CHEMICAL ENGINEERING TRANSACTIONS

VOL. 63, 2018

A publication of AIDIC

The Italian Association
of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jeng Shiun Lim, Wai Shin Ho, Jiří J. Klemeš

ISBN 978-88-95608-61-7; **ISSN** 2283-9216

DOI: 10.3303/CET1863068

Process Optimisation of Effective Partition Constant in Coconut Water via Progressive Freeze Concentration

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Concentration technique via progressive freeze concentration was applied to increase the concentration of coconut water for commercialisation. The process will eliminate portion of water from coconut water and retain pure nutritional compound with high sugar content. To obtain the optimum condition, which is the objective of this study, optimisation process was conducted using Response Surface Methodology (RSM) through STATISTICA Software. RSM was utilised to optimise the process parameters for effective partition constant (K) in progressive freeze concentration (PFC) of the coconut water. The effects of circulation flowrate, circulation time, initial solution concentration and coolant temperature on effective partition constant were observed. Results show that the data adequately fit the second-order polynomial model. The linear and quadratic independent variables, circulation flowrate, circulation time, initial concentration and coolant temperature have significant effects as well as interactions on the effective partition constant. It was observed that the optimum process parameters within the experimental range for the best K would be with circulation flowrate of 3,400 mL/min, circulation time of 23 min, initial concentration of 3.4 % Brix and coolant temperature of -7 °C. Under these conditions, the K can be enhanced up to 0.3.

1. Introduction

Coconut water (CW) has become prominent among athletes as natural sports drink because of its electrolytes content, low calorie, high nutrition content with high content of potassium, antioxidants, mineral and sugar content. As consumers come from many countries around the world, the coconut fruit has to be transported to thousands of miles away with only 20 % of the transported fruit is the wanted water and 80 % is the coconut fibers (Jusoh et al., 2014). This makes the transportation, storage and handling costs to be a major part of the sales price. New or improved concentration techniques are required to eliminate portion of the water from the aqueous solution and henceforth ease the handling of CW by reducing its volume and weight. At present, there are three commercial methods for concentrating the fruit juices, namely evaporation concentration, membrane concentration (reverse osmosis) (Couto et al., 2011) and freeze concentration (FC) (Sánchez et al., 2011). Evaporation is considered to be the simplest and widely used methods, but it consumes high energy for evaporators (Ramteke et al., 1993). It is not suitable to be engaged if the fruit juice to be concentrated is heat sensitive due to loss of their volatiles and aromas when heated. Reverse osmosis (RO) gives greater retention of product quality but in most cases, clogging of membrane can easily occur which produces low flux and limited yield due to high osmotic pressure (Cassano et al., 2007). Another concentration technique is freeze concentration (FC), which consists of suspension freeze concentration (SFC) and progressive freeze concentration (PFC). Separation of ice crystals from the concentrated solution is crucial in the SFC. But, because there are lots of ice crystals with limited size in this method, the separation process tends to be more difficult. PFC on the other hand, involves the formation of a single ice crystal that grows layer by layer from the mother solution, making separation from the mother liquor much easier to be handled and at a lower cost. The efficiency of PFC system can be affected by many factors including circulation flowrate, circulation time, initial concentration and coolant temperature. The best condition or level for each of the

Please cite this article as: Mazura Jusoh, Noor Naimah Mohamed, Norshafika Yahya, Rohashimah Musa, Zurina Mohamad, Norzita Ngadi, Roshanida A. Rahman, Anwar Johari, Zaki Yamani Zakaria, 2018, Process optimisation of effective partition constant in coconut water via progressive freeze concentration, Chemical Engineering Transactions, 63, 403-408 DOI:10.3303/CET1863068

