Production of Methyl Laurate from Coconut Cream through Fractionation of Methyl Ester

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Abstract. This paper concerns the production of methyl laurate from coconut cream through fractionation of methyl esters. Coconut oil was produced by wet processing of coconut cream. The esters were prepared by reacting coconut oil and methanol using homogeneous catalyst KOH in a batch reactor, followed by fractionation of fatty acid methyl esters (FAME) at various reduced pressures applying differential batch vacuum distillation. Experimental data were compared with simulation of a batch distillation employing the simple Raoult's model and modified Raoult's model of phase equilibria. Activity coefficients (γ_i) were determined by optimization to refine the models. The modified Rault's model with activity coefficients gave better agreement with the experimental data, giving the value of γ_i between 0,56-0,73. For a given boiling temperature, lower operating pressure produced higher purity of C10 and C12 FAME for respective distillates.

1   Introduction

Indonesia is the second largest coconut producer in the world. Coconut oil (CNO) is rich in medium saturated fatty acids (up to 93% in triglyceride form), about 50-60% of which consist of lauric acid (C12:0) in triglyceride form [1-3]. Conversion of medium and long chain fatty acids into methyl or ethyl esters is used to produce intermediate oleo-chemical, biofuels or surfactants [4-8]. Methyl laurate is an intermediate for producing biopolymers, fatty acids, fatty acid alcohols, monolaurine or lauric acid. Vacuum batch distillation is suitable for high-boiling point components such as FAME mixture, which makes it an attractive route for fractionating medium fatty acid ester from coconut oil or seed oil compared with other routes such as saponification, crystallization, supercritical extraction, among others [9-12]. The objective of this paper is to evaluate the production and fractionation potential of FAME from coconut cream and to compare the results of distillation of FAME with those from a

distillation simulation employing the modified Raoult's model of vapor-liquid equilibrium.

2   Methodology

Coconut oil was produced by wet processing of coconut cream as in the method given in detail by Khayam and Sitompul [13] after which it was converted to fatty acid methyl esters with KOH as catalyst. The FAME was separated from the bottom phase (glycerol) and fed into a 500-ml batch vacuum distillation unit for fractionation of the FAME to produce methyl laurate. A schematic diagram of the FAME production is not shown here due to space limitations but it can be found elsewhere [13]. Distillate and bottom product composition were measured by gas chromatography and estimated by saponification value. The composition of the FAME was analyzed with a Shimadzu® GC-2010 Plus, FID type gas chromatograph using a Stabilwax® capillary column (30 m length and 0.25 mm ID with particle diameter 0.25 µm). The standard FAME was bought from Merck. The acid value and saponification value were determined according to FBI A01-03 and FBI-A03-03 standards, respectively [14,15].

Figure 1 shows the experiment's flowchart and Figure 2 shows the vacuum distillation schematic diagram.
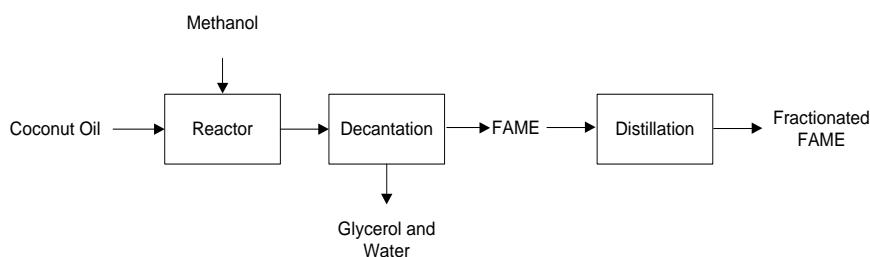
Figure 1 Schematic diagram for producing and fractionation of FAME from coconut oil.

