Global Journal of Science Frontier Research
Chemistry
Volume 12 Issue 4 Version 1.0 Year 2012
Type : Double Blind Peer Reviewed International Research Journal
Publisher: Global Journals Inc. (USA)
Online ISSN: 2249-4626 & Print ISSN: 0975-5896

Directional Crystallization Kinetics of Coconut Oil Under Temperature Gradient

By Jie Peng, Xue Bai, Yunzhu Zhang & Xingpeng Bai
Hainan University, Haikou, China

Abstract - The directional crystallization kinetics of coconut oil was studied under the temperature gradient from 13℃ to 15℃. During the crystallization of coconut oil, the overall crystal growth rate Rg decreased over time, but it increased with the growth of temperature difference. While the change of crystallization yields Y first increased then decreased to constant. And the variation trend of crystallization yield with temperature difference was the same with crystal growth rate. The Avrami equation was basically fit for the analysis of coconut oil's crystallization. Some deviations also existed during the last stage of crystallization. What's more, the crystalline form and the methods of crystal growth both changed with different temperature.

Keywords : *Coconut oil, temperature gradient, Avrami, crystallization kinetics.*

GJSFR-B Classification : *FOR Code: 030502*

Strictly as per the compliance and regulations of :

Directional Crystallization Kinetics of Coconut Oil Under Temperature Gradient

Jie Peng [α] , Xue Bai [σ], Yunzhu Zhang [ρ] & Xingpeng Bai [ω]

Abstract - The directional crystallization kinetics of coconut oil was studied under the temperature gradient from 13℃ to 15℃. During the crystallization of coconut oil, the overall crystal growth rate Rg decreased over time, but it increased with the growth of temperature difference. While the change of crystallization yields Y first increased then decreased to constant. And the variation trend of crystallization yield with temperature difference was the same with crystal growth rate. The Avrami equation was basically fit for the analysis of coconut oil's crystallization. Some deviations also existed during the last stage of crystallization. What's more, the crystalline form and the methods of crystal growth both changed with different temperature.

Keywords : *Coconut oil, temperature gradient, Avrami, crystallization kinetics.*

I. Introduction

Fats have many physical and chemical characteristics, such as the melt point, the crystallization behavior and the crystalline form. These special characteristics played an important role in the food quality control and food processing[1]. For some oil and fat food, such as cakes, chocolates, candies, ice creams, margarines, shortening, cocoa butter; the unique plastic grease can extend their shelf-life, enhance their quality and stability, and provide special mouth-feel[2, 3].In order to improve the characters of oil and fat food, acquire some special products, making some studies about oil fractionation and crystallization is really essential.

Oil fractionation aims at separating solid lipid and liquid oil according to the temperature. Three main methods can be taken: fractional crystallization, liquid-liquid extraction and distillation[4]. Dry fractionation, which belongs to fraction crystallization, is the simplest and the most economic method among oil fractionation.

Different types of triglycerides have different melting points under different temperature, so we can achieve the purpose of solid-liquid separation by cooling[4, 5].

Dry fractionation is a physical modification process, it can avoid the produce of trans fatty acid and decrease vanadium pollution. Low temperature brings the directional suspended crystal separation, which decreased the separating efficiency and purity of the products, mixed the crystal with a large number of low-melting compositions. Dry fractionation contains three main stages: the produce of crystal nucleus, the growth of crystal and the separation and purification of crystal. In order to give an exact description of grease crystallization behavior, some relevant parameters should be determined.

Coconut oil is one of the Laurel acids grease, which contains about 90% saturated fatty acid. It's main compositions are lauric acid(C12:0,45.9%~50.3%) and myristic acid(C14:0,16.8%~19.2%). This fatty acid makes coconut oil much easier to oxidize, then provide energy to the body in a short time. What's more, it can also reduce the risk of atherosclerosis and heart disease, benefit to our health [6].

In order to acquire the solid lipid with the same characters of butter, a series of temperature gradients were built to give a step-by-step separation of coconut oil in this study. The experimental data was simulated by means of molecular diffusion Fick's Law and the Avrami equation. The fundamental crystallization parameters such as the crystal morphology (n), the crystallization rate (k) were obtained and the mathematical model was established. The purpose was to get the improved mathematical model of the crystallization behavior of coconut oil under the temperature gradient, and this model would be used to guide the experimental to get the ideal value of the crystallization parameters. The results will lay the foundation for exploring the effect of the temperature gradient on the nucleation mechanism and molecular orientation aggregation structure.