process parameters was determined using Response Surface Methodology (RSM). Design of experiment (DOE) is important for multifactor experiments to save time and make it capable of predicting the optimum condition of the combined factors (Keshani et al., 2010). In previous studies, the parameter conditions have been merely optimised by one-variable-at-a-time technique (Humaidah et al., 2017). The results do not reflect actual changes in concentration as the interactions between factors that are present were ignored (Jusoh et al., 2013) and inefficient to detect any interaction amongst the independent variables. To overcome such drawback, the technique of RSM has been chosen as a powerful tool for determining the effect of the factors and their interactions. This is a useful feature in modelling and analysis of the problem, in which the response of interest is influenced by several variables (Abhang and Hameedullah, 2010) and can provide a complete optimal condition to improve a process (Chan et al., 2009). Keshani et al, (2010) optimised the concentration process using RSM for pomelo fruit juice meanwhile Jusoh et al. (2013) used RSM for PFC of wastewater. Optimisation of coconut water concentration via progressive freeze concentration method has not been reported yet. Concentration of coconut water using this particular and newly designed crystalliser has also not been studied. This study aims to investigate the best condition based on the lowest effective partition constant, K, with multifactor condition through RSM.

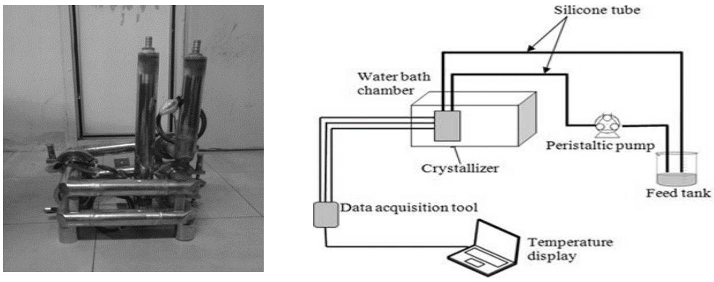
2. Material and Method

2.1 Materials

The raw material used was CW with concentrations ranging from 3 to 5 % Brix, measured using a Brix refractometer (Milwaukee MA871). The CW was taken from young green coconuts obtained from a local plantation in Johor, Malaysia. The coconuts were perforated for the purpose of collecting its water. The water obtained was filtered before being used as raw material. Other materials include distilled water which was used in making ice crystal seeds in the crystalliser and ethylene glycol 50 vol% which was used as coolant after being mixed with 50 % of distilled water.

2.2 Experimental Methods

Procedures for formation of seed ice lining on the surface of the crystalliser was first carried out in each experiment conducted. In this step, distilled water was fed into the system and circulated. When the crystalliser was full, it was then immersed in a refrigerated waterbath at the investigated coolant temperature and circulated within 5 min. The distilled water was flushed out and the ice lined crystalliser was then filled with CW solution, pre-cooled at 2 ºC, to start the PFC. The filled crystalliser was then immersed in the refrigerated water bath. The solution was circulated at the desired circulation flowrate using peristaltic pump and circulation time. At the end of the circulation time, the crystalliser was then taken out from the water bath for the ice layer to be thawed and the concentrate flushed. Then thickness of the ice layer formed was measured at each flange point after being unassembled and a sample of ice produced was taken. Finally, Brix refractometer was used to determine the final sugar concentration in the concentrate and also in the ice. The experiment was repeated with different values of circulation flowrate, circulation time, initial concentration and coolant temperature. The range used for circulation flowrate is from 2,000 to 2,800 mL/min, 10 to 18 min for circulation time, 3.0 to 5.0 % Brix for initial concentration and from -16 to -8 °C for coolant temperature. To select the range of values for the variables which are likely to be important in preparing the CW concentrates experimental, screening process was already done which required fewer runs or test. The equipment and experimental set-up for this system used in this study is shown in Figure 1a and Figure 1b. Figure 1a shows the crystalliser which was made of stainless steel and Figure 1b shows the crystalliser was connected to a peristaltic pump using a pair of silicon tube, which was immersed in a water bath at the desired cooling temperature during experiment.



(a) (b)

Figure 1: (a) Stainless steel crystalliser, (b) Schematic drawing for experimental set-up

2.3 Experimental Design

In this study, four variables which are circulation flowrate, circulation time, coolant temperature, and initial concentration were chosen as the factors that will most likely influence the efficiency of PFC system. The effects of these variables were investigated toward K value in concentrated solution which was chosen as response variables. The low, middle and high range for each process parameter were fixed and coded as (-1), (0) and (+1). The extreme value outside the range (±α) was denoted as (-2) for lower limit of the parameter and (+2) for the upper limit. The selected factors with their limit are given in Table 1.

