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Mechanisms and Factors of Oil in the Fruit and Seeds of Neem

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ABSTRACT

In this experiment, Neem oil extraction from Neem seeds (*Azadirachta indica A. Juss*) with n-hexane and ethanol are presented. Effects of particle size, temperature and type of solvent on the extraction kinetic and thermodynamic parameters were studied. Results showed that the maximum oil yields were 41.11% for ethanol and 44.29% for n-hexane at 50°C, and 0.425-0.71 mm particle size. Based on psycho-chemical characteristics analysis showed that increasing temperature decreased iodine value but caused saponification, acid, and peroxide value became higher, which means higher extraction temperature result on higher oil yield but lower oil quality. The kinetic of neem oil extraction was derived from mass transfer rate equation. It also found that ΔH is positive, ΔS is positive, and ΔG is negative indicating that this process are endotermic, irreversible, and spontaneous.

***Keywords*—** oil, neem, extraction, kinetic, thermodynamic.

I. INTRODUCTION

Neem (*Azadirachta indica A. Juss*) is one of the very few trees known in the Indian subcontinent. This tree is belonged to *Meliceae* family, and grows rapidly in the tropic and semi-tropic climate. It is also observed that this tree could survive in very dry and arid conditions. Neem tree is an evergreen tree, but it may become leafless for a short period in certain conditions [1]. Neem tree also found in Indonesia in several areas such as Bali, Lombok, West Java, East Java (Situbondo, Ngawi), Central Java, and Nusa Tenggara Barat. All parts of Neem plant such as leaves, bark, flower, fruit, seed and root have advantages in medical treatment and industrial products. Its leaves can be used as drug for diabetes, eczema and reduce fever. Barks of Neem can be used to make toothbrush. Neem roots has an ability to heal diseases and against insects [1, 2]. However, this tree is not very popular in Indonesia because it is only used as a canopy tree.

Neem seed is a part of Neem tree which has high concentration of oil. Neem oil is widely used as insecticides, lubricant, drugs for variety of diseases such as diabetes and tuberculosis [1-3]. This oil could also prolong leather goods when it is applied on them [1].There are several methods to obtain Neem oil from the seeds like mechanical pressing, supercritical fluid extraction, and solvent extraction [1]. Mechanical extraction is the most widely used method to extract Neem oil from Neem seed. However, the oil produced with this method usually has a low price, since it turbid and contains a significant amount of water and metals contents. Extraction using supercritical fluid, the oil produced has very high purity; however the operating and investment cost is high. Extraction using solvent has several advantages. It gives higher yield and less turbid oil than mechanical extraction, and relative low operating cost compared with supercritical fluid extraction.

In this study we used solvent extraction to extract the oil from Neem seed. The effects of parameter process such as temperature and particle size were studied and kinetic and thermodynamics model were developed. As the solvents, we used ethanol and hexane.

II. MATERIALS AND METHODS

Material preparation:

Neem seed used in this study were obtained from Bali. This raw material has water content of 7.8% and oil content of 49.58%. Prior to use, the Neem seeds were repeatedly washed to remove dirt and other impurities material, and subsequently dried in oven at 50°C until it reached constant moisture content. Then, Neem seeds were ground to get three different particle sizes (0.85-1.40 mm, 0.71-0.85 mm, and 0.425-0.71 mm).

Oil extraction:

Neem seeds were extracted using two solvent (n-hexane and ethanol) for 3 hours with ratio Neem seed powder weight to solvent volume of 1:5. In certain time intervals, the samples were taken and centrifuged to separate the solid fraction from solution. Filtrate was heated and evaporated to obtain solvent-free oil. Then the oil was weighed to calculate the concentration of oil in the solution. Extractions were conducted at 5 temperature level (30°, 35°, 40°, 45° and 50°C).

III. RESULTS

Effect of temperature to quality of oil:

Oil quality was affected by temperature, hydrolysis, oxidation, lipase enzyme, and another compounds in the oil. The effect of extraction temperature to psychochemical characteristics of Neem oil is shown in Figure-1.

