0.01$. The graphs were drawn by Microsoft Excel 2003.

3. RESULTS AND DISCUSSION

3.1. Retention of flavours during spray and freeze drying

The retention of 1,8-cineole was affected by the method of the drying. The results showed that higher final retention of 1,8-cineole could be achieved by spray drying, indicating that this spray drying was a better method to encapsulate 1,8-cineole than freeze drying. Retention of 1,8-cineole during spray and freeze drying were 0.95 and 0.86, respectively. Rosenberg, Kopelman and Talmon (1990) observed similar results at a higher load of ethyl butyrate. They observed at spray-dried powder, an early crust formation on the surface of the droplet resulted in entrapping much of the flavor inside the droplet.

3.2. Influence of relative humidity on the release of 1,8-cineole from the powder

The release time-courses of 1,8-cineole from the spray and freeze-dried powder were measured at 25 and 50 °C and at 45, 60, and 75% relative humidity (RH). The effects of RH on the release of 1,8-cineole during storage are shown in Figures 1 and 2. In these Figures, the relative humidity greatly affected the release rate of 1,8-cineole. The dependence, however, was not simple. In constant temperature, the release of 1,8-cineole increased with increasing RH. However, when comparing the different temperature, the release of 1,8-cineole at 50 °C was higher than that observed at and 25 °C. These results suggested that the release of 1,8-cineole was closely related at least to the water activity of the powder, which is in agreement with many earlier

observations. The loss of 1,8-cineole during storage may be caused by two mechanisms: diffusion of 1,8-cineole through the matrixes of the wall material and the oxidation of 1,8-cineole. However, as will be mentioned in the following section, the loss by oxidation was at most 5-6% of the initial 1,8-cineole content. Therefore, the release of 1,8-cineole may result mainly from diffusion as suggested by Whorton (1995). However, when comparing the two methods of drying, the release rate was observed to be slower for spray drying in this study.

3.3. Analysis of the release rate by avrami's equation

To evaluate the release rate constant of 1,8-cineole in the powder, Avrami's equation (eq 1) was applied to the release time-courses of the encapsulated 1,8-cineole as reported by yoshii et. al (2001) and soottitantawat et. al (2003),

$$R = \exp[-(kt)^n] \quad (1)$$

where R is the retention of 1,8-cineole, t is the storage time, k is the release rate constant, and n is a parameter representing the release mechanism.

The release time-courses could be correlated well with Avrami's equation, as shown by the solid line in Figures 3 and 4. Eq (1) is also called the Weibull distribution function, which is successfully applied to describe the shelflife failure (Gacular and Kubala 1975). As can be seen from Figures 3 and 4 the relative humidity had a pronounced effect on the release of 1,8-cineole, which was greatly accelerated by an increase in relative humidity. This suggested that the release of ethyl butyrate was closely related to the presence and concentration of water molecules surrounding the powder. Whorton and Reineccius 1995 have reported similar results for several esters. Also, for encapsulated powder, the release of 1,8-cineole markedly influenced by drying method. There was appreciable increase in the release rate when the freeze drying was used. On the other hand, freeze-dried powder was more lost at relative humidity in storage time than spray-dried powder. Spray drying was a better-controlled release agent than freeze drying.

Sun and Davidson (1998) successfully applied Avrami's Eq. (1) to analyze the time-dependent protein inactivation in amorphous sucrose and trehalose matrices. As is easily recognized, n=1 represents the first order reaction. In case of solid-gas reaction, if the molecular diffusion of the reactant and product compounds through the ash layer is rate limiting, n=0.54. Taking double logarithm of both sides, Eq. (1) yields Eq. (2):

$$\ln(-\ln R) = n\ln k + n\ln t \quad (2)$$

From Eq. (2). one can get the parameter n as a slope by plotting $\ln(-\ln R)$ vs. $\ln t$, and the release rate constant k from the interception at $\ln t=0$.

The release time-course of 1,8-cineole at different conditions were analyzed by plotting $\ln(-\ln R)$ against $\ln t$. Figures 4 and 5 shows an example of the analysis by Eq. (2). As can be seen, the release of encapsulated powder prepared by spray and freeze drying fitted well to Eq. (2). As compared with the release rate at RH of 45%, the higher rate was observed at around RH of 75%.

This implies that the slower release in the low water activity region is most likely due to the lower mobility of 1,8-cineole molecules in the glassy state of the capsule matrixes (Whorton 1995). When RH increased up to a value of around 75%, the powders began to be rehydrated. At this stage, it may be assumed that the effective surface area decrease resulted in a decrease of 1,8-cineole evaporation from the surface of the powder particles. Most particles were detected to be clumped and adhered together into a paste like mass, which explains the rubbery form of the capsule matrixes. A similar speculation was also proposed by Whorton and Reineccius 1995.

