Central composite design applied to purify lemongrass essential oil using vacuum distillation

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Abstract. Vacuum distillation process can be applied for purification of lemongrass essential oil by increasing the concentration of citral in lemongrass essential oil. In this study, the relationship between experimental parameters of purification of lemongrass oil was investigated. The effect of pressure, temperature and pH was examined to determine the best performance of the product yield. Central Composite Design was applied to optimize the operating parameters of the process. It was found that the product yield of bottom product achieved an optimum level of 98.4% yield at the following reaction conditions, i.e. pressure of 55.9 mbar, temperature of 104.6^{o}C and pH of 4.8.
Key words: Central composite desgn, citral, lemongrass essential oil, vacuum distillation

Introduction

Cymbopogon citratus (DC) Stapf. (lemongrass) is perennial herb largely cultivated in tropical and subtropical countries. Lemongrass essential oil is characterized by a high content of citral (composed of neral and geranial isomers), which is widely used in fragrance formulations and incorporated into numerous consumer products (Lalko & Api, 2008). Citral is a racemic mixture of two monoterpene aldehydes; the geranial (*cis-citral*) and the neral (*trans-citral*).

Distillation is frequently used for the purification of essential oil because of operational ease and low operating costs. Vacuum distillation is used for the separation of mixtures with thermolabile compounds. It operates at low temperatures, thereby avoiding degradation of the compounds in the extract. The process involves heating a mixture and vaporizing the compounds, which depends on the volatility of the compounds. Initially, the more volatile compounds are vaporized, followed by intermediately volatile compounds, and so on. At the end of the process, the less volatile fraction remains in the reboiler. More volatile compound have lower boiling point compared than less volatile compound. The separation efficiency depends on the mass and energy transfer promoted between the liquid and vapor phases of the mixture. As consequence, the packing type, diameter and height of the packed column are variables that directly influence the results (Torres et al. 2012). On a laboratory scale, it is evident that the packing used affects vacuum distillation efficiency. The packings of the columns have different structures and are produced with different materials, such as ceramics, glass, metals and polymers. Determining the appropriate type of filling material depends on the properties of the mixture to be separated (Seader and Henley 1998).

Previous studies have reported on the use of vacuum distillation for successful production of essential oil. Belsito et al. (2007) was used vacuum distillation for removal bergapten, a phytotoxic compound, from bergamot (*Citrus bergamia*) essential oil. This process was also used to enrich the essential oil of citronella or geraniol to citronellal and citronellol (Beneti et al. 2011).

In this work, the vacuum distillation process was applied for purification of lemongrass essential oil by increasing the concentration of citral in lemongrass essential oil. Central composite design (CCD) technique was used to obtain the operating conditions of the vacuum distiller for concentration of citral in the bottom streams. This pocess has two product streams: bottom and top.

Material and Method

The lemongrass essential oil was purchased from CV. Eteris Nusantara, Yogyakarta. This volatile mixture was extracted by steam distillation from the aerial parts of these aromatic plants.

The lemongrass essential oil was purifieded using a laboratory vacuum distillation apparatus. A lemongrass essential oil volume of 250 mL (equivalent to 175 g) was introduced in a round bottom flask equipped with electrical resistance. In the reboiler, a temperature sensor was introduced for measuring the lemongrass essential oil temperature and for avoiding an overly high temperature in the flask.

The fractionating column was 1.5 m in height and was packed with titanium alloy. The experiments were conducted at specified pressure, temperature and pH as experimental variables. Due to the high concentration of citral (neral and geranial) in bottom product, we decided to use this product as the base of yield calculation. Then, the experimental results were reported in terms of bottom product yield calculated by Eq. (1).

$$\text{Product yield} = \frac{\text{Weight of bottom product}}{\text{Weight of lemongrass oil introduced in a round bottom flask}} \times 100\% \quad (1)$$

Gas chromatography/mass spectrometry

The chemical composition of lemongrass essential oil was analyzed by a gas chromatograph coupled with a mass spectrometer detector, GC-MS (Shimadzu, Japan, Model QP 5090A), using a capillary column DB5 (30 m, 0.25 mm, 25 μm). The column temperature gradient was as follows: 333 K / 2.5 min, 3 $Kmin^{-1}$ to 423 K, 5 $Kmin^{-1}$ to 523 K, 10 $Kmin^{-1}$ to 563 K / 10 min. Helium was used as carrier gas and the injector and detector temperatures were maintained at 553 K and 583 K, respectively. The sample components were identified by matching their mass spectra with those from the library database.

Results and Discussion

The vacuum was intended to increase the citral concentration in lemongrass essential oil. The results of the average yield of product were calculated from the relationship between the weight of bottom product and the weight of oil introduced in the round bottom flask. Compositions of lemongrass essential oils were analyzed by gas chromatography-mass spectrometry (GC-MS). The lemongrass essential oil components analysis results by GC-MS are presented in Table 1. Only main component is presented. The GC-MS analysis indicated that lemongrass essential oil mainly contained four components and α-citral was the highest component. The results are shown in Table 1.