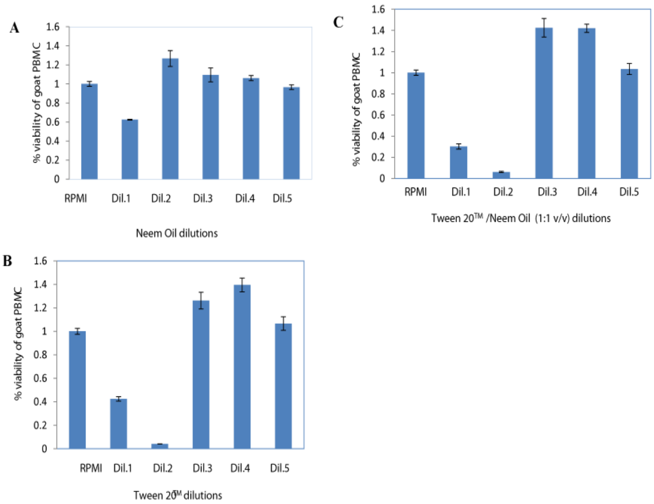


Figure-1. The effect of Neem oil extraction temperature on (a) acid value; (b) saponification value; (c)peroxide

The quality of Neem oil decreased as the temperature increased. This is shown in Figure-1(a) to (d) where the acid, saponification and peroxide value increase while iodine value decrease. Acid value indicates the amount of free fatty acids presents in an oil. Acid value is good indicator of oil degradation caused by hydrolysis. Figure-1(a) shows that higher extraction temperature increased the acid value because the extraction temperature influenced the hydrolysis of Neem oil [5 - 6]. Vegetable oil contains lipase enzyme which has an optimum temperature about 35-40o C [7-9]. Lipase enzyme hydrolyzes oil become free fatty acid and glycerol.

Saponification value indicates the average molecular weight of triglycerides in the oil [5-6, 10]. Figure-1(b) shows that an increase in temperature, increased the saponification value because higher temperature caused lipid to breakdown therefore reduced the average molecular weight of the oil [5, 10]. Peroxide value is used as an indicator of oil rancidity [5]. Figure-1(c) shows that an increase in temperature increased the peroxide value. Increasing the temperature extraction caused the oil to be rancid, thus leading to reduce its oxidative stability. Rancidity is caused by aldehydes, ketones, and oxidation [4, 11]. Iodine value expresses the unsaturation level of the oil [9, 12]. Figure-1(d) shows that higher temperature reduced the iodine value, since higher temperature initiate the breakdown of carbon chain bonding thus leading to form the saturated carbon chain. This results on decrease the iodine value of oil.

The type of solvent did not affect on the saponification and iodine value, however it influenced the acid value. It implies that n-hexane as non-polar solvent suitable for free fatty acid extraction compare to ethanol, which is polar solvent, is able to extract bio-active compounds [13].

Extraction kinetics :

A relevant kinetic data is required to analyze and design an extraction process especially in industrial scale. In these experiments, we used mass transfer kinetic model to represent our experiment data because there is no reaction between the Neem oil with both solvent, n-hexane and ethanol. Neem oil, as an organic material, contains several organic compounds such as nimbin, nimbidin, salannin, etc. Since Neem oil is an organic material, it readily dissolved in organic solvents like n-hexane and ethanol. Here, the mechanism control for extraction of Neem oil in n-hexane and ethanol is mass transfer, and we propose mass transfer kinetic model to represent the yield data of Neem oil extraction.