4. CONCLUSION

The retention of 1,8-cineole was influenced by the the type of drying method. spray drying was found to be a superior method over freeze drying to retain 1,8-cineole during storage. The release time-course of 1,8-cineole fitted well to the Avrami's equation. Inspecting the results obtained for the effect of temperature and moisture content on the release of 1,8 cineol indicated that at water activities and all temperatures under question, the spray-dried microcapsules showed slower release rates than the freeze-dried ones.

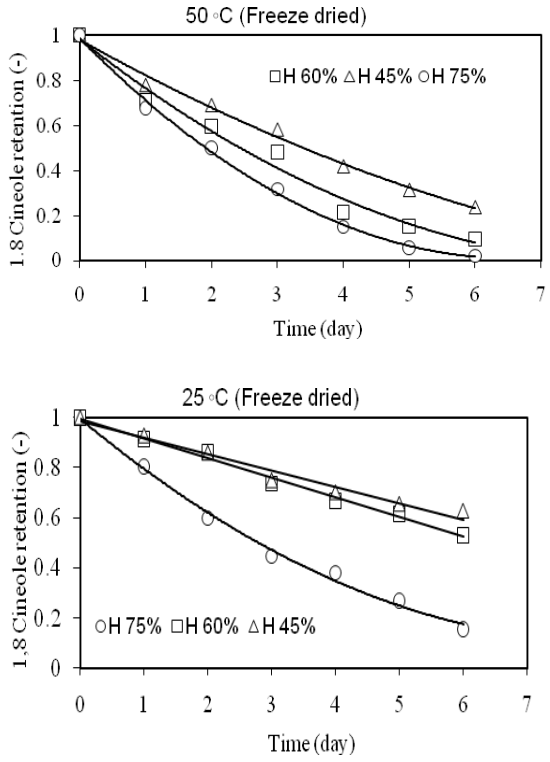

Figure 2: Effects of relative humidity and storage temprature on the release of 1,8-cineole from freeze-dried powder.

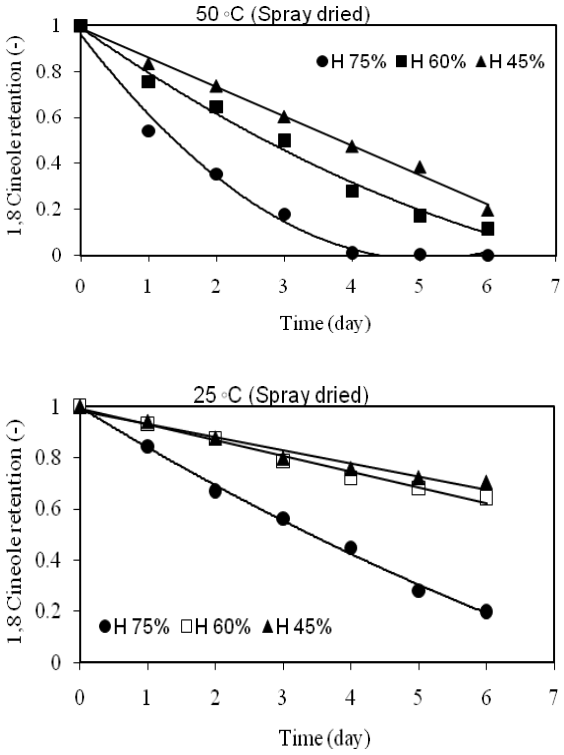

Figure 2: Effects of relative humidity and storage temprature on the release of 1,8-cineole from spray-dried powder.

