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# Evaluation of ethanolamide based nonionic biosurfactant materials from chemically modified castor oil and used palm oil waste

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Successful preparation of the ethanolamide based nonionic biosurfactant materials from castor oil and used palm oil waste through a chemical modification process has been reported. Both oil wastes have been transesterified with methanol under the alkaline condition to yield 93.32 and 80.30% of methyl esters. The ricinoleic acid and 9,10,12-trihydroxystearic acid compounds are obtained in 93.44 and 94.86% yield; while the amidation of the methyl esters in a solvent-free reaction gives ricinoleyl ethanolamide in 49.81% yield, and biomaterials containing lauryl ethanolamide, myristyl ethanolamide, palmityl ethanolamide derivatives yielded in 74.48%. The chemical structures of the products have been confirmed by FTIR, GC-MS, and <sup>1</sup>H-NMR spectrometers. Almost all biosurfactant materials gave higher HLB and lower surface tension compared with the Tween 80 as a positive control. Even though only ricinoleic acid and ethanolamide derivatives from used palm oil give a stable foam volume up to 70 mL for 90 min and also give a stable emulsion between distilled water and gasoline to 5 days, which is remarkable. These findings show that the ethanolamide derivatives from castor oil and used palm oil waste are promising nonionic biosurfactant materials for industrial applications.

Keywords: Castor oil, Ethanolamide, Nonionic Biosurfactant, Oil waste, Used palm oil

Biomaterials are attracting world attention as future alternative materials due to the scarcity of crude oil, abundant natural resources, environmentally friendly material, and so on<sup>1-10</sup>. Biosurfactant becomes a pivotal commercial product for surface science due to its biodegradable property as well as its ability to reduce the surface tension between two immiscible phases<sup>11</sup>. Biosurfactant is a biochemical based surfactant mostly derived from the plant oil containing hydrophilic and hydrophobic moieties on its chemical structure<sup>12-14</sup>. In general, there are three types of biosurfactants, *i.e.*, nonionic, cationic, and anionic biosurfactants in which depend on the type of functional groups. Either cationic or anionic biosurfactant contains positive or negative charge of the polar functional groups, respectively. While nonionic biosurfactant contains neutral-polar functional groups, such as alcohol, ester, ether, etc. Tween80 is one of the commercially available nonionic biosurfactants. However, its application is limited due to its low Hydrophilic Lipophilic Balance (HLB) value (3.450). Therefore, researchers are putting their effort into the design and development of nonionic biosurfactants from the available raw materials<sup>15</sup>.

Hundreds of nonionic biosurfactant materials have been developed due to their high chemical and thermal stability, as well as their possibility to be used for an enhanced oil recovery process<sup>16-21</sup>. According to Griffin's theory, the physicochemical properties of the biosurfactants depend on the balance of the hydrophilic and lyophilic functional groups. Vanavil et al. prepared biosurfactant material from fermentation of palm oil and glucose using Pseudomonas aeruginosa while Amruta et al. prepared a biosurfactant material from Bacillus subtilis, however the technical procedure for preparation of microorganism needs certain temperature, viscosity and pH condition making their process was unfavourable for industrial application<sup>15,17</sup>. In 2006, Awang and coworkers prepared 9,10dihydroxystearyl ethanolamide derivative through a synthetic pathway and it was able to form a stable foam and emulsion in alkaline media<sup>21</sup>. However, practice preparation and application from the abundantly available raw materials such as edible oil or used oil waste have not been approached yet.

In the present work, ethanolamide based nonionic biosurfactant materials were prepared from castor and used palm oil waste to increase their economic value and reduce the amount of their disposed waste. Both castor oil and used palm oil waste were utilized because they contain around 80% of ricinoleic acid and around 40% of oleic acid<sup>22,23</sup>. The ricinoleic acid and oleic acid can be chemically modified to produce ethanolamide based nonionic biosurfactant materials through a solvent-free reaction method. Their chemical modification process is shown in Figure 1 Furthermore, their nonionic biosurfactant properties such as HLB value determination, surface tension, and critical micelle concentration measurement and foam and emulsion stability investigation were also evaluated and compared with Tween 80 as a positive control.

