Refining and Physicochemical Test of Tengkawang oil *Shorea stenoptera* Origin Sintang District West Kalimantan

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**Abstract.** The oil from Tengkawang fruit (*Shorea stenoptera*) has been processed by indigenous people in West Kalimantan as cooking oil and margarine. This research examined the degumming process, neutralization and bleaching of Tengkawang oil to reduce the high acid and peroxide numbers resulted from traditional processes. The oil produced at each stage of the refining process were tested for their physicochemical properties by calculating the acid, iodine and peroxide numbers. Respectively, the values of acid number (mg NaOH/100 g sample), iodine number (g I$_2$/100 g sample), and peroxide number (mg equivalent O$_2$/kg sample) for initial Tengkawang fat were 10.14; 32.49 and 10.98; for Tengkawang fat after degumming were 10.25; 28.81 and 10.88; for Tengkawang fat after neutralization were 6.09; 30.52 and 5.57; and for Tengkawang fat after bleaching were 6.14; 31.39 and 5.55. The acid number of Tengkawang oil after neutralization process with variation of volume 5, 7.5 and 10 % were 7.83; 6.14 and 3.12 mg NaOH/100 g sample, respectively. The refining process increased the quality of physicochemical properties of Tengkawang oil to fall into industrial grade.

1. **Introduction**

One of the export commodities of non-timber forest product group is Tengkawang fruit. Tengkawang fruit is produced by several types of *Shorea* that belong to *Dipterocarpaceae* family [1]. Tengkawang can grow naturally on the mountain slopes at an altitude of 5 - 1,000 mdpl, on all soil types, provided it is not sandy and sufficient sunlight [2]. There are 12 types of Tengkawang protected by PP. 7 of 1999, namely: *Shorea stenoptera*, *S. gysbertiana*, *S. pinanga*, *S. compressa*, *S. seminis*, *S. martiana*, *S. mexistopteryx*, *S. beccariana*, *S. micrantha*, *S. palembanica*, *S. lepidota*, and *S. singkawang* [3]. The trade name of Tengkawang fruits is Illipé nut or borneo tallow nut [4].

Total consumption of vegetable oil in Indonesia increased by 335 % since 1980 [5]. Tengkawang is one of the potential bio-based sources. The use of bio-based resources for the production of added value products is a key element of sustainable development. The fat content of Tengkawang ranged from 50-70 % [6]. However, the physicochemical properties of Tengkawang fat are influenced by the type, seed size, seed maturity, and storage time [2].

Tengkawang fruit processing into fat can be done in three ways, namely the way of forging, boiling and dissolving (extraction) using organic solvents [6]. The current practice of extracting Tengkawang fat by indigenous people in Kalimantan is through the seed pressing. This current processing is still traditional so that the yield and quality of processed oil is not optimal [7]. It is characterized by high acid and peroxide number that is 10.14 mg NaOH/100 g sample and 10.98 mg equivalent O$_2$/kg sample.

Tengkawang oil is reported to have the same type of triglyceride as palm oil [4]. The fat refining stages of palm oil generally consist of degumming, neutralization, bleaching and deodorizing. Steam-stripping is commonly used to reduce the free fatty acid content in the palm oil refining processes to an acceptable level. In this study, we used NaOH in neutralization process to remove free fatty acids from Tengkawang oil.
Degumming is an early stage purification process whereby the principle is to remove or separate gum (sap or mucus) without reducing the amount of free fatty acids in fat. Neutralization is the process of separating free fatty acids by reacting free fatty acids with alkaline or other reagents to form soap. Free fatty acids it is easily oxidized and can cause rancidity, so that the presence of free fatty acids in palm oil is undesirable [8].

FFA levels of various types of Tengkawang are not much different. FFA levels of fat Tengkawang type *S. pinanga*, the extraction results in an amount of FFA 1.94, after degumming rose to 2.31 and after neutralization fell back to 1.77 [4]. Bleaching is the purification step of removing unwanted substances in oil, which can be done by mixing the oil with a small amount of adsorbents such as absorbent soil, active clay and activated charcoal or with chemicals [6].