For this model we assumed that the main mechanism which controls the rate of Neem oil extraction is mass transfer of Neem oil from Neem seeds (solid) to bulk liquid n-hexane and ethanol. Mass transfer rate of Neem oil from Neem seed to organic solvents can be written as,

$$\frac{dW_A}{dt} = k.A.(C_{Ai} - C_A)$$

Where dW_A/dt is the mass transfer rate of neem oil (g/s), C_A and C_{Ai} are the concentration of neem oil in bulk liquid (organic solvents) at time t (g/L) and at equilibrium (g/L), respectively. Here k is mass transfer coefficient and A is surface area for mass transfer process. Since the extraction was taken in batch process and its volume was kept constant during process, therefore

$$\frac{dW_A}{dt} = k.\frac{A}{V}.(W_{Ai} - W_A)$$

$$\frac{dW_A}{dt} = k.a.(W_{Ai} - W_A)$$

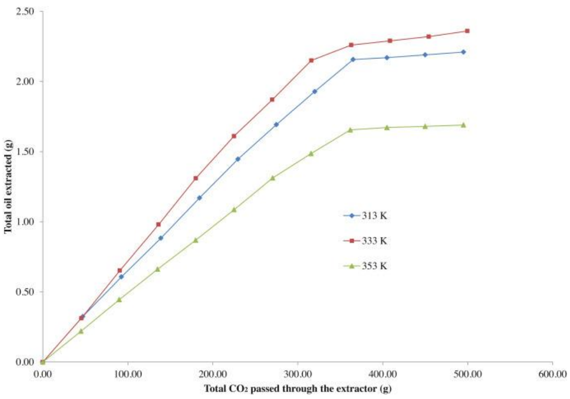
Where *k.a* is volumetric mass transfer coefficient. To solve Eq. (3), we used some conditions as follows:
At the beginning of extraction process (t = 0), the mass of Neem oil in bulk liquid is zero, WA = 0.
At any time t, mass of Neem oil in bulk liquid is WA = WAi. With those conditions, integration of Eq. (3) gives the following result,

$$W_A = W_{Ai}\left[1 - \exp(-k.a.t)\right]$$

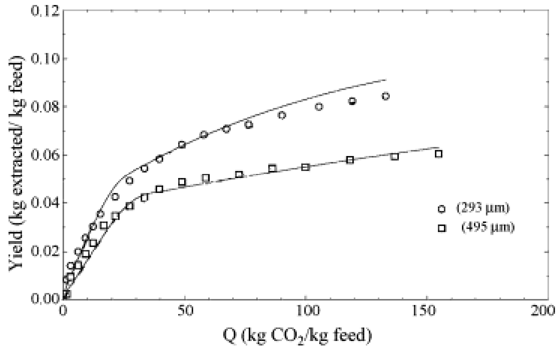
Eq. (4) can be rearrange so it can be written in terms of yield per mass of Neem seed,

$$Y_A = Y_{Ai}\left[1 - \exp(-k.a.t)\right]$$

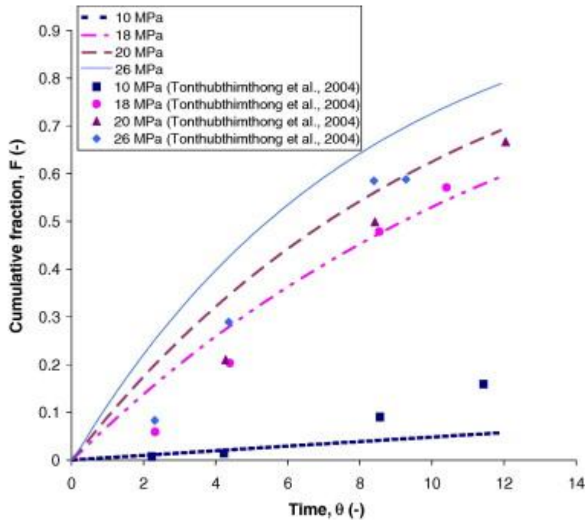
Where Y_A andi Y_{Ai} are yield of Neem oil in bulk liquid at time t and at equilibrium per mass of Neem seed.