# **Experimental Section**

### Materials

The used chemicals such as potassium hydroxide, sodium hydroxide, glacial acetic acid, methanol, ethanolamine, sodium thiosulfate, hydrochloric acid, anhydrous sodium sulfate, chloroform, acetonitrile, ethanol, and N,O-bis(trimethylsilyl)trifluoroacetamide (BSTFA) were purchased from Merck in pro analysis grade and used without further purification. Meanwhile, the castor oil and used palm oil were supplied by the Organic and Biochemistry Laboratory of Chemistry Department, Universitas Gadjah Mada.

# Procedure

# Determination of free fatty acid content and peroxide value

The plant oil (2.00 g) was dissolved in methanol (50 mL) and the mixture was refluxed for 30 min. The mixture was cooled down to room temperature ( $\pm 25$  °C) and titrated by 0.10 M KOH standard solution with phenolphthalein as an indicator. The free fatty acid content (%FFA) is calculated by equation (1).

$$\% FFA = \frac{V \times MW \, fa}{20,000} \times 100\% \qquad \dots (1)$$

whereas V is the required volume of 0.10 M KOH solution to reach the titration endpoint, and MW fa is the average molecular weight of fatty acids<sup>24</sup>.



Fig. 1 — The synthesis scheme of ethanolamide derivatives from castor oil and used palm oil

On the other hand, the peroxide value (*PV*) was determined by a standard method as described by Kuselman *et al.*<sup>25</sup>. The plant oil (0.50 g) was dissolved in chloroform:glacial acetic acid 2:3 v/v (30 mL). The saturated potassium iodide solution (0.5 mL) was added and the mixture was kept in the darkroom for 30 min. The mixture was titrated by 0.10 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> standard solution with amylum as an indicator. The *PV* is calculated by equation (2).

$$PV = 200 V' \qquad \dots (2)$$

whereas V' is the required volume of 0.10 M Na<sub>2</sub>S<sub>2</sub>O<sub>3</sub> solution to reach the titration endpoint.

#### Transesterification of plant oil

The plant oil (50.0 g) was added into 1.25 M NaOH in methanol (150 mL) and the mixture was heated at 60°C for 90 min. The mixture was then neutralized by 6.0 M HCl and extracted with petroleum ether (150 mL) in a separatory funnel. The organic phase was dried over anhydrous sodium sulfate and evaporated to obtain the desired product as a yellowish liquid.

Methyl ricinoleate of castor oil was yielded in 93.32%. Retention time 7.40 min with 86.10% methyl ricinoleate. FTIR (wavenumber/cm<sup>-1</sup>): 3425 (O-H alcohol stretching), 3009 (C-H sp<sup>2</sup> stretching), 2939-2855 (C-H sp<sup>3</sup> stretching), 1736 (C=O ester stretching), 1458 (-CH<sub>2</sub>- bending), 1361 (-CH<sub>3</sub> bending), 1196 (C-O ester stretching), 725 (cis C=C bending).

Methyl esters of used palm oil was produced in 80.30% yield. Retention time 22.0 min (9.53%) for methyl laurate (M<sup>+</sup>-OCH<sub>3</sub> found at m/z = 183), 26.9 min (2.91%) for methyl myristate (M<sup>+</sup>-OCH<sub>3</sub> found at m/z = 211), 31.3 min (36.7%) for methyl palmitate (M<sup>+</sup> found at m/z = 270) and 34.8 min (42.2%) for methyl oleate (M<sup>+</sup> found at m/z = 296). FTIR (wavenumber/cm<sup>-1</sup>): 3000 (C-H sp<sup>2</sup> stretching), 2924-2854 (C-H sp<sup>3</sup> stretching), 1743 (C=O ester stretching), 1458 (-CH<sub>2</sub>-bending), 1373 (-CH<sub>3</sub> bending), 1165 (C-O ester stretching), 725 (cis C=C bending).