Studies of oil extraction from Tengkawang fruit using n-hexane solvent against *S. pinanga*, *S. stenoptera*, *S. mexistopteryx*, and *S. parvivolia* showed that oleic acid is the largest content of Tengkawang fats produced for the *S. stenoptera*. The study was then continued by extracting oil from seeds and continued with degumming and neutralization of *S. pinanga* and *S. mexistopteryx* [4]. Research on Tengkawang oil production using apit (traditional tool of indigenous people of Kalimantan) on *S. stenoptera* and *S. mexistopteryx* showed that the density and refractive index of both types of Tengkawang were the same, but differed on the iodine number, the saponification number and the FFA content [9].

In this research, the process of refining Tengkawang oil with degumming, neutralization and bleaching of *S. stenoptera* originating from Sintang regency of West Kalimantan was investigated. The purpose of this research is to improve the quality of vegetable oil with low acid number and peroxide number. Thus, it will increase the quality and the economic value.

2. Methods

2.1. Materials

Tengkawang fat was obtained from *S. stenoptera* harvested in 2017 from Sintang District, West Kalimantan. Other chemicals used were KI, NaOH, KOH, Na$_2$S$_2$O$_3$, iodine monochloride (ICl), glacial acetic acid, chloroform, alcohol, acetone, indicator of phenolphthalein, starch solution. All chemicals were obtained from Merck, Germany.

2.2. Purification Process

At room temperature the Tengkawang fat is in solid phase. 150 grams of Tengkawang was inserted into 300 mL beaker glass and was heated until it melted perfectly at temperatures 60-70 °C. The melted Tengkawang fat was then added with 20 % phosphoric acid by 1 % (w/w). The mixture was stirred using a magnetic stirrer at 400 rpm.

After 10 minutes of stirring, the mixture was inserted into the separating funnel to wash the remaining phosphoric acid and the impurities. Then, 5 % warm water was added to wash the mixture and was shaken for several minutes. The mixture was allowed to form two phase layers of fat and water. The weight of Tengkawang fat was measured. Then, Tengkawang fat was neutralized with NaOH concentration of ± 1 M added to the mixture with variation of volume 5, 7.5 and 10 % (w/w). The purpose of this variation is to examine the effect of NaOH concentration on the acid number. The mixture was then stirred for 15 minutes at 400 rpm at temperature of 60-70 °C.

After 15 minutes, the soap phase began to separate with the fat of the Tengkawang. The Tengkawang fat was then inserted into the separating funnel to remove the residual soap. Afterward, 5 % of warm water was added to wash the mixture and was shaken for a few minutes to let the mixture to form two phase layers of water and fat. The weight of Tengkawang fat was measured. The bleaching process was carried out by adding 1 % (w/w) of activated carbons into Tengkawang fat and heated at 70 °C for 30 min. After stirring, Tengkawang fat was then separated from the activated carbons.

2.3. Acid Numbers, Iodine and Peroxides

The number of acids, iodine number and peroxide number were examined in duplo at each stage of the refining process. In the acid number test, as much as 2 grams of sample was incorporated into the 100
mL Erlenmeyer. Subsequently, 25 mL of neutral ethanol was added to the Erlenmeyer and shaken to form two layers of ethanol and fat layer followed by the addition of 3 to 4 drops of phenolphthalein indicator. The sample was titrated with 0.1 N NaOH to form a pink solution [10]. The calculation of the numbers of acids was as follows:

\[
\text{Acid Number} = \frac{V \times T \times 40}{m}
\]

where \(V\) is the volume of NaOH required [mL]; \(T\) is the standard normality of NaOH; \(40\) is the molecular mass of NaOH [gram/mol]; and \(m\) is the sample weights [gram].