Run A was operated at pressure 10 kPa, 160°C and 190°C. SV-testing and gas chromatography were used to determine the product's SV and composition. Run B was operated at pressure 13.5 kPa, 185°C and 195°C, and SV was determined. The experimental data were compared with the simulated data by applying the simple and the modified Raoult's model for phase equilibria modeling of multi-component mixtures. Figure 3 shows a scheme of the FAME batch distillation process.
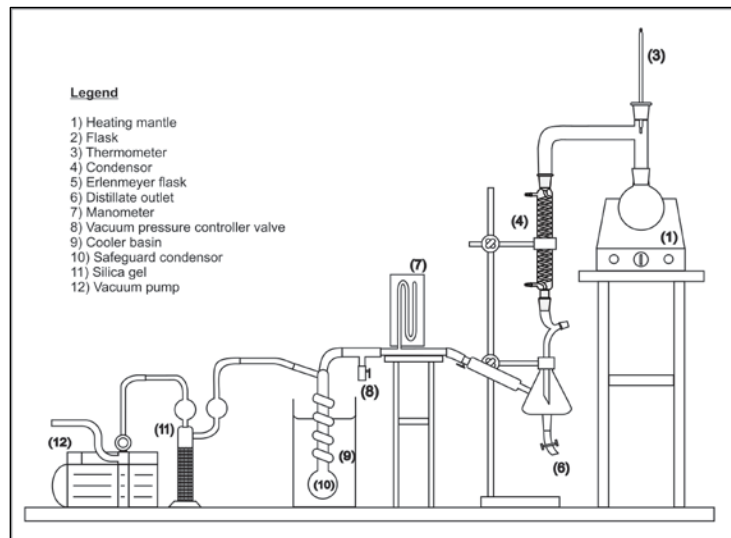
Figure 2 Schematic diagram of vacuum distillation for methyl laurate fractionation.
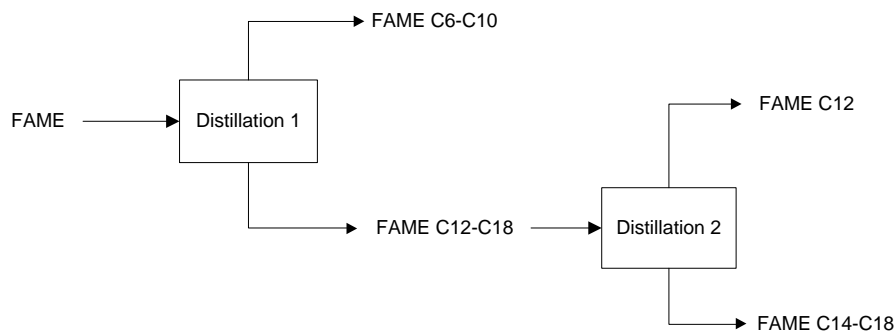
Figure 3 Differential batch vacuum distillation for fractionation of FAME from coconut oil.

Modeling of differential batch vacuum distillation was derived by total mass and component mass balance. In a batch vacuum distillation, total mass balance of distillate (D) and bottom product (L) are described below.

$$0 - dD = dL \tag{1}$$

$$-\int_d^D dD = \int_{L_0}^L dL \tag{2}$$

$$D = L_0 - L \tag{3}$$

For component mass balance, we include mole fraction of component in liquid form (x_i) and vapor form (y_i).

$$0 - d(y_i.D) = d(x_i.L) \tag{4}$$

$$0 - y_i.dD - D.y_i = x_i.dL + L.dx_i \tag{5}$$

By considering the differential of more fractions of dy_i quite small ($dy_i \approx 0$), then