Table 1. Composition of main components in lemongrass essential oil

Components	**Composition of lemongrass essential oil (%)**		
	Before vacuum distillation	**After vacuum distillation**	
		Top product	**Bottom product**
Myrcene	10.7	17.8	2.23
β-citral	32.8	28.9	33.25
Geraniol	3.46	3.69	5.58
α-citral	44.09	37.33	50.04
Total (%)	91.05	87.72	91.1

The percentages of each component of lemongrass essential oil obtained by vacuum distillation are reported as raw percentages without standardization. The lemongrass essential oil before and after vacuum distillation have very different concentrations, mainly in terms of their primary components. There was an increasing of citral concentration in bottom product after vacuum distillation. After vacuum distillation, the more volatile component of myrcene as the principal component was obtained in top product, while the bottom product had a high citral concentration and a low myrcene concentration.

The effect of process parameters on the yield of bottom product was studied using Design of Experiments (DOE). The DOE selected was RSM using Design Expert version 7.1.6 (Stat-Ease, Inc.) software. Table 2 indicates the independent variables and their levels used in the response surface design. To optimize the process parameters a Central Composite Design with a three-level-three-factor design that addressed pressure, temperature and pH was selected.

Table 2. Experimental Design Matrix and Results

Pressure (mbar)	**Temperature (°C)**	**pH (-)**	**Bottom product yield (%)**
70	140	5	89.4
70	100	5	96.9
80	130	6	89.5
70	120	5	95.8
70	120	5	94.2
80	110	6	93.7
60	130	6	90.1
70	120	3	91.6
70	120	7	71.7
70	120	5	95.2
50	120	5	95.5
70	120	5	95.2
80	110	4	94.0
70	120	5	93.2
90	120	5	92.8
60	110	4	96.5
60	110	6	92.1
60	130	4	92.8
80	130	4	94.0

The experimental parameters, ranges and levels of the independent variables investigated in this study and the results on the basis of the Central Composite Design are shown in Table 2. All of the 19 designed experiments were conducted and the results analyzed by multiple regression. Five duplicates are included at the center of the design. The predicted values were obtained from model fitting technique and were seen to be sufficiently correlated to the observed values. Fitting of the data to various models (linear, two factorial, quadratic and cubic) and their subsequent ANOVA showed that the process was most suitably described with quadratic polynomial model. The following quadratic model equation (in coded factors) that correlates the yield of product to the various process parameters is given by Eq. (2).

$$\text{Yield (g)} = 95.14-0.36A-1.56B-3.23C+0.19AB+0.29AC-0.31BC+0.013A^2-0.24B^2-3.11C^2 \quad (2)$$

Where A, B and C were pressure (mbar), temperature (^oC) and pH, respectively.

The high F value (F model = 6.03) with low probability value ($P < 0.0001$) indicates the significance of the fitted model. The low value of the coefficient of variation (CV = 3.16%) indicates that results of the fitted model are reliable. The quality of the model fit was evaluated by the coefficient of determination (R^2), this value being calculated to be 0.858 for the response, indicating that the developed model equation successfully captured the correlation between the process parameters to the yield of bottom product. The adjusted coefficient of determination (R^2Adj.) value reconstructs the expression with all the significant terms included. The value of the adjusted coefficient of determination (R^2 Adj. = 0.715) is also very high, supporting the significance of the model. As the fitted model Eq. (2) provides a good approximation to the experimental condition, the model was employed to find the values of the process variables for optimum yield of biodiesel.