Table 1: Experimental range and level recorded

Factors	Range and levels				
	-α (-2)	-1	0	+1	+α (+2)
Circulation Flowrate, X_1 (mL/min)	1,600	2,000	2,400	2,800	3,200
Circulation Time, X_2 (min)	6	10	14	18	22
Initial Concentration, X_3 (% Brix)	2.0	3.0	4.0	5.0	6.0
Coolant Temperature, X_4 (°C)	-20	-16	-12	-8	-4

To determine a critical point such as maximum, minimum, or saddle, it is necessary to use the polynomial function which contains quadratic terms. In this study, the full quadratic models of K value was established according to polynomial function as shown in the Eq(1) where β_o represents the intercept coefficient, β_i, β_{ii} and β_{ij} represents the linear terms, quadratic terms and interaction terms, and ε is the residual associated to the experiments.

$$y = \beta_0 + \sum_{i=1}^{k} \beta_i x_i + \sum_{i=1}^{k} \beta_{ii} x^2{}_{ii} + \sum_{1 \le i \le j}^{k} \beta_{ii} x_i x_j + \epsilon \quad (1)$$

3. Result and Discussion

The experimental results of response variables that are correlated with four parameters studied for each run are shown in Table 2.

Table 2: Design of Experiment (DOE) and the response

Exp/Run	CFlowrate (X_1)	CTime (X_2)	Initial Con. (X_3)	CTemp (X_4)	K
1	2,000 (-1)	10 (-1)	3 (-1)	-16 (-1)	0.62
2	2,000 (-1)	10 (-1)	3 (-1)	-8 (+1)	0.59
3	2,000 (-1)	10 (-1)	5 (+1)	-16 (-1)	0.97
4	2,000 (-1)	10 (-1)	5 (+1)	-8 (+1)	0.93
5	2,000 (-1)	18 (+1)	3 (-1)	-16 (-1)	0.84
6	2,000 (-1)	18 (+1)	3 (-1)	-8 (+1)	0.47
7	2,000 (-1)	18 (+1)	5 (+1)	-16 (-1)	0.84
8	2,000 (-1)	18 (+1)	5 (+1)	-8 (+1)	0.94
9	2,800 (+1)	10 (-1)	3 (-1)	-16 (-1)	0.58
10	2,800 (+1)	10 (-1)	3 (-1)	-8 (+1)	0.57
11	2,800 (+1)	10 (-1)	5 (+1)	-16 (-1)	0.77
12	2,800 (+1)	10 (-1)	5 (+1)	-8 (+1)	0.58
13	2,800 (+1)	18 (+1)	3 (-1)	-16 (-1)	0.53
14	2,800 (+1)	18 (+1)	3 (-1)	-8 (+1)	0.36
15	2,800 (+1)	18 (+1)	5 (+1)	-16 (-1)	0.82
16	2,800 (+1)	18 (+1)	5 (+1)	-8 (+1)	0.56
17	1,600 (-2)	14 (0)	4 (0)	-12 (0)	0.69
18	3,200 (+2)	14 (0)	4 (0)	-12 (0)	0.54
19	2,400 (0)	6 (-2)	4 (0)	-12 (0)	0.75
20	2,400 (0)	22 (+2)	4 (0)	-12 (0)	0.60
21	2,400 (0)	14 (0)	2 (-2)	-12 (0)	0.37
22	2,400 (0)	14 (0)	6 (+2)	-12 (0)	0.71
23	2,400 (0)	14 (0)	4 (0)	-20 (-2)	0.75
24	2,400 (0)	14 (0)	4 (0)	-4 (+2)	1.00
25	2,400 (0)	14 (0)	4 (0)	-12 (0)	0.58
26	2,400 (0)	14 (0)	4 (0)	-12 (0)	0.60