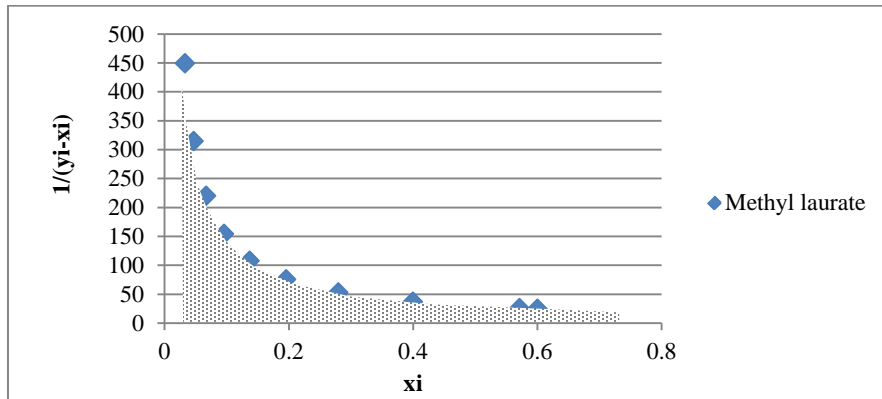$$-y_i.dD = x_i.dL + L.dx_i \tag{6}$$

$$\int_{L_0}^{L} \frac{dL}{L} = \int_{x_{i_0}}^{x_i} \frac{dx_i}{(y_i - x_i)} = \tag{7}$$

$$\ln\left(\frac{L}{L_0}\right) = \int_{x_{i_0}}^{x_i} \frac{1}{(y_i - x_i)}.\Delta x_i \tag{8}$$

$$L = e^{area\ below\ curve}.L_0 \tag{9}$$

The area below integration in Eq. (8) was calculated using a numerical method available such as the trapezoidal method as illustrated in Figure 4 below.

Figure 4 Typical profile of area of below integration for Distillate 2 in the modeling of FAME batch distillation.

Modeling of phase equilbria was conducted by introducing constant equilbrium, K_i, the ratio of y_i to x_i. The Raoult's model or the modified Raoult's model for K_i is given below.

$$K_i = \frac{y_i}{x_i} = \frac{\gamma_i P_i^{sat}}{P} \tag{10}$$

γ_i is the activity coefficient for each component in the mixture. Note that γ_i is equal to 1 for the Raoult's model's so called ideal model, while for non-ideal models γ_i is determined by the optimization routine for the modified Raoult's

model. Note that the saturated vapor pressure data of components (P_i^{sat}) were calculated using the Antoine equations with respect to Antoine constants for FAME, available in the literature [4,16].

3   Results and Discussion
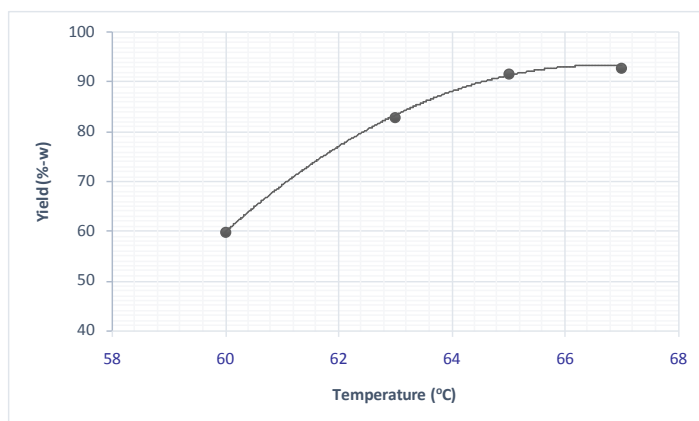
3.1   Production of FAME

Table 1 shows the composition of the coconut oil produced from coconut cream compared to literature data [3,6], indicating differing characteristics based on its origin, especially for lauric acid content. Note that the composition of the sample and standard FAME were determined by gas chromatography as mentioned in the section above and the %-mole was converted from %-weight given the average molecular weight of CNO.

Table 1 Coconut oil (CNO) composition from experimental data and comparison with literature data [3,6].

Components	Experimental data %-mole	Literature data %-mole
Caproicacid (C6 carboxylic acid)	0.00%	0.00%
Caprylic acid (C8 carboxylic acid)	18.64%	0.00%
Capric acid (C10 carboxylic acid)	11.98%	8.68%
Lauric acid (C12 carboxylic acid)	49.07%	56.49%
Myristic acid (C14 carboxylic acid)	11.11%	19.63%
Palmitic acid (C16 carboxylic acid)	5.12%	9.16%
Stearic acid (C18 carboxylic acid)	3.53%	0.00%
Oleic acid (C18:1 carboxylic acid)	0.16%	6.05%
Linoleic acid (C18:2 carboxylic acid)	0.39%	0.00%
Linolenicacid (C18:3 carboxylic acid)	0.00%	0.00%
Total	**100.00%**	**100,00%**

A graph of reaction yield versus temperature from four runs of trans-esterification is shown in Figure 5. Note that the percentage (weight) yield of the reaction is defined as the ratio of amount of FAME produced to initial CNO.