(a)

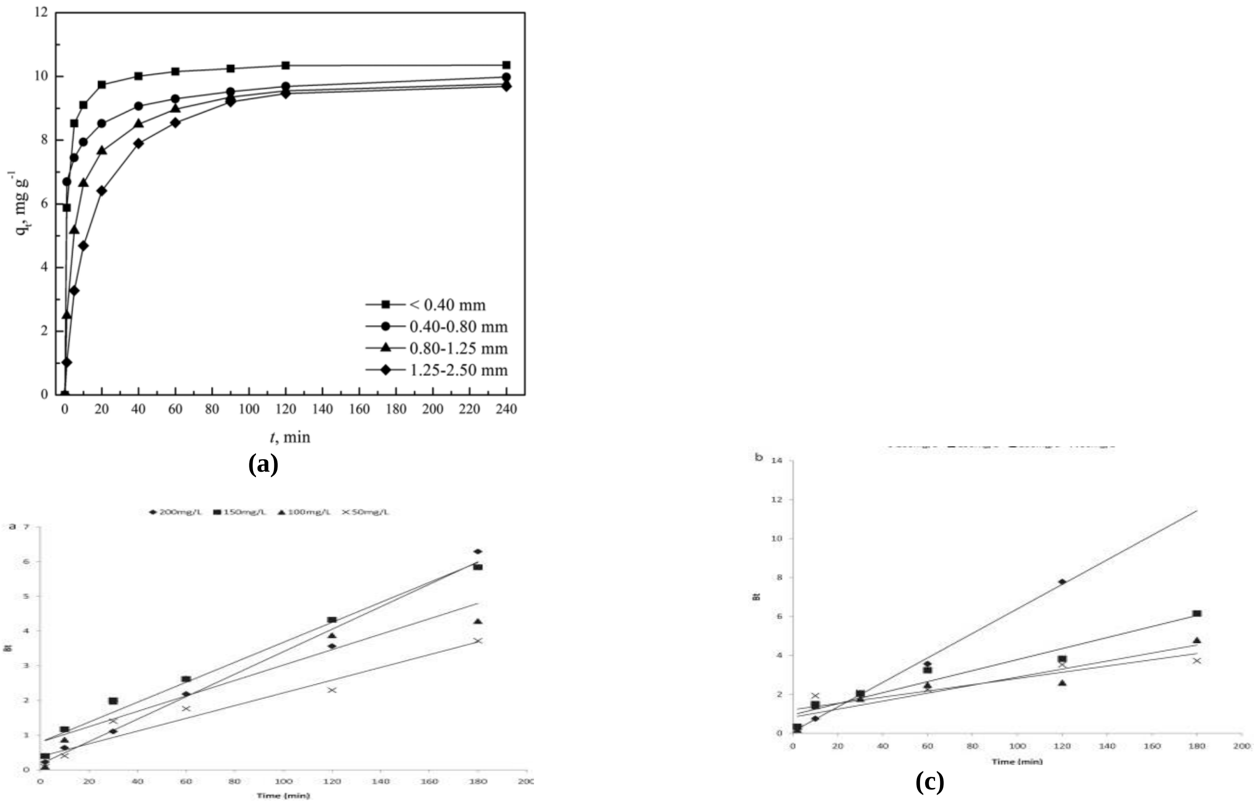


(b)



(c)

Figure-2. Extraction kinetic of Neem seeds powder at particle size (a) 0.85-1.40 mm; (b) 0.71-0.85 mm; (c) 0.425-0.71 mm using n-hexane as solvent.



(a)

(b)

(c)

Figure-3. Extraction kinetic of Neem seeds powder at particle size (a) 0.85-1.40 mm; (b) 0.71-0.85 mm; (c) 0.425-0.71 mm using ethanol as solvent.

Table-1. Parameters fitting of Neem oil extraction kinetics using n-hexane.

T	**0.85-1.40 mm**			**0.71-0.85 mm**			**0.425-0.71 mm**		
(^{0}C)	**Y_{Ai} Fitted**	**Y_{Ai} Experimental**	**k.a**	**Y_{Ai} Fitted**	**Y_{Ai} experimental**	**k.a**	**Y_{Ai} fitted**	**Y_{Ai} experimental**	**k.a**
30	35.8700	35.8901	0.3587	36.9500	36.9612	0.3695	38.0100	38.0266	0.3801
35	37.8300	37.8522	0.3783	38.5000	38.5585	0.3850	40.0000	40.0123	0.4001
40	39.1300	39.1514	0.3943	40.2100	40.2264	0.4021	41.6200	41.6302	0.4162
45	39.9800	39.9902	0.3998	41.4800	41.4983	0.4148	42.8800	42.8911	0.4287
50	41.0400	41.1429	0.4104	42.2900	42.3060	0.4228	43.7200	43.7263	0.4372

Table-2. Parameters fitting of Neem oil extraction kinetics using ethanol.