The efficiency of cooling system or freeze concentration is best described by effective partition constant, K, that represents the amount of separation of solute in liquid phase or solid phase. The efficiency of the system also portrays higher degree of solute in concentrated than in ice (solid phase). The result was then used to empirically quantify the relationship that exists between the response variables and the process parameters studied through some form of the mathematical model as Eq(2) as followed:

$$Y1 = 1.38394 - 0.00024X_1 - 0.05502X_2 + 0.37080X_3 + 0.14369X_4 + 0.00163X_2^2 - 0.00820X_3^2 + 0.00468X_4^2 - 0.00001X_1X_2 - 0.00007X_1X_3 - 0.00001X_1X_4 + 0.00108X_2X_3 - 0.00164X_2X_4 + 0.00319X_3X_4 \qquad (2)$$

Y1 is predicted value of the effective partition constant, K whereas X_1, X_2, X_3, and X_4 are independent variables or factors with influence on K. The coefficient without the factor is the constant, while coefficient with one factor represents the particular factor or linear coefficient. Coefficient with two factor and second-order are significantly the interaction of two terms and quadratic effect of the factor. The negative and positive signs indicate the signal of parallel and adverse effect relying on the factor. The model was selected based on highest order of polynomials where the models were significant and not aliased (Tan et al., 2008).

3.1 Model Adequacy Check

Model adequacy of RSM is generated by the regression model which affects each variable including the interaction with each other that relies on the K. The response of K is also closely bonded or correlated with four variables applied using multiple regression analysis and second-order model as polynomial function. The regression analysis would determine the relationship between factor and response that was carried out using STATISTICA software, generating the mathematical model as Eq(2). The response K can be expressed as a second order polynomial equation as a function of circulation flowrate (X_1), circulation time (X_2), initial concentration (X_3) and coolant temperature (X_4). The derivation of the equation was designed by using the interactions of linear and quadratic regression coefficients of main factors and linear- by-linear regression coefficients. Besides the mathematical model, the data was necessary to examine the fitted model to ensure that it provides an adequate approximation to the true system. A more reliable way to make the evaluation is by application of analysis of variance (ANOVA). The purpose of ANOVA table is to represent the sources that contribute to the total variation in the data which included total, regression and residual sums of squares as well as the mean squares for the model that relate K to the operating parameters or factors as shown in Table 3. The important criterion that has been firstly evaluated is by referring to the dominant and appropriateness of the model to determine the regression coefficient and represent the value of R-squared, R2. The function of R2 itself is to reveal the total variance of the observed value and measure the proportion of variation that is explained by the model relative to the mean (overall average of the response) (Carley et al., 2004) and measure of the reduction in variability of response (Bas and Boyaci, 2007). From Table 3, the R2 for the model is 0.7679 (76.79 %), which demonstrates that 23.21 % of the total variability in the K is not explained by the regression in the fitted model. According to Myers and Montgomery (1995), it is possible for the models that have large values of R2 to give poor predictions or estimates of the response. Therefore, although the value of R_2 is not really high, it can still be used to indicate that the model obtained will be able to give a reasonably good estimate of K in the range studied. The accuracy of the model cannot be measured using only the R_2. It can also be determined through the ratio between the mean square regression and the mean square residual (F calculated). According to Barros Neto et al. (1996), the regression model is said to be significant if the calculated F-value is larger than the tabulated value (F calculated > F tabulated). Since the calculated F-value given in Table 3 is larger than the tabulated value at 0.10 probability level, the empirical model is still considered to be well adjusted to the experimental data.

Figure 2 illustrates the K from the empirical model (Eq(2)) versus those obtained from the experimental works. In the figure, the deviations of the observed point from the predicted data of the K from the empirical model is quite large, which reflects that the R^2 of the model is only 0.7679. However, the distributed residuals lie in a straight line. This means that the model is still adequate to fit the observed data. This model is adopted for subsequent prediction and optimisation. The figure clearly shows that K_{pred} as calculated K-value from regression model and K_{exp} is slightly deviated from the line of $K_{exp} = K_{pred}$.