For iodine number test, 1 gram sample was inserted into 250 mL Erlenmeyer with addition of chloroform. Wijs solution (iodine monochloride in glacial acetic acid) of 25 ml was added, where iodine as a reagent and glacial acetic acid as an acid catalyst. The mixture was shaken for one minute strongly, and then the mixture was kept in the dark for 60 minutes. KI solution (20%) was added with 100 mL of aquadest and mixed titration with 0.1 N Na\(_2\)S\(_2\)O\(_3\) solution with kanji indicator [10]. Calculations of iodine Numbers were as follows:

\[
\text{Iodine Number} = \frac{12.69 \times T \times (V_0 - V_1)}{m}
\]

where \(V_0\) is the volume Na\(_2\)S\(_2\)O\(_3\) which required in the blank spreading [mL]; \(V_1\) is the volume Na\(_2\)S\(_2\)O\(_3\) which required in sampling [mL]; \(T\) is the standard normality of Na\(_2\)S\(_2\)O\(_3\); and \(m\) is the sample weights [gram].

For the test of peroxide number, 2 grams of sample yield was added to 250 mL of Erlenmeyer with chloroform and was shaken until completely dissolved. Then, glacial acetic acid as catalyst and saturated KI solution was mixed for one minute strongly. Aquadest was added as much as 75 mL into mixture and mixed titration with 0.02 N Na\(_2\)S\(_2\)O\(_3\) solution with kanji indicator [10]. Calculations of the Peroxide Numbers were done as follows:

\[
\text{Peroxide Number} = \frac{T \times (V_1 - V_0)}{m}
\]

The Tengkawang fat was also characterised regarding to Melting Point (SNI.7348:2009), Saponification Number (SNI.01-3555-1998) as well as Monounsaturated, Polyunsaturated and Trans Fat (IUPAC 2, 301 7th edition) standard methods.

3. Results and discussion

The Tengkawang fat from Sintang District was obtained in the form of brownish yellow solid. Analysis of the acid number (mg NaOH/100 g sample), peroxide number (mg equivalent O\(_2\)/kg sample) and iodine number (g I\(_2\)/100 g sample) was done prior to degumming. The results were 10.14; 10.98 and 32.49, respectively. The values of acid number and peroxide number in Tengkawang Sintang fat sample before the initial degumming were big. Therefore, further treatment was needed to reduce the values of the acid number and peroxide number.

The value of iodine number of sample Tengkawang was small (<35 g I\(_2\)/100 g sample). This indicates that the Tengkawang sample treated has resistance to rancidity. The Tengkawang remained in good conditions after 1.5 months of lack of lighting and low temperatures storage. Therefore, the Tengkawang sample had a typical of Tengkawang flavor and did not undergo easily rancid.

The degumming process was carried out by adding a phosphoric acid into melted fat. Phosphoric acid, polybasic organic acids, and hydration with water are usually used to remove phospholipids either individually or in combination. Phospholipids must be removed because they have emulsifying properties. After degumming, the colour of the fat turned to a clear yellow. The Tengkawang oil formed was analysed to determine the acid number, peroxide number and iodine number with the following results as follows 10.25; 10.88 and 28.81, respectively.

These results showed an increase in acid numbers. Although the increase was not too large, the increase in the acid numbers was expected due to the hydrolysis reaction that occurred due to the addition of acid during the degumming process [11]. In the degumming process, there were free fatty acids due
to reaction with residual phosphoric acid thus increasing the value of fatty acids and acid numbers. There was an increase in the free fatty acids and acid numbers. The impurities such as phosphatide bonds were detached and dissolved in the aqueous phase (containing residual phosphoric acid).

The degummed oil was neutralized with the addition of NaOH 7.5 % (w/w). During the process of addition and stirring, it formed soap (soap stock). Besides, the glycerol was still mixed in Tengkawang fat. The longer the time of neutralization, the more soaps were formed as more free fatty acids were accumulated. After the stirring process was completed, the soap floated to the surface of the mixture so that the soap layer can be removed and separated. After the soap layer was separated, the oil layer was washed several times with warm water to obtain a clear yellow oil layer. The acid number, peroxide number and iodine number of Tengkawang oil after neutralization were 6.09; 5.57 and 30.52, respectively.