#### Synthesis of ricinoleic acid

The methyl ester (32.0 g, 102 mmol) was added into 1.75 M KOH in ethanol (100 mL) and the mixture was refluxed for 120 min. The mixture was acidified by 0.6 M HCl into pH 2.0 and extracted with chloroform (50 mL) in a separation funnel. The organic phase was dried and evaporated to obtain the desired product as a yellow liquid in 93.44% yield. FTIR (wavenumber/cm<sup>-1</sup>): 3393 (O-H carboxylic acid stretching), 3009 (C-H sp<sup>2</sup> stretching), 2930-2856 (C-H sp<sup>3</sup> stretching), 1713 (C=O carboxylic acid stretching), 1466 (-CH<sub>2</sub>- bending), 1357 (-CH<sub>3</sub> bending), 1124 (C-O carboxylic acid stretching), 725 (cis C=C bending). <sup>1</sup>H-NMR (CDCl<sub>3</sub>, chemical shift/ppm): 6.40 (broad singlet, 2H, -OH and -CO<sub>2</sub>H), 5.40 (multiplet, 2H, -HC=CH-), 3.65 (multiplet, 1H, -CH-OH), 2.25-1.20 (multiplet, 26H, -CH<sub>2</sub>-), 0.90 (triplet, 3H, -CH<sub>3</sub>).

# Synthesis of 9,10,12-trihydroxystearic acid

Ricinoleic acid (3.50 g, 12 mmol) and KOH (0.81 g, 14 mmol) were dissolved in distilled water (450 mL) at 0-5 °C. The 1.30% b/v KMnO<sub>4</sub> solution (250 mL, 21 mmol) was added dropwise into the cooled mixture. After 30 min, Na<sub>2</sub>SO<sub>3</sub> (7.5 g, 59 mmol) and two drops of concentrated sulfuric acid were added into the mixture. The formed precipitation was collected and washed with cooled distilled water. The solid product was recrystallized with ethanol to obtain the desired product as a white solid in 94.86% vield. m.p. 138°C. FTIR (wavenumber/cm<sup>-1</sup>): 3377 (O-H carboxylic acid stretching), 2922-2851 (C-H sp<sup>3</sup> stretching), 1701 (C=O carboxylic acid stretching), 1468 (-CH<sub>2</sub>- bending), 1357 (-CH<sub>3</sub> bending), 1193 (C-O carboxylic acid stretching). <sup>1</sup>H-NMR (DMSO-d<sub>6</sub>, chemical shift/ppm): 3.30 (multiplet, 3H, -CH-OH), 2.10-1.25 (multiplet, 24H, -CH<sub>2</sub>-), 0.90 (triplet, 3H, -CH<sub>3</sub>).

#### Amidation of methyl ester

The methyl ester (64.0 mmol) and ethanolamine (7.68 g, 128 mmol) were mixed, and it was refluxed for 180 min. The mixture was diluted by methanol: distilled water 1:1 v/v and extracted with chloroform. The organic phase was dried and evaporated, and then the product was recrystallized with acetonitrile to obtain the desired product.