The trans-esterification reaction is exothermic and at a higher temperature will reach equilibrium and will decrease after a further raise in temperature. The acid value of the FAME product was 0.54-0.65 mg KOH/gr sample, showing low fatty acid content in the product and representing the possibility of a low deterioration rate caused by hydrolysis during storage of the sample.

Figure 5 Yield vs temperature for trans-esterification of coconut oil.

3.2   Distillation of FAME

Two runs of distillation or fractionation were conducted, run A (with reduced pressure 10 kPa, differential temperature 160°C and 190°C for two distillate products respectively) and run B (with pressure 13 kPa, differential temperature 185°C and 195°C for two distillate products respectively).

Comparison and deviation of quantity, and saponification values of experimental and simulation data are shown in Table 2. For run A, the composition of the final product (Distillate 1, theoretically rich in methyl caprate, and Distillate 2, methyl laurate) obtained from the experimental data was compared to the simulation data obtained with the simple Raoult's model, as shown in Table 3.

Table 2 Comparison of product amount and saponification values from simulation and experimental data with Raoult's model ($\gamma_i = 1$).

	Quantity			Saponification Value		
	Experimental data (mL)	Simulation data (mL)	Deviation	Experimental data	Simulation data	Deviation
Run A (10 kPa), initial sample 61 mL						
Distillate 1	9.20	5,32	-42.2%	334.88	345.66	3.2%
Distillate 2	32.10	32.14	0.1%	254.26	274.88	8.1%
Bottom product 2	23.80	21.04	-11.6%	246.28	246.70	0.2%
Run B (13 kPa), initial sample 139 mL						
Distillate 1	28.00	20.11	-28.2%	334.88	343.69	2.6%
Distillate 2	56.00	69.97	24.9%	254.26	283.07	11.3%
Bottom product 2	55.00	55.06	0.1%	246.28	247.52	0.5%

To refine the model, known as the modified Raoult's model, the activity coefficient for each component (γ_i) was determined by the optimization routine, which resulted in a smaller deviation between the experimental and the simulation data (see Table 3) and γ_i values for each component, as shown in Table 4.

Table 3 Comparison of deviation between experimental and simulation data with simple ($\gamma_i = 1$) and modified (γ_i = optimized) Raoult's model of phase equilibria.

	Run A		Run B	
	Simple	Modified	Simple	Modified
Deviation mean of product's quantity	25,35%	17,99	23,92%	17,75%
Deviation mean of saponification value	3,86%	3,83	4,41%	4,82%

Table 4 Activity coefficients for each component (γ_i) from data optimization.

Components	Activity Coefficient Calculated		
	Run A	Run B	Deviation
Methyl caproic (FAME C6)	0,7100	0,7300	-3%
Methyl caprylic (FAME C8)	0,6922	0,7263	-5%
Methyl capric (FAME C10)	0,6749	0,7227	-7%
Methyl lauric (FAME C12)	0,6580	0,7191	-8%
Methyl myristic (FAME C14)	0,6416	0,7155	-10%
Methyl palmitic (FAME C16)	0,6255	0,7119	-12%
Methyl stearic (FAME C18)	0,6099	0,7083	-14%
Methyl oleic (FAME C18:1)	0,5946	0,7048	-16%
Methyl linoleic (FAME C18:2)	0,5798	0,7013	-17%
Methyl linolenic (FAME C18:3)	0,5653	0,6978	-19%

Table 3 shows that the data gave a better agreement when the activity coefficient was applied in the batch distillation model. Further, Table 4 shows that the two experiments produced similar values of γ_i. Deviation was higher for longer esther chains, which indicates a linear profile of activity coefficient deviation versus chain length of FAME. Hence, the modified Raoult's phase equilibria of the distillation model produced better prediction due to the FAME mixture being a non-ideal solution, as can be seen from the activity coefficients determined from the simulation shown in the Table 4, in the range of 0.56-0.73 [17].