II. Experimental

a) Materials

Refined, bleached and deodorized coconut oil was used in this work. It was a kind of clear liquids and presented full-bodied coconut taste at room temperature(25℃).

b) Mpparatus

Fig.1 illustrates the apparatus used in this study. A cylindrical container (15cm in the typical radius) was put on the magnetic stirring apparatus (5).The container was double-layered and its temperature was controlled by the heating and temperature controlled system (4). Another temperature controlled cylinder (condenser pipe (6), 7cm in the typical radius) was put into the middle of double-wall beaker. It was refrigerated by the refrigeration and temperature controlling system (7).

Author α ρ ω : *College of Food Science and Engineering, Hainan University,Haikou,570228,P.R. China. E-mail : xinpeng2001@126.com*
Author σ : *College of Horticulture and Landscape Architecture, Hainan University, Haikou 570228, China.*

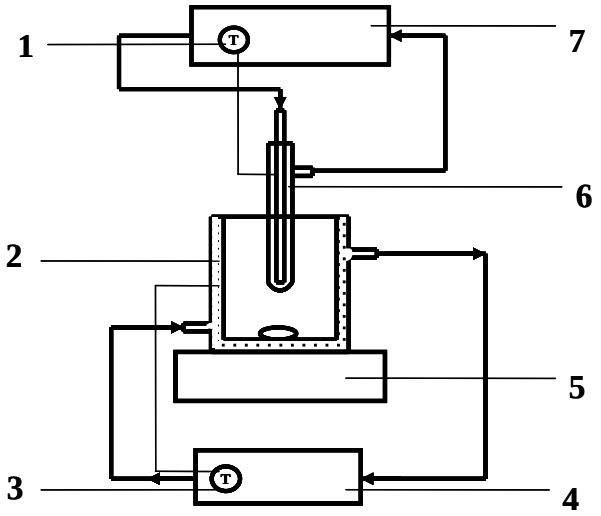


Figure 1 : Schematic of the apparatus used: 1.Temperature controller 2.Container's interlayer 3.Temperature controller 4.Heating and temperaturecontrolling system5.Magnetic stirring apparatus 6.Condenser pipe 7.Refrigeration and temperature controlling systemFig

c) Methods

Two of the above apparatus were used to decrease the error and shorten the repetitive experimental period. The coconut oil (about 100-120g) was conditioned at 60℃ for 10 to 20 min to destroy the crystal structures and subsequently poured into the double-wall breaker, the temperatures of condenser pipe and double-wall breaker were set according to the desired crystallization temperature. When the system was stable, the condenser pipe was dipped into the melt, which was agitated by a magnetic stirrer. The examined process parameters are summarized in Table1. Weight the crystal of condenser every 2 hours until 22hours.

Table 1: Experimental conditions

Groups	Temperature of condenser pipe/℃	Temperature of double-wall breaker/℃	stirring rate	Indoor temperature/℃
1	19			
2	17	32	minimum	25-27
3	15			

All the data we obtained were the mean values of six times' experiments. So the accuracy of the data was much higher. The data were simulated by means of the Avrami equation, with the help of Microsoft Excel Solver, some fundamental crystallization parameters were obtained, and a mathematical model of directional solidification was also established.

i. *Determination of crystal growth rate*

The overall crystal growth rate was calculated via Eq. (1) [6]:

$$Rg=\frac{dMc}{Adt}[gcm^{-2}h^{-1}] \quad (1)$$

Where Rg is the crystal growth rate (assumed as a constant crystal growth rate), Mc is the mass of crystal deposited on the surface of the condenser pipe [g], A is the surface area of the condenser pipe [cm2] ($A=2\pi rL+\pi r^2$) and t is the crystallization time [*h*].

ii. *Yield of crystallization*

The crystallization yield was calculated via the following Eq.(2) [6]:

$$Yield=\frac{M_{solid}}{M_{melt}}\times 100\% \quad (2)$$

Where Msolid is the mass of the solid fraction crystallized on the condenser pipe's surface[g] and Mmelt is the mass of the melt[g].

iii. *Crystallization kinetics*

Avrami equation (Eq.3) was used to simulate the course of crystallization[7]. The half period of the crystallization was measured by Eq.4:

$$Xt=1-\exp(-kt^n) \quad (3)$$

Where Xt is the relative crystallinity, k is the crystallization rate, n is the Avrami index.

$$t_{1/2}=(0.693/k)^{1/n} \quad (4)$$

III. Results and Discussion

a) Analyses of crystal growth rate and crystallization yield

Fig.2 shows the changes of crystal growth rate (Rg) under different temperature. The overall trend was decreasing. The greater the difference in temperature was, the more obvious of the downtrend, and the greater the crystal growth rate was. At the beginning of crystallization (about 2 hours), the crystal growth rate in 15℃ was about 0.0224, while in 19℃ was about 0.0449. 12hours later, the downtrend became mild. Fig.3 shows the change of crystallization yield(Y). Its main trend was first increasing then declining. The value of Y reached the maximum between 10 hours to 15 hours.