The results showed that the acid and peroxide numbers significantly decreased. In the sample after neutralization there was a decrease in the acid number from 10.25 to 6.09 and in the value of peroxide number from 10.88 to 5.57. The decrease in the acid numbers was the result of acid-base reactions between free fatty acids in the oil with a NaOH base. Decreasing acid numbers improved the quality of oil; a low acid number indicates a longer shelf life [4].

The iodine number increased slightly from 28.81 to 30.52. The higher the iodine number, the more the C = C bonds present in the oil. Fats with lots of unsaturated trace bonds are particularly susceptible to oxidative resistance which can be stimulated at high temperatures and light. In contrast, fats with low iodine indicate a lot of saturated bonds [4].

After the neutralization process, the next step was bleaching using activated carbon. After bleaching, the acid number, peroxide number and iodine number were analyzed. The results showed 6.14; 5.55 and 31.39, respectively. The values of those three numbers were stagnant. In the bleaching process the activated carbon played a role to absorb unwanted dyestuffs without oxidizing the oil, so the color of the fat Tengkawang become darker white than before bleaching.

**Table 1.** Acid Numbers, Peroxide Numbers and Iodine Numbers of Tengkawang Fat

| Sample                      | Value of acid number (mg NaOH/g fat) | Peroxide Numbers Value (mek O_2/kg) | Iodine Value (gram iodine/100 gram) |
|-----------------------------|-------------------------------------|--------------------------------------|-------------------------------------|
| Early Tengkawang sample    | 10.14                               | 10.98                                | 32.49                               |
| Tengkawang sample after degumming | 10.25                           | 10.88                                | 28.81                               |
| Tengkawang sample after neutralization | 6.09                           | 5.57                                 | 30.52                               |
| Tengkawang sample after bleaching | 6.14                           | 5.55                                 | 31.39                               |

There were variations of iodine number, yet the iodine values contained in Tengkawang sample came within the standard ranges of Tengkawang fats established by SNI No 2903: 2016. The value of acid number was analyzed after bleaching using NaOH ± 1 N as much as 5 and 10 % as can be seen in Table 2.

**Table 2.** Tengkawang Fatty Acid Numbers with Variation of NaOH Levels

| Sample                      | Value of acid number (mg NaOH/g sample) |
|-----------------------------|----------------------------------------|
| Sample + NaOH 5 % (w/w)     | 7.83                                   |
| Sample + NaOH 7.5 % (w/w)   | 6.14                                   |
Sample + NaOH 10 % (w/w )  3.12

Table 2 showed that the concentration of NaOH used was inversely proportional to the acid value. The greater the NaOH used, the lower the yield percentage of Tengkawang fat. The triglycerides of the fatty ester in the Tengkawang were broken and saponified. The use of 10 % NaOH (w/w) is effective if there is a system capable of separating the Tengkawang fat and other side-effects such as soap stock and glycerol.

Table 3. Fatty Acid (18:2) Compositions from Different Studies

| Butter Name | Fatty Acid (18:2)* | References |
|-------------|-------------------|------------|
| Shea Butter | 4.3 - 6.65        | [12], [13], [14], [15] |
| Sal Fat     | 2.2 - 2.8         | [12], [16], [17] |
| Tengkawang  | 6.65              | From this study |

*in %

According to the Table 3. The results from our study showed that fatty acid content of Tengkawang was 6.65 %. These results were similar to Shea butter which belongs to the family of Sapotaceae, Shea butter come from edible vegetable fat obtained from the shea kernel Vitellaria paradoxa which mostly growth in West African and sub-saharan African. This trees also called Butyrospermum parkii L. [18]. Casten and Synder, 1985 reported that Shea kernel contains 40–55% valuable fat [19], according to Table 4 the results from our study showed that the monounsaturated and polyunsaturated fat content of Tengkawang was 28.7 % and 2.43 %.