Table 5 also shows a comparison of the final product from the experimental and the simulation data. A larger deviation was found for C14 and C16 FAME in Distillate 2 due to fluctuation in the temperature during operation.

As can be seen from Table 5, the methyl ester composition of Distillate 2 in the FAME (thus representing the fatty acid components in the coconut oil) was dominated by C12:0 FAME. The simulation data of the FAME composition for

Distillate 2 at different pressures and temperatures are summarized and tabulated in Table 6. Table 6 shows that distillation with higher pressure resulted in a smaller deviation and hence produced a better prediction by simulation.

Table 5   Comparison of Distillate 2 (Final Product) from Experimental Data and Simulation Data.

Components	Composition of CNO from experiment		
	Experimental Data	Simulation Data	Deviation
Methyl caproic (FAME C6)	0.0%	0.0%	0.00%
Methyl caprylic (FAME C8)	0.0%	15.0%	0.00%
Methyl capric (FAME C10)	8.5%	15.8%	86.33%
Methyl lauric (FAME C12)	68.8%	48.6%	-29.43%
Methyl myristic (FAME C14)	15.9%	15.6%	-2.20%
Methyl palmitic (FAME C16)	3.8%	5.1%	32.04%
Methyl stearic (FAME C18)	0.0%	0.0%	0.00%
Methyl oleic (FAME C18:1)	1.7%	0.0%	-100.00%
Methyl linoleic (FAME C18:2)	0.0%	0.0%	0.00%
Methyl linolenic (FAME C18:3)	0.0%	0.0%	0.00%
Total	99.0%	100.0%	1.23%

Table 6   Fractionation result with simulation for operating pressure of run A (10 kPa) and run B (13 kPa) for Distillate 2.

Components	Simulation Results	
	Run A (10 kPa, 160 and 190 °C)	Run B (13 kPa, 185 and 195 °C)
Methyl caproic (FAME C6)	0.0%	0.0%
Methyl caprylic (FAME C8)	15.0%	23.2%
Methyl capric (FAME C10)	15.8%	12.8%
Methyl lauric (FAME C12)	48.6%	44.1%
Methyl myristic (FAME C14)	15.6%	15.3%
Methyl palmitic (FAME C16)	5.1%	4.6%
Methyl stearic (FAME C18)	0.0%	0.0%
Methyl oleic (FAME C18:1)	0.0%	0.0%
Methyl linoleic (FAME C18:2)	0.0%	0.0%
Methyl linolenic (FAME C18:3)	0.0%	0.0%
Total	**100.0%**	**100.0%**
Saponification Value (data)	**274.38**	**281.15**

Further, fractionation was conducted based on the batch distillation model, producing the composition distribution of the Distillate 2 as shown in the Table 6. Note that the SV for each distillate is shown and used as a comparison of the total quality of the product. Table 6, with the same composition of feed and operation conditions in run A (10 kPa, 160°C and 190°C) gave better purity of methyl lauric than in run B (13 kPa, 185°C and 195°C). Furthermore, Table 6 also shows the experimental data for the SV, representing the overall FAME of

the distillate. The SV's were in good agreement for both runs. In general, a higher composition of medium-chain FAME was produced at lower operating pressure and hence fractionation can be produced at a lower boiling point (Run A at 10 kPa) by differential batch distillation.

4   Conclusion

Methyl laurate was produced from coconut cream, after initially being converted to CNO by methyl ester fractionation. Experimental data of fractionation were compared with the simple Raoult's model of phase equilibria, which was refined into the modified Raoult's model by employing the activity coefficient (γ_i) for each component. The activity coefficients found from optimization were in the range of 0.56-0.73, showing the non-ideal mixture. Two runs of the experiment showed similar values for γ_i, although deviations were higher for longer ester chains, indicating a linear profile of activity coefficient deviation versus chain length. A larger deviation was found for the composition of FAME produced at a higher boiling point, such as C14 and C16. Regarding the quantity and composition of the distillate, the experimental and simulated data showed that a lower operation pressure produced a higher content of medium-chain FAME, especially C10 FAME and C12 FAME for Distillate 1 and Distillate 2 during differential batch vacuum distillation. Hence, a lower pressure of batch vacuum distillation produced a higher distillate and overall higher purity for more volatile components such as C10 and C12 FAME.