Ricinoleyl ethanolamide of castor oil was produced as brownish powder in 49.81% yield. m.p. 53°C. Retention time 27.9 min with 43.77% ricinoleyl ethanolamide. FTIR (wavenumber/cm<sup>-1</sup>): 3294 (O-H alcohol stretching), 3009 (C-H sp<sup>2</sup> stretching), 2924-2855 (C-H sp<sup>3</sup> stretching), 1643 (C=O amide stretching), 1466 (-CH<sub>2</sub>- bending), 1361 (-CH<sub>3</sub> bending), 1056 (C-N amide stretching), 718 (cis C=C bending). MS derivatization using silylation method with BTSFA reagent: m/z = 514 (M<sup>+</sup>-C<sub>3</sub>H<sub>8</sub> for C<sub>26</sub>H<sub>55</sub>NO<sub>3</sub>Si<sub>3</sub><sup>+</sup>), 498 (M<sup>+</sup>-C<sub>4</sub>H<sub>11</sub> for C<sub>25</sub>H<sub>52</sub>NO<sub>3</sub>Si<sub>3</sub><sup>+</sup>), 408 (M<sup>+</sup>-C<sub>7</sub>H<sub>21</sub>O Si for C<sub>22</sub>H<sub>42</sub>NO<sub>2</sub>Si<sub>2</sub><sup>+</sup>), 338 (M<sup>+</sup>-  $C_{10}H_{27}O$  Si<sub>2</sub> for  $C_{19}H_{36}NO_2Si^+$ ), 160 ( $C_6H_{14}NO_2Si^+$ ), 146 (base peak,  $C_5H_{12}NO_2Si^+$ ), 73 ( $C_3H_9Si^+$ ).

Ethanolamide derivatives of used palm oil yielded as a yellowish powder in 74.48%. m.p. 78.0 °C. FTIR (wavenumber/cm<sup>-1</sup>): 3294 (O-H alcohol stretching), 3011 (C-H sp<sup>2</sup> stretching), 2924-2854 (C-H sp<sup>3</sup> stretching), 1643 (C=O amide stretching), 1465 (-CH<sub>2</sub>- bending), 1389 (-CH<sub>3</sub> bending), 1056 (C-N amide stretching), 717 (cis C=C bending).

MS derivatization using silulation method with BTSFA reagent:

Retention time 15.2 min (9.31%) for lauryl ethanolamide with m/z = 299 (M<sup>+</sup>-C<sub>4</sub>H<sub>12</sub>Si for C<sub>16</sub>H<sub>33</sub>NO<sub>2</sub>Si<sup>+</sup>), 271 (M<sup>+</sup>-C<sub>6</sub>H<sub>16</sub>Si for C<sub>14</sub>H<sub>29</sub>NO<sub>2</sub>Si<sup>+</sup>), 173 (M<sup>+</sup>-C<sub>13</sub>H<sub>30</sub>Si for C<sub>7</sub>H<sub>15</sub>NO<sub>2</sub>Si<sup>+</sup>), 144 (C<sub>6</sub>H<sub>14</sub>NOSi<sup>+</sup>), 117 (C<sub>5</sub>H<sub>13</sub>OSi<sup>+</sup>), 73 (base peak, C<sub>3</sub>H<sub>9</sub>Si<sup>+</sup>), 43 (C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>).

Retention time 17.1 min (4.52%) for myristyl ethanolamide with m/z = 327 (M<sup>+</sup>-C<sub>4</sub>H<sub>12</sub>Si for C<sub>18</sub>H<sub>37</sub>NO<sub>2</sub>Si<sup>+</sup>), 299 (M<sup>+</sup>-C<sub>6</sub>H<sub>16</sub>Si for C<sub>16</sub>H<sub>33</sub>NO<sub>2</sub>Si<sup>+</sup>), 283 (M<sup>+</sup>-C<sub>6</sub>H<sub>16</sub>OSi for C<sub>16</sub>H<sub>33</sub>NOSi<sup>+</sup>), 247 (M<sup>+</sup>-C<sub>12</sub>H<sub>24</sub> for C<sub>10</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>2</sub><sup>+</sup>), 173 (M<sup>+</sup>-C<sub>15</sub>H<sub>34</sub>Si for C<sub>7</sub>H<sub>15</sub>NO<sub>2</sub>Si<sup>+</sup>), 168 (C<sub>12</sub>H<sub>24</sub><sup>+</sup>), 73 (base peak, C<sub>3</sub>H<sub>9</sub>Si<sup>+</sup>), 43 (C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>).