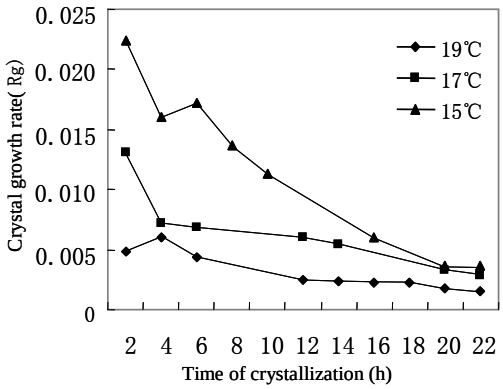
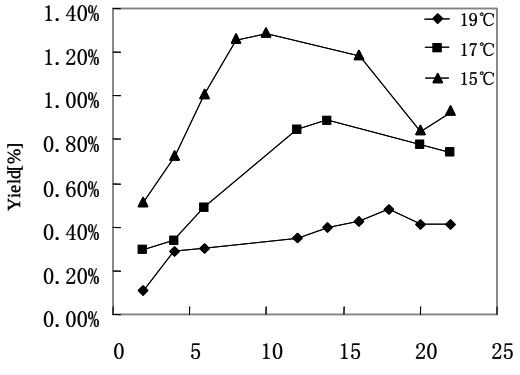


Figure 2 : Curves of coconut oil 's crystal growth rate under different temperatures. The temperatures in the figure stand for the temperatures of the condenser pipe.



Figuer 3 : Curves of coconut oil's crystallization yield under different temperatures. The temperatures in the figure stand for the temperatures of the condenser pipe.

The degree of the saturation in solid fat changed with the temperature. That is to say, per unit of volume of the maximum dissolved solid fats varied with the change of temperature, Stable temperature gradient was built during the experiments, and then the concentration gradient of solid fats formed, because of the molecular diffusion, when the solid fats contacted with the cold wall, crystal formed. The higher the temperature was, the greater the degree of the saturation was and the more crystal we got, so both Rg and Y became bigger. After a long time of crystallization, the coconut oil trended to the saturated state, then Rg declined. When the oil reached the saturated state, some crystal would be dissolved again until it became stable, so at later stage of crystallization, Y dropped to stable.

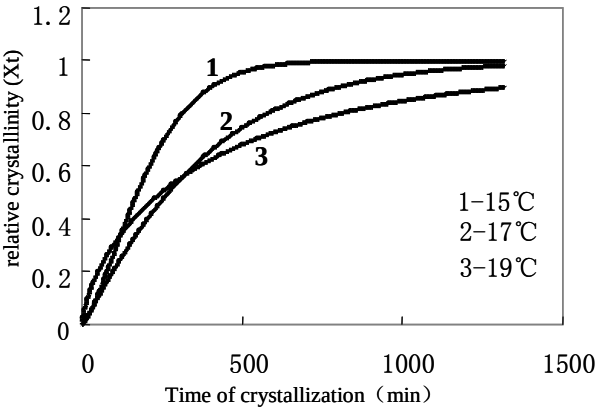


Figure 4 : Fitting curves of crystallization about coconut oil under different temperatures. The temparatures in the figure stand for the temperature of condenser pipe.

b) Analysis of crystallization kinetics

Avrami equation was used to stimulated the data we got.Fig.4 shows the fitting curves of the crystallization. Three curves were similar to S type, that suggested the crystallization were heterogeneous nucleation. At the beginning, the relative crystallinity (Xt) in 19℃ was the biggest, and 15℃ was the smallest; 8 hours later, the condition was just the reverse. All curves' variation trend was similar, slopes of the curves and Rg both increased with the increasing of temperature gradient, which was agree with the change in Fig.2. The greater the temperature gradient was, the shorter time was needed to reach the stable state during the crystallization. The time of 15℃ was about 500min, but the times of 17℃ and 19℃ were much longer than 22hours. Fig.5 can be used to examine the fitness of the Avrami equation. t0 means the initial moments of the crystallization, it's equal to 0 in this experiment. The curves were straight line, so the Avrami equation was basically fit for the crystallization of coconut oil. And the curves also told us that the crystallization rate in 19℃ was the max, but it was similar in 15℃ and in 17℃, which could be examined by comparing the values of k in Tab.2.