T	**0.85-1.40 mm**			**0.71-0.85 mm**			**0.425-0.71 mm**		
(^{0}C)	**Y_{Ai} Fitted**	**Y_{Ai} experimental**	**k.a**	**Y_{Ai} fitted**	**Y_{Ai} experimental**	**k.a**	**Y_{Ai} fitted**	**Y_{Ai} experimental**	**k.a**

30	30.9760	33.43	0.0594	31.4472	33.6847	0.0635	32.4377	33.9500	0.0675
35	32.8000	34.85	0.0584	33.302	35.3500	0.061	33.7679	35.9500	0.0615
40	34.1317	35.63	0.0651	34.574	35.9883	0.0655	34.9842	36.6300	0.0711
45	35.6329	37.64	0.0774	36.0747	37.9400	0.0776	36.5482	38.5400	0.0777
50	37.2790	39.1733	0.109	37.7718	39.7733	0.1085	38.3562	41.0823	0.1083

Thermodynamic parameters:

Thermodynamics parameters (ΔH , ΔS , and ΔG) for the extraction of neem oil using n-hexane and ethanol as solvents can be estimated using following equations,

$$\ln K = -\frac{\Delta G}{R}\frac{1}{T} = -\frac{\Delta H}{R}\frac{1}{T} + \frac{\Delta S}{R} \quad (6)$$

$$K = \frac{Y_T}{Y_u} = \frac{m_L}{m_S} \quad (7)$$

Where K is equilibrium constant, Y_T is yield percent of oil at temperature T, Y_u is percent of oil remaining in Neem seed, m_L is amount of Neem oil in liquid at equilibrium temperature T, m_S is amount of Neem oil in solid at equilibrium temperature T, R is gas constant, while ΔH , ΔS , and ΔG are enthalpy, entropy, and free energy of extraction, respectively.

The values of K and ΔG for extraction of Neem oil using n-hexane and ethanol as solvents were calculated using Eqs. (6) and (7) are given in Tables 3 and 4. The values of enthalpy and entropy of extraction are given in Table-5. The negative values of ΔG indicate that the extraction of Neem oil using n-hexane and ethanol are spontaneous process. The positive value of enthalpy indicates that the process is endothermic and require energy during process.

Table-3. Equilibrium constant of Neem oil extraction using n-hexane and ethanol.

T (K)	**1/T** (1/K)	**Equilibrium constant** (K)					
		0.85-1.40 mm		**0.71-0.85 mm**		**0.425-0.71 mm**	
		n-Hexane	**Ethanol**	**n-Hexane**	**Ethanol**	**n-Hexane**	**Ethanol**
303	0.00330033	3.3872	4.3516	3.1268	4.5351	2.9447	4.7401
308	0.003246753	4.3930	5.5650	3.7434	6.1347	3.7062	6.9640
313	0.003194888	5.6973	6.4991	4.7115	7.0235	4.3930	8.1721
318	0.003144654	6.9588	10.840	5.6973	11.9598	4.8067	14.9827
323	0.003095975	8.4149	20.2028	6.5535	29.7037	5.5845	55.4572

Table-4. Free energy of Neem oil extraction using n-hexane and ethanol.