Retention time 18.8 min (44.9%) for palmityl ethanolamide with m/z = 355 (M<sup>+</sup>-C<sub>4</sub>H<sub>12</sub>Si for C<sub>20</sub>H<sub>41</sub>NO<sub>2</sub>Si<sup>+</sup>), 327 (M<sup>+</sup>-C<sub>6</sub>H<sub>16</sub>Si for C<sub>18</sub>H<sub>37</sub>NO<sub>2</sub>Si<sup>+</sup>), 311 (M<sup>+</sup>-C<sub>6</sub>H<sub>16</sub>OSi for C<sub>18</sub>H<sub>37</sub>NOSi<sup>+</sup>), 283 (M<sup>+</sup>-C<sub>8</sub>H<sub>20</sub>OSi for C<sub>16</sub>H<sub>33</sub>NOSi<sup>+</sup>), 186 (M<sup>+</sup>-C<sub>15</sub>H<sub>33</sub>OSi for C<sub>9</sub>H<sub>20</sub>NOSi<sup>+</sup>), 173 (M<sup>+</sup>-C<sub>15</sub>H<sub>38</sub>Si for C<sub>7</sub>H<sub>15</sub>NO<sub>2</sub>Si<sup>+</sup>), 117 (base peak, C<sub>5</sub>H<sub>13</sub>OSi<sup>+</sup>), 73 (C<sub>3</sub>H<sub>9</sub>Si<sup>+</sup>).

Retention time 20.2 min (37.4%) for oleyl ethanolamide with m/z = 396 (M<sup>+</sup>-C<sub>3</sub>H<sub>8</sub>Si for C<sub>23</sub>H<sub>47</sub>NO<sub>2</sub>Si<sup>+</sup>), 381 (M<sup>+</sup>-C<sub>4</sub>H<sub>12</sub>Si for C<sub>22</sub>H<sub>43</sub>NO<sub>2</sub>Si<sup>+</sup>), 353 (M<sup>+</sup>-C<sub>6</sub>H<sub>16</sub>Si for C<sub>20</sub>H<sub>39</sub>NO<sub>2</sub>Si<sup>+</sup>), 235 (M<sup>+</sup>-C<sub>17</sub>H<sub>30</sub> for C<sub>9</sub>H<sub>25</sub>NO<sub>2</sub>Si<sub>2</sub><sup>+</sup>), 205 (M<sup>+</sup>-C<sub>10</sub>H<sub>42</sub>NO<sub>2</sub>Si<sub>2</sub> for C<sub>16</sub>H<sub>13</sub><sup>+</sup>), 173 (M<sup>+</sup>-C<sub>17</sub>H<sub>36</sub>Si for C<sub>7</sub>H<sub>15</sub>NO<sub>2</sub>Si<sup>+</sup>), 43 (base peak, C<sub>2</sub>H<sub>3</sub>O<sup>+</sup>).

# Physicochemical properties evaluation as nonionic biosurfactant material

The HLB values of the nonionic biosurfactant were calculated according to the proposed equation by Griffin, as shown in equation (3), whereas H and L are the amount of the hydrophilic and lyophilic substituents, respectively.

$$HLB = 7 + \sum H + \sum L \qquad \dots (3)$$

The interfacial tension value of the nonionic biosurfactant was determined by the capillary rise

method. Concisely, the nonionic biosurfactant was dissolved in ethanol at 0.5, 1.0, and 1.5 g  $L^{-1}$  concentration. The capillary rise method was carried out by pulling up to the sample solution on the capillary glass to increase the fluid position. After releasing the pressure, the fluid was dropped slowly and returned to the equilibrium position, and the difference in traveling distance from the initial and equilibrium position was observed. The measurement was replicated three times.