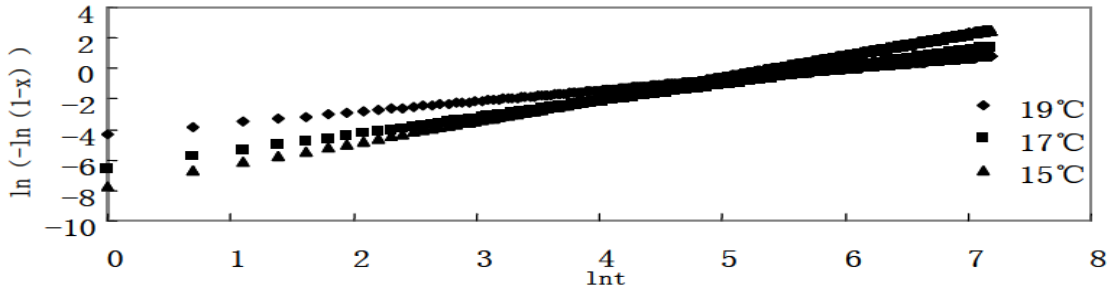


Figure 5 : The relationship between ln（-ln（1-x）） and ln（t-t0）

Table 2 : The parameters of Avramiequation during the crystallization of coconut oil

Temperature of condenser pipe（T）	Crystal morphology (n)	Crystallization rate (k)	Half period of crystallization($t_{1/2}$)
292	0.714	0.252	4.130
290	1.105	0.131	4.509
288	1.425	0.152	2.901

Table 3 : The relationship between Avramiparameters and crystallization behavior[10]

The mechanism of crystal growth \ Nucleation method	Homogeneous nucleation	Heterogeneous nucleation
One-dimensional growth (acicular crystal)	n=1+1=2	n=1+0=1
Two-dimensional growth (flat crystal)	n=2+1=3	n=2+0=2
Three-dimensional growth (spherical crystal)	n=3+1=4	n=3+0=3

Generally, the value of n varied with the temperature. It is the function of the number and the size of crystal, which reflects the mechanism of nucleation. Relevant data shows the value of n is generally integer, between 1 to 4.But in this experiment, the data we got were non-integer and all less than 2. There were following reasons suggested: (1) The production of fractal geometry during the crystallization; (2) Different crystallization mechanism exited at the same time; (3) The existence of secondary crystallization [9].

The non-integer value also showed the existence of heterogeneous nucleation, it also predicted the fitness of the Avrami equation was not perfect.. Especially in the later stage of crystallization, some deviations existed. According to the data in Tab.3, we could find that in 17℃ and 15℃, the mechanism of crystal growth was heterogeneous nucleation and one-dimensional growth, the crystal was acicular crystal. But in 19℃, the mechanism were not sure, and the crystal morphology was also different. The half period of crystallization is some contribution of both k and n.. In 19℃ and 17℃, the value of t1/2 was much higher than in 15℃, that is, at this temperature (15℃), the time to produce 50% crystal was the shortest.

IV. Acknowledgements

This research work was supported by a grant from National Natural Science Foundation of the Republic of China (Nos.31160325).

References Références Referencias

1. Xie Bijun, Food chemistry (the third edition),Beijing: Science Press, (2011)122.
2. Aini, I. N .and Miskandar, M. S.(2007).Utilization of palm oil and palm products in shortenings and margarines. European Journal of lipid Science and Technology,109(4),422-432.
3. Goh, E. M.(2002).Applications and uses of palm and palm kernel oils in specialty products. Malaysian Oil Science and Technology,11(1),46-50.
4. Liu Haijun, Qiu Aiyong. Dry fractionation of oils and

fats and application. China Oils and Fats. 28(10) (2003) 14-17.
5. Hua Pinpin, Dry fractionation of fat or oil with the addiction of seed crystals. Journal of Wuxi University of Light Industry, 6(2) (1987) 1-9.
6. Chaleepa, K., Szepes, A. and Ulrich, J*. Dry fractionation of coconut oil by melt crystallization.Chemical Engineering Resarch and Design,2010,88:1217-1222.
7. Mo Zhishen, Zhang Hongfang. Static polymer structure and X ray diffraction. Beijing: Science Press,(2003) 115.
8. Saberi, A.H.,Lai, O.M, Toro-Vazquez, J.F. Crystallization kinetics of palm oil in blends with palm-based diacylglycerol[J].Food Research International.2010:1-11.
9. Bian Jie, Ye Sheng-Rong, Feng Lin-Xian. Investigation on Avrami Equation of PET and PBT in Crystallization. Chemical Journal of Chinese Universities. 21(9) (2000) 1481-1484.
10. Yu Xiang, Zhu Chengshen, He Suqin, Liu Wentao. Avrami Kinetics Study of the Isothermal Crystallization of Poly(ε-caprolactone). Materials Review, 24(10) (2010) 108-112.