Table 3: ANOVA results for the model of K

Source	Sum of Square	Degree of Freedom	Mean Square	F	$F_{0.10}$	R^2
Regression	0.5944	14	0.0425	2.60	2.17	0.7679
Residual	0.1797	11	0.0163			
Total	0.7741	25				

The significance of each coefficient was determined by p-value. All the terms at $p > 0.05$ levels are considered not significant (Cai et al., 2012). The p-values of each model terms are given in Table 4. Regarding the initial concentration and circulation flowrate, their linear terms are highly significant ($p < 0.05$), suggesting that changes in those factors have a significant effect on the K-value. For coolant temperature, only the quadratic effect was verified to be statistically significant. The circulation time was found to be insignificant. No significant interactions terms were found to exist between the main factors. This indicates that the main driving force in high purity of ice in PFC system is governed solely by the main factors, and changes in their magnitude towards the K do not depend on the levels of other factors.

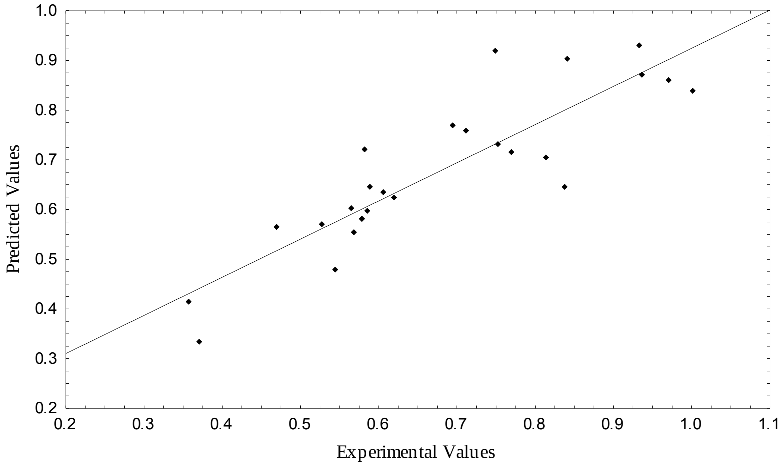


Figure 2: Observed verses predicted values of response

Table 4: Result of regression analysis for K

Factor	Coefficient Estimation	p-value
X_3	0.37080	0.001869
X_1	-0.00024	0.018095
X_4^2	0.00468	0.032297
X_1X_3	-0.00007	0.378315
X_2	-0.05502	0.387734
X_2^2	0.00163	0.413111
X_2X_4	-0.00164	0.427820
X_4	0.14369	0.470003
X_1X_4	-0.00001	0.599128
X_1X_2	-0.00001	0.677886
X_3X_4	0.00319	0.697082
X_1^2	-0.00000	0.720112
X_3^2	-0.00820	0.793545
X_2X_3	0.00108	0.894621

3.2 Optimum Condition

The aim of the process optimisation is to find the operating conditions that lead to a maximum purity of ice (low K), and at the same time to simultaneously increase the sugar content in the concentrate produced at the end of the process. The optimal condition to obtain the highest response was determined in the range of experimental conditions by the prediction of computing program, StatSoft 8.0 as shown in Table 5.

Table 5: Comparison between the predicted value and observed value for the response variables

Response	Observed value	Predicted value	Optimised condition			
			X_1 (mL/min)	X_2 (min)	X_3 (%Brix)	X_4 (°C)
K-value	0.3010	0.33848	3,400	23	3.4	-7

The K-value was validated through an experimental run using the predicted optimum condition to observe how accurate is the optimisation done by STATISTICA. From Table 5, the result for observed K-value does not differ significantly with the predicted value determined under the predicted optimal condition. The optimisation was successfully performed to identify the best operating parameters and it generally shows that the PFC system is well operated at very dilute solution in coconut water process.

4. Conclusions

The results of this optimisation process has confirmed that a minimum K value (0.3) can be obtained simultaneously at circulation flowrate of 3,400 mL/min, circulation time of 23 min, initial concentration of 3.4 % Brix and coolant temperature of -7 °C. This result supports that the objective of this study has been accomplished.

Acknowledgments

The author would like to express gratitude and special thank for the financial support from Ministry of High Education (MOHE) under vote Q.J130000.2546.16H86 (FRGS).

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