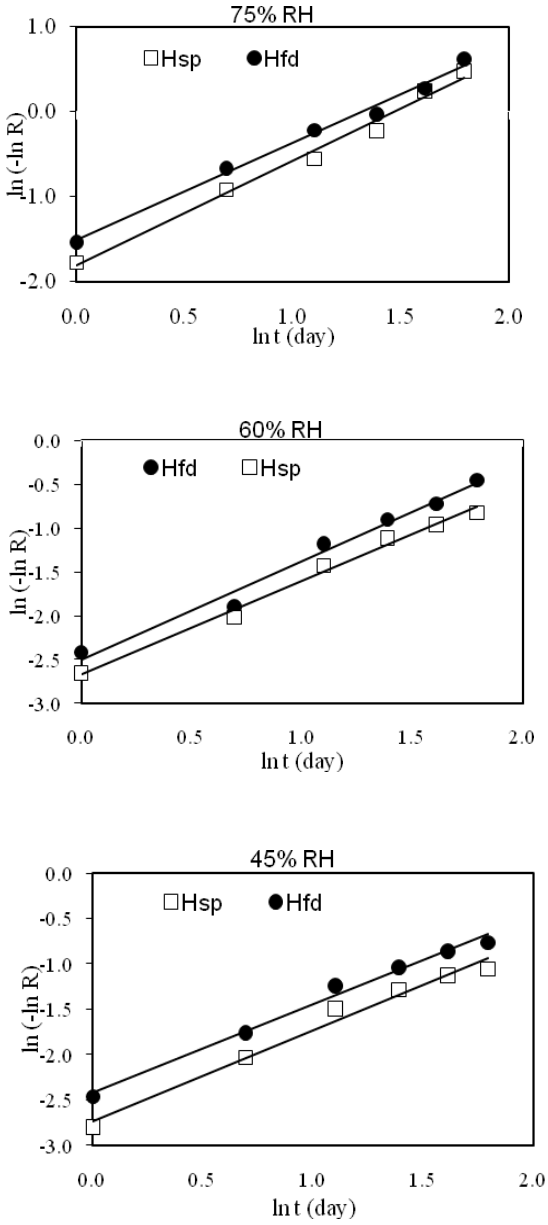

Figure 3: Correlation of release time-course of 1,8-cineole by Avrami's equation at 25°C for spray (sp) and freeze-dried (fd) powders.

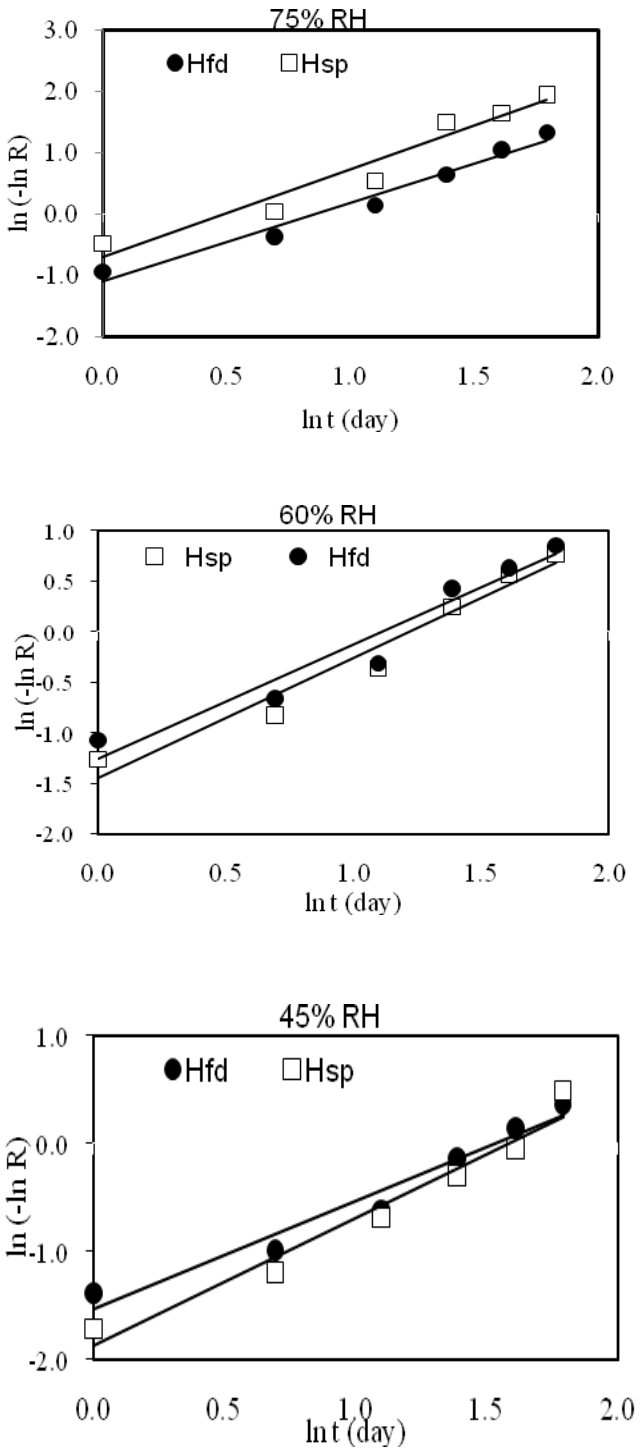

Figure 4: Correlation of release time-course of 1,8-cineole by Avrami's equation at 50°C for spray (sp) and freeze-dried (fd) powders.

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