The critical micelle concentration of the nonionic biosurfactant was carried out by a turbidimetry method at 28 °C as reported before. The turbidimeter was calibrated by using AMCOTM 2020 1.0 and 10 NTU standard solutions. The turbidity measurements of the nonionic biosurfactant in distilled water at 0.5, 1.0, and 1.5 g L<sup>-1</sup> concentrations were measured three times.

Finally, the foam and emulsion stability of the nonionic biosurfactant was investigated. The nonionic biosurfactant in distilled water at 5, 10, and 15 g L<sup>-1</sup> concentration was stirred for 1 room temperature. Afterward, the foam stability was evaluated by measuring the formed foam volume above the fluid after 15, 30, 45, 75, and 90 min. Meanwhile, the emulsion stability was investigated by mixing gasoline and the nonionic biosurfactant solution in 1:1 volume ratio and measuring the emulsification index after 1, 2, 3, 4 and 5 days.

# **Results and Discussion**

# Synthesis of ethanolamide derivatives from castor oil and used palm oil waste

In the present work, castor oil and used palm oil were evaluated as possible resources to prepare ethanolamide based nonionic biosurfactant materials. At first, the free fatty acid content and peroxide value of those oils were characterized because both parameters reflect the quality of the oil for industrial applications. The free fatty acid contains measured the hydrolyzed fatty acids from their triglyceride forms due to humidity or long storage condition. Meanwhile, peroxide value measured the peroxide content on the plant oil due to the oxidation process. According to the Indonesian standard regulation<sup>26</sup>, the free fatty acid content and of the resources should be less than 2.5% and 3.00 meq kg<sup>-1</sup> while the peroxide value should be less than 3.00 meq kg<sup>-1</sup>. From the present study, it was found that the free fatty acid contents of castor oil and used palm oil waste were 0.24 and 0.73%, while the peroxide value of castor oil and used palm oil waste were 1.85 and 5.34 meq kg<sup>-1</sup>, respectively. Those values are still less than the Indonesian standards except for used palm oil waste because of the impurities content in the used palm oil waste. Even though they were found as waste, this preliminary investigation was good enough for their chemical modification process.

First of all, both oils were transformed into the form of their methyl esters through а transesterification process under alkaline conditions. It was found that the yields of the transesterification process of castor oil and used palm oil were satisfied enough in 93.32 and 80.30%. The transesterification process gave methyl ricinoleate (86.10%) from the castor oil, and a mixture of methyl laurate (9.53%), methyl myristate (2.91%), methyl palmitate (36.7%) and methyl oleate (42.2%) from the used palm oil by GC-MS analysis. Furthermore, from the FTIR characterization, the presence of the C=O and C-O ester stretching peaks at 1743-1736 and 1196-1165 cm<sup>-1</sup> confirmed that the transesterification of castor oil and used palm oil has been successfully performed.

Afterward, the ricinoleic acid and 9,10,12trihydroxystearic acid biosurfactants were prepared via hydrolysis and oxidation reactions of the methyl ricinoleate, respectively. The hydrolysis process of methyl ricinolate gave ricinoleic acid in 93.44% yield. The chemical structure of ricinoleic acid was confirmed by FTIR and <sup>1</sup>H-NMR analysis by the presence absorption peak of O-H and C=O carboxylic acid functional groups at 3393 and 1713 cm<sup>-1</sup> as well as a broad singlet signal at 6.40 ppm for the proton of -CO<sub>2</sub>H. The oxidation reaction of ricinoleic acid gave 9,10,12-trihydroxystearic acid in 94.86% yield. It was confirmed by FTIR and <sup>1</sup>H-NMR analysis that the 9,10,12-trihydroxystearic acid compound had been successfully obtained by a bathochromic shift of O-H stretching peak from 3393 to 3377 cm<sup>-1</sup> due to more stable hydrogen bonding as well as the disappearance of cis C=C peak at 725 cm<sup>-1</sup>. From the <sup>1</sup>H-NMR analysis, the -CO<sub>2</sub>H signal at 6.40 ppm was disappeared, proving that the transformation of ricinoleic acid to 9,10,12-trihydroxystearic acid has been successfully carried out.