T (K)	**1/T** (1/K)	ΔG (J/mol)					
		0.85-1.40 mm		**0.71-0.85 mm**		**0.425-0.71 mm**	
		n-Hexane	**Ethanol**	**n-Hexane**	**Ethanol**	**n-Hexane**	**Ethanol**
303	0.00330033	-2663.0574	-4298.1595	-2759.5630	-4425.2737	-3252.0303	-4562.6751
308	0.003246753	-3336.3060	-5158.0664	-3232.9716	-5485.8683	-3515.1134	-5928.8767
313	0.003194888	-3714.3888	-5777.2473	-3910.6174	-6056.1254	-4413.4913	-6627.2622
318	0.003144654	-3962.3262	-7951.8484	-4137.4696	-8437.8957	-5054.1845	-9763.0717
323	0.003095975	-4298.2758	-12855.1204	-4723.4840	-13370.9323	-5451.8852	-16968.0632

Table-5. Enthalpy and entropy of Neem oil extraction using n-hexane and ethanol at various particle size.

Particle size (mm)	ΔH (J/mol)		ΔS (J/mol)	
	n-Hexane	**Ethanol**	**n-Hexane**	**Ethanol**
0.85-1.40	37.03	115505.1730	0.13	392.0458
0.71-0.85	31.02	86687.0813	0.11	299.2475
0.425-0.71	25.33	75340.2695	0.09	263.7695

IV. CONCLUSIONS

The maximum yield obtained from extraction of neem oil research were 44.29% for n- hexane and 41.11% for ethanol at 50°C and 0.425-0.71 mm particle size. Based on psycho-chemical characteristics analysis, increasing temperature decreased iodine value but increased saponification, acid, and peroxide value which means increasing temperature increased neem oil yield but decreased neem oil quality. This extraction follows first order kinetic with smaller *k.a* value as decrease of temperature. It also found that ΔH is positive, ΔS is positive, and ΔG is negative indicating that this process are endotermic, irreversible, and spontaneous.

REFERENCES

[1]Puri H.S. 1999. Neem-The Divine Tree. Harwood Academic Publishers, Amsterdam.
[2]Ragasa C.Y., Nacpil Z.D., Natividad G.M., Tada M., Coll J.C. and Rideout J.A. 1997. Tetranortriterpenoids from Azadirachta Indica. Journal of Phytochemistry. 46: 555-558.
[3]Johnson S., Morgan E.D. and Peiris C.N. 1996. Development of the Major Triterpenoids and Oil in the Fruit and Seeds of Neem (Azadirachta indica). Journal of Annals Botany. 78: 383-388.
[4]Mongkholkhajornsilp D., Douglas S., Douglas P.L., Elkamel A., Teppaitoon W. and Pongamphai S. 2004. Supercritical CO2 Extraction of Nimbin from Neem Seeds-A Modeling Study. Journal of Food Engineering. 71: 331-340. 53
[5]Adeeko K.A. and Ajibola O.O. 1990. Processing Factors Affecting Yield and Quality of Mechanically Expressed Groundnut Oil. Journal of Agricultural Engineering. 45: 31-43.
[6]Khraisha Y.H. 2000. Retorting of Oil Shale Followed By Solvent Extraction of Spent Shale: Experiment and Kinetic Analysis. Journal of Energy Sources. 22: 347-355.
[7]Levenspiel O. 2003. Chemical Reaction Engineering. 3rd Ed., John Wiley and Sons Inc., New York.
[8]Choe E. and Min D.B. 2006. Mechanisms and Factors for Edible Oil Oxidation (Comprehensive Reviews in Food Science and Food Safety, Volume 5), Institute of Food Technologies, Ohio. ZMin D.B. and Steenson D.F. 1998. Crude Fat Analysis. Food Analysis. pp. 201-216.
[9] Fasina O.O. and Ajibola O.O. 1989. Mechanical Expression of Oil from Conophor Nut. Journal of Agricultural Engineering. 44: 275-287.
[10] Nielsen S.S. 1998. Food Analysis. An Aspen Publication, Maryland, USA. Engineers S.B.o.C. 1998. SBP Handbook of Oil Seeds, Oils, Fats and Derivatives. SBP Consultant &Engineers Pvt. Ltd., New Delhi.
[11] Herodez S.S., Hadolin M., Skerget M. and Knez Z. 2002. Solvent Extraction Study of Antioxidants from Balm (Melissa officinalis L.) Leaves. Journal of Food Chemistry.80:275-282.