Acknowledgements

References

[1]   Bhatnagar, A.S., Kumar, P.K.P., Hemavathy, J. & Krishna, A.G.G., *Fatty Acid Composition, Oxidative Stability, and Radical Scavenging Activity of Vegetable Oil Blends with Coconut Oil*, JAOCS, **86**, pp. 991-999, 2009.

[2]   Anneken, D.J., Both, S., Christoph, R., Fieg, G., Steinberner, U. & Westfechtel, A., "*Fatty Acids*", *Ullmann's Encyclopedia of Industrial Chemistry*, Wiley-VCH, Weinheim, 2006.

[3]   Salunkhe, D.K., *World Oilseeds Chemistry. Technology and Utilization*, Van Nostrand Remhol, USA, pp. 281-291, 1992.

[4]   Stage, H., *Fatty Acid Fractionation by Column Distillation: Purity, Energy Consumption and Operating Conditions*, JAOCS, **61**, pp. 204-214, 1984.

[5]   Bono, A., Pin, O.P. & Jiun, C.P., *Simulation of Palm based Fatty Acids Distillation*, Journal of Applied Sciences, **10**(21), pp. 2508-2515, 2010.

[6]   Krishna, G., Raj, G., Bhatnagar, A.S., Kumar, P. & Chandrashekar, P., *Coconut Oil: Chemistry, Production and Its Applications – A Review*, Indian Coconut Journal, pp. 15-27, July 2010.

[7]   Cao, P., Dubé, M.A. & Tremblay, A.Y., *High-Purity Fatty Acid Methyl Ester Production from Canola, Soybean, Palm, and Yellow Grease Lipids by Means of A Membrane Reactor*, Biomass and Bioenergy, **32**(11), pp. 1028-1036, 2008.

[8]   Elraies, K.A., Awang, M., Tan, I.M. & Saaid, I., *The Synthesis and Performance of Sodium Methyl Ester Sulfonate for Enhanced Oil Recovery*, Petroleum Science and Technology, **28**(17), pp. 1799-1806, 2010.

[9]   Vyas, A.P., Verma J.L. & Subrahmanyam, N., *A Review on FAME Production Processes*, Fuel, **89**(1), pp. 1-9, 2010.

[10] Brown, J.B. & Kolb, D.K., *Progress in Chemistry of Fats and Other Lipids*, Vol. 3, Holman, R.T., Lundberg, W.A. & Malkin, T., eds, Pergamon Press, pp. 58-230, 1955.

[11] Markley, K.S., *Fatty Acids,* Part 3, Markley, K.S., ed., Interscience Publishers, pp. 1983-2123, 1964.

[12] Palumpitag, W., Prasitchoke, P., Goto, M. & Shotipruk, A., *Supercritical Carbon Dioxide Extraction of Marigold Lutein Fatty Acid Esters: Effects of Cosolvents and Saponification Conditions*, Separation Science and Technology, **46**(4), pp. 605-610, 2011.

[13] Khayam, U. & Sitompul, J.P., *Preliminary Studies of Production of Coconut Oil from Coconut Cream*, National Conference of Chemical Engineering, University of Indonesia, Jakarta, 2012.

[14] FBI A01-03 Standard (in Indonesian), *Standard Method for Analysis of Acid Value for Biodiesel*, 2010.

[15] FBI-A03-03 Standards (in Indonesian), *Standard Method for Analysis of Saponification Number and Composition of Alkyl Ester Biodiesel*, 2010.

[16] Yuan, W., Hansen, A.C. & Zhang, Q., *Vapor Pressure and Normal Boiling Point Predictions for Pure Methyl Esters and Biodiesel Fuels*, Fuel, **84**, pp. 943-950, 2005.

[17] Smith, J.M., Van Ness, H.C. & Abbot, M.M., Chapter 13, *Introduction to Chemical Engineering Thermodynamics*, 7th Edition, McGraw Hill Co., New York, 2005.