The final chemical modification process was an amidation reaction to obtain the ethanolamide derivative as the nonionic biosurfactant material. The amidation process was performed by a solvent-free process between methyl ester and ethanolamine reagents. The desired biomaterials were purified by a recrystallization process with acetonitrile to yield ricinoleyl ethanolamide and ethanolamide derivative of used palm oil in 49.81 and 74.48%, respectively. The success of amidation process was reflected by the FTIR and GC-MS of the products. From the FTIR spectra of the ethanolamide derivatives, the presence of O=C-N group was indicated by the presence of its absorption peaks at 1643 (C=O) and 1056 (C-N) cm<sup>-1</sup>. Further characterization was employed by a silvlation method with BTSFA reagent to decrease the boiling point of those ethanolamide derivatives. The ricinoleyl ethanolamide, lauryl ethanolamide, myristyl ethanolamide, palmityl ethanolamide and oleoyl ethanolamide derivatives gave m/z = 514 (M<sup>+</sup>-C<sub>3</sub>H<sub>8</sub> for  $C_{26}H_{55}NO_3Si_3^+$ ), 299 (M<sup>+</sup>-C<sub>4</sub>H<sub>12</sub>Si for C<sub>16</sub>H<sub>33</sub>NO<sub>2</sub>Si<sup>+</sup>), 327 ( $M^+-C_4H_{12}Si$  for  $C_{18}H_{41}NO_2Si^+$ ), 355 ( $M^+-C_4H_{12}Si$  $C_{20}H_{41}NO_2Si^+$ ), and 396 (M<sup>+</sup>-C<sub>3</sub>H<sub>8</sub>Si for for  $C_{23}H_{47}NO_2Si^+$ ) on their corresponding MS spectra, respectively.

# Evaluation of the physicochemical properties of ethanolamide derivatives as the nonionic biosurfactant materials

The physicochemical properties of ethanolamide derivatives from castor and used palm oil were investigated to evaluate their potential application as the nonionic biosurfactant materials. At first, the theoretical HLB value was calculated according to the Griffin method, as listed in Table 1. The HLB values of ricinoleic acid, 9,10,12-trihydroxystearic acid, ricinoleyl ethanolamide, and ethanolamide derivatives from used palm oil were 2.925, 6.724, 11.18, and 10.04, respectively. Except for ricinoleic acid, those HLB values were higher than the HLB value of Tween 80, demonstrating that they were potential to be applied for nonionic biosurfactant materials.

The surface tension values were pivotal since the low surface tension determine the efficiency of the emulsion formation between two immiscible fluids. The surface tension values of the materials were listed in Table 2. The surface tension of ethanol was 21.70 dyne cm<sup>-1</sup>, and it was decreased by increasing the concentration of the biosurfactant materials. The order of the surface tension of the ethanolic solution

Table 1 — The HLB values of the evaluated sample and Tween
80 as the positive control

Sample name	HLB values
Ricinoleic acid	2.925
9,10,12-Trihydroxystearic acid	6.724
Ricinoleyl ethanolamide	11.180
Ethanolamide derivatives from used palm oil	10.040
Tween 80	3.450

Table 2 — Surface tension values of the evaluated sample and   Tween 80 as the positive control			
Sample name	Concentration (g L <sup>-1</sup> )	Surface tension (Dyne cm <sup>-1</sup> )	
Ricinoleic acid	0.5 1.0	21.00 19.38	
	1.5	18.90	
9,10,12-Trihydroxystearic acid	0.5	18.81	
	1.0	17.70	
	1.5	15.73	
Ricinoleyl ethanolamide	0.5	19.59	
	1.0	17.57	
	1.5	14.44	
Ethanolamide derivatives from	0.5	21.24	
used palm oil	1.0	19.97	
	1.5	18.70	
Tween 80	0.5	21.60	
	1.0	19.34	
	1.5	17.38	

containing 0.5 g  $L^{-1}$  from a higher to a lower value was Tween80 > ethanolamide derivatives from used palm oil > ricinoleic acid > 9,10,12-trihydroxystearic acid > ricinoleyl ethanolamide. It means that the prepared nonionic biosurfactant materials in this work gave lower surface tension compared with the positive control, *i.e.*, Tween80, which is remarkable.