Compared with Sal fat in Table 3, fatty acid content of Tengkawang fat were not similar. Several researchers reported that the variety, climate and regional differences influence the quality of fatty acid compositions in several fat source [18, 20-21]. Sal fat (Shorea robusta) is obtained from the seed kernel of sal trees, which grown in India, Malaysia, Borneo, Java, and Philippines.

Approximately 5% of the total forest area in India is occupied by Sal trees. The sal seed kernels contain 19–20% of oil which is known as Sal butter. The iodine value of sal fat is 31–45 and the melting point is 30–36 °C [22]. This properties were similar with Tengkawang fat, the results from our study showed that the melting point and iodine value of Tengkawang butter were 30.4 and 31-35 respectively (Table 1 and 4).

This shows that both tengkawang and sal fat have resistance to rancidity. Based on the triglyceride compositions, both shea butter and sal fat can be used as cocoa butter substitutes in making chocolate [23-24]. The Tengkawang in our study can also be used as a substitute for cocoa butter as the properties come into the properties of commercial cocoa butters from different countries [25].

Table 4. Physicochemicals of Tengkawang oil Shorea stenoptera Origin Sintang District West Kalimantan

| Parameter                  | Unit | Result | Test Method                                      |
|----------------------------|------|--------|-------------------------------------------------|
| pH                         | -    | 12.8   | SNI. 01-2891-1992, point 16                     |
| Melting Point              | °C   | 30.4   | SNI. 7348 : 2009, attachment A.4               |
| Monounsaturated Fat        | %    | 28.7   | IUPAC method 2, 301 7th edition                 |
| Polyunsaturated Fat        | %    | 2.43   | IUPAC method 2, 301 7th edition                 |
| Trans Fat                  | %    | <0.005 | IUPAC method 2, 301 7th edition                 |
As can be seen in Table 3 and 4, the physicochemicals of Tengkawang oil Shorea stenoptera meet some requirements as an alternative source to substitutes in cocoa butter and confectionary industries. With the right purification process, it is possible for Tengkawang as a potential food source in the future.

4. Conclusion
The value of acid number for Tengkawang fat; Tengkawang after degumming; Tengkawang after neutralization; and Tengkawang after bleaching were 10.14; 10.25; 6.09 and 6.14 (mg NaOH/100 g sample), respectively. The iodine number value of the initial Tengkawang; Tengkawang after degumming; Tengkawang after neutralization; and Tengkawang after each bleaching were 10.98; 10.88; 5.57; 38. The value of the initial Tengkawang peroxide number; Tengkawang after degumming; Tengkawang after neutralization; and Tengkawang after each bleaching were 32.49; 28.81; 24.67; 30.52; 31.39 (g I₂/100 g sample), respectively. The bleaching process was not necessary to reduce the acid number, peroxide number and iodine number. But it was useful to make the fat look clearer. All the samples were in the standard ranges for iodine number of Tengkawang fat according to SNI 2903:2016, i.e 25 - 38. The value of the initial Tengkawang peroxide number; Tengkawang after degumming; Tengkawang after neutralization; and Tengkawang after each bleaching were 10.98; 10.88; 5.57 and 5.55 (mg equivalent O₂/kg sample), respectively. This indicates that the treated Tengkawang sample has resistance to rancidity. The results from the 5; 7.5 and 10 % NaOH neutralization were 7.83; 6.14 and 3.12 (mg NaOH/100 g sample), respectively. Only the 10% neutralization Tengkawang sample had the lowest acid number of 3.12 and came within the standard of SNI 2903: 2016 (maximum of 3.50). Outnotes should be avoided whenever possible. If required they should be used only for brief notes that do not fit conveniently into the text.

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