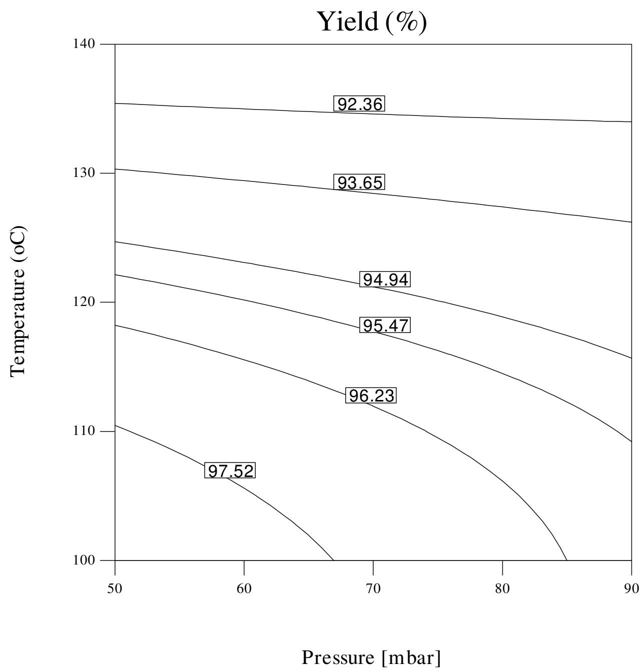

Figure 1. Combined effect of pressure and temperature on yield of bottom product

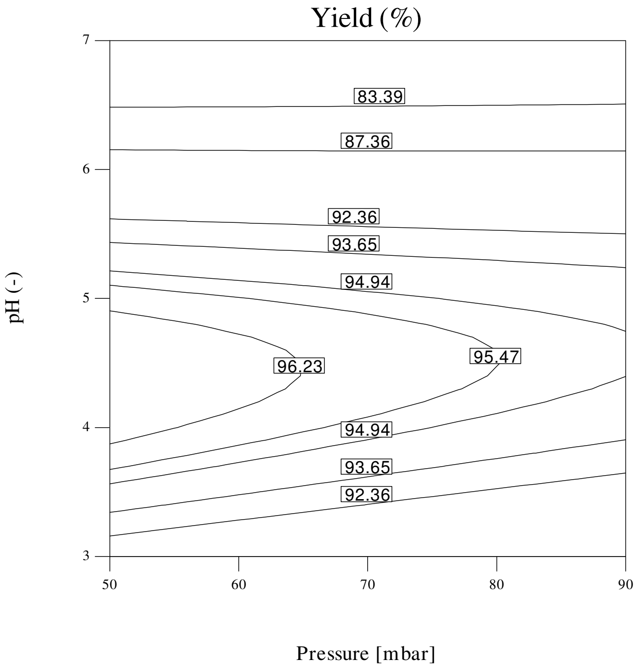

Figure 2. Combined effect of pressure and pH on yield of bottom product

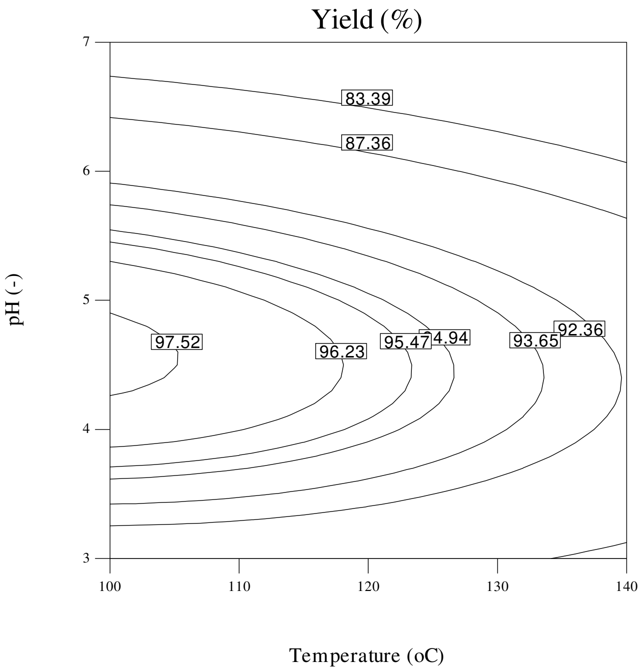

Figure 3. Combined effect of temperature and pH on yield of bottom product

The graphical representation of the regression Eq. (2), and the contour plot are presented in Figures 1-3. Shape of the contour plot indicated different interaction between the variables. The optimal values of the selected variables were obtained by solving the regression equation of Eq. (2). This model was employed to find the value of the process variables that gives optimum yield of bottom product. The predicted optimal value, that obtained from the model equation are pressure of 55.9 mbar, temperature of 104.6 ^{o}C and pH of 4.8. The model predicts that the maximum product yield that can be obtained under these optimum conditions of the variables is 98.4%.

Conclusions

It was possible to isolate citral with high vacuum and low temperatures, avoiding, so, the possible thermal degradation of the material, when compared to conventional process. Vacuum distillation process can be applied for purification of lemongrass essential oil by increasing the concentration of citral in lemongrass essential oil. The mathematical models obtained by the complete central composite design are efficient to represent the process of vacuum distillation in the experimental range. In this way, with these equations, it is possible to estimate the yield of bottom product that will be obtained by the processing of the lemongrass essential oil by vacuum distillation. It was found that the product yield of bottom product achieved an optimum level of 98.4% yield at the following reaction conditions, i.e. pressure of 55.9 mbar, temperature of 104.6^{o}C and pH of 4.8.

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References

Lalko J. and Api A.M. 2008. Citral: Identifying a threshold for induction of dermal sensitization. Regulation Toxicology Pharmacology 52: 62–73.

Beneti SC, Rosset E, Corazza ML Caren D. Frizzo C.D., Luccio, M.D. and Oliveira, J.V. 2011. Fractionation of citronella (*Cymbopogon winterianus*) essential oil and concentrated orange oil phase by batch vacuum distillation. Journal of Food Engineering. 102:348–354

Belsito E.L., Carbone C., Di Gioia M.L., Leggio A., Liguori A., Perri F., Siciliano C. and Viscomi M.C. 2007 Comparison of the volatile constituents in cold-pressed bergamot oil and a volatile oil isolated by vacuum distillation. Journal of Agriculture Food Chemistry 55:7847–7851

Seader, J.D. and Henley, E.J. 1998. Separation process principles. Wiley, New York

Torres, F.C., Lucas, A.M., Ribeiro, V.L.S., Martins, J.R., von Poser, G., Guala, M.S., Elder, H.V. and Cassel E. 2012. Influence of essential oil fractionation by vacuum distillation on acaricidal activity against the cattle tick. Brazilian Archives of Biology and Technology, 55:613–621