EXTRACTION OF NEEM OIL (Azadirachta indica A. Juss) USING N-HEXANE AND ETHANOL: STUDIES OF OIL QUALITY, KINETIC AND THERMODYNAMIC

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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 ∆H is positive, ∆S is positive, and ∆G is negative indicating that this process are endotermic, irreversible, and spontaneous.

Keywords: oil, neem, extraction, kinetic, thermodynamic.

INTRODUCTION
Neem (Azadirachta indica A. Juss) is one of the very few trees known in the Indian subcontinent. This tree is belonged to Meliaceae 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. Bark 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.

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).

RESULTS AND DISCUSSIONS

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.
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 35-40°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,

\[
\frac{dW}{dt} = k_A(C_{At} - C_A)
\]

Where \(dW/dt\) is the mass transfer rate of neem oil (g/s), \(C_A\) and \(C_{At}\) 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

\[
\frac{dW}{dt} = \frac{k_A}{V}(W_{At} - W_A)
\]

\[
\frac{dW}{dt} = k_A(W_{At} - W_A)
\]

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, \(W_A = 0\).
- At any time \(t\), mass of Neem oil in bulk liquid is \(W_A = W_{At}\).

With those conditions, integration of Eq. (3) gives the following result,

\[
W_A = W_{At}[1 - \exp(-k_A t)]
\]

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

\[
Y_A = Y_{At}[1 - \exp(-k_A t)]
\]

Where \(Y_A\) and \(Y_{At}\) are yield of Neem oil in bulk liquid at time \(t\) and at equilibrium per mass of Neem seed.
The thermodynamic parameters (\(\Delta H\), \(\Delta S\), and \(\Delta G\)) for the extraction of neem oil using n-hexane and ethanol as solvents can be estimated using the following equations:

\[
\ln K = \frac{-\Delta G}{R} = \frac{-\Delta H}{RT} + \frac{\Delta S}{R}
\]

\[
K = \frac{Y_f}{Y_i} = \frac{m_L}{m_S}
\]

Where \(K\) is the equilibrium constant, \(Y_f\) is the yield percent of oil at temperature \(T\), \(Y_i\) is percent of oil remaining in Neem seed, \(m_L\) is amount of Neem oil in liquid at equilibrium temperature \(T\), and \(m_S\) is amount of Neem oil in solid at equilibrium temperature \(T\), \(R\) is gas constant, while \(\Delta H\), \(\Delta S\), and \(\Delta G\) are enthalpy, entropy, and free energy of extraction, respectively. The values of \(K\) and \(\Delta G\) 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 \(\Delta G\) 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 requires energy during process.
Table 3. Equilibrium constant of Neem oil extraction using n-hexane and ethanol.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (1/K)</th>
<th>n-Hexane</th>
<th>Ethanol</th>
<th>n-Hexane</th>
<th>Ethanol</th>
<th>n-Hexane</th>
<th>Ethanol</th>
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<tr>
<td></td>
<td></td>
<td>0.85-1.40 mm</td>
<td></td>
<td>0.71-0.85 mm</td>
<td></td>
<td>0.425-0.71 mm</td>
<td></td>
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<td>303</td>
<td>0.00330033</td>
<td>3.3872</td>
<td>4.3516</td>
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<td>4.5351</td>
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<td>4.7401</td>
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<td>4.3930</td>
<td>5.5650</td>
<td>3.7434</td>
<td>6.1347</td>
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<td>5.6973</td>
<td>6.4991</td>
<td>4.7115</td>
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<td>10.840</td>
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<td>29.7037</td>
<td>5.5845</td>
<td>55.4572</td>
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Table 4. Free energy of Neem oil extraction using n-hexane and ethanol.

<table>
<thead>
<tr>
<th>T (K)</th>
<th>1/T (1/K)</th>
<th>ΔG (J/mol)</th>
<th>n-Hexane</th>
<th>Ethanol</th>
<th>n-Hexane</th>
<th>Ethanol</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>0.85-1.40 mm</td>
<td></td>
<td>0.71-0.85 mm</td>
<td></td>
<td>0.425-0.71 mm</td>
</tr>
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<td>303</td>
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<td>-2663.0574</td>
<td>-4298.1595</td>
<td>-2759.5630</td>
<td>-4425.2737</td>
<td>-3252.0303</td>
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<tr>
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<td>-13370.9323</td>
<td>-5451.8852</td>
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Table 5. Enthalpy and entropy of Neem oil extraction using n-hexane and ethanol at various particle size.

<table>
<thead>
<tr>
<th>Particle size (mm)</th>
<th>ΔH (J/mol)</th>
<th>ΔS (J/mol)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>n-Hexane</td>
<td>Ethanol</td>
</tr>
<tr>
<td>0.85-1.40</td>
<td>37.03</td>
<td>115505.1730</td>
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<tr>
<td>0.71-0.85</td>
<td>31.02</td>
<td>86687.0813</td>
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<td>0.425-0.71</td>
<td>25.33</td>
<td>75340.2695</td>
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</table>

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,α 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.

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