The critical micelle concentration of the samples determined through a turbidimetry was also technique. The critical micelle concentration reflects the minimum required concentration to form a micelle structure of the surfactant. A lower critical micelle concentration is favorable because it is economically feasible for industrial applications. Figure 2 shows the turbidity profile of the nonionic biosurfactant materials from 0.1-2.0 g  $L^{-1}$  concentration in the distilled water. It was found that the critical micelle concentration of Tween80, ricinoleic acid, 9,10,12trihydroxystearic acid, ricinoleyl ethanolamide and ethanolamide derivatives from used palm oil were 1.1, 0.7, 1.4, 1.7 and 0.5 g  $L^{-1}$ , respectively. From this experiment, only ricinoleic acid and ethanolamide derivatives from used palm oil exhibit lower critical micelle concentration than Tween 80 as a positive control. Therefore, further characterization will be focused on ethanolamide derivatives from used palm oil due to its lowest critical micelle concentration in the present study.

The foam and emulsion stability study of the ethanolamide derivatives from used palm oil was carried out to evaluate the durability application as the nonionic biosurfactant material and shown in



Fig. 2 — The turbidity profile of ricinoleic acid (cross), 9,10, 12-trihydroxystearic acid (square), ricinoleyl ethanolamide (star), ethanolamide derivatives from used palm oil (circle) and Tween80 (triangle).



Fig. 3 — (a) The foam stability of the ethanolamide derivatives from used palm oil at 10 (circle), 15 (square) and 20 (triangle) g  $L^{-1}$  concentration. (b) The emulsion stability of the ethanolamide derivatives from used palm oil at 10 g  $L^{-1}$  concentration in gasoline:surfactant solution 1:1 volume ratio.

Figure 3. The foam volume was increased by increasing surfactant concentration, and the foam was stable for 0-90 min with a negligible change in its volume (Figure 3(a)). Furthermore, the emulsion between distilled water and gasoline in 1:1 volume ratio was also stable up to 5 days (Figure 3(b)), which is remarkable. These findings are pivotal for the utilization of used palm oil as the raw material to prepare the nonionic biosurfactant materials.

#### Conclusions

The ethanolamide derivatives from castor oil and used palm oil has been successfully prepared through a chemical modification process involving transesterification, hydrolysis, oxidation. and amidation reactions. Transesterification reaction of castor oil and used palm oil are achieved in 93.32 and 80.30%, while the hydrolysis of methyl ricinoleate and oxidation of ricinoleic acid give the desired compounds in 93.44 and 94.86% yield, respectively; and the amidation reaction of methyl ester and ethanolamine produced ricinoleyl ethanolamide and ethanolamide of used palm oil in 49.81 and 74.48%.

From the physicochemical properties' evaluation, the HLB values of 9,10,12-trihydroxystearic acid, ricinoleyl ethanolamide, and ethanolamide of used palm oil are higher than the HLB value of Tween 80 as a positive control. All of those products are found to decrease the surface tension at a concentration of  $1.5 \text{ g L}^{-1}$ . While the ricinoleic acid and ethanolamide derivatives of used palm oil exhibit lower critical micelle concentrations than that of Tween 80 as a positive control. Furthermore, the ethanolamide derivatives from used palm oil gave a stable foam volume for 90 min and also gave a stable emulsion between distilled water and gasoline in 1:1 volume ratio up to 5 days.

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