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Sulphurization of Kapok (*Ceiba Pentandra*) Seed Oil *via* H_2S Bubbling Under UV Radiation and The Product's Performance as Extreme Pressure Additives for Lubricant

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Abstract. In this research, extreme pressure additive (EP additive) for lubricants was manufactured from *Ceiba pentandra* seed oil (kapok oil) *via* sulfurization reaction at a low temperature (50°C) by using a photochemical reactor under UV-radiation (254 nm). The sulfurization process was conducted by recirculating bubbling H_2S gas through kapok oil filled in a glass chamber. The sulfurization reaction has been proven successful, as shown from the FTIR spectrum of the sulfurized kapok oil, where carbon-sulfur bond (C-S) vibration appears at a peak of 581 cm^{-1}. It was also found that within 20 hours, the recirculated-bubbling sulfurization produced sulfurized kapok oil with a sulfur content of 32,682 ppm, viscosity of 72.17 cSt, and density of 0.92 g/cm^3. The product was then used as an EP additive by mixing it with mineral oil and testing it using a 4-ball wear tester. The mineral oil containing sulfurized kapok oil 10% v/v or equal to sulfur content 3,268 ppm reduced wear amount by 98%. Results of corrosion tests *via* copper strip corrosion ASTM D130 showed that the copper strip's color only had level 1a, meaning that mineral oil containing 10% Kapok oil as EP additives is not corrosive.

Keywords: Anti-Wear Additives, EP Additive, 4-Ball Wear Tester, Recirculated Bubbling, Sulfurization UV-Radiation, Sulfurized Kapok Oil, Sulphur Content

INTRODUCTION

Kapok (*Ceiba pentrandra*) is a tropical tree native to South America country, which is also easily found in Indonesia, especially in Java, and cultivated for its cotton-like fiber. The tree's seed contains 25 - 40% oil; the oil's triglycerides contain poly and monounsaturated 80 - 85% and free fatty acid (FFA) more than 4%. The *Ceiba pentandra* seed oil or kapok oil has linoleic acid at 33.6 %, oleic acid at 23.4 %, and palmitic acid at 22.4 %. Since it contains relatively high poly-unsaturated content, the kapok oil is relatively easy to get rancid and not appropriate for food uses (Anwar *et al.*, 2014). In terms of oxidation stability, kapok oil is worse than palm oil, which contains 10% linoleic acid (poly-unsaturated), 40% oleic acid (monounsaturated), 44% palmitic acid, and 5% stearic acid (Papin Sourou and Léopold, 2018).

Since oxidation stability is required for many vegetable oil applications, many

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attempts are made to increase stability by converting the unsaturated into saturated (Karmakar *et al.*, 2017; Cecilia *et al.*, 2020). However, containing too much unsaturated would cause the oil to have a high pour point, which is unsuitable for lubricant application. Therefore, high oleic oils (monounsaturated) are considered a compromise or an optimum property for both oxidative stability and fluidity, and they are gaining in popularity for food uses and lubricants. The high oleic oil can be made *via* partial hydrogenation of vegetable oil (Zambelli, 2021).

Another popular method for increasing stability of oil is *via* epoxidation reaction of the unsaturated. From an oxidation stability point of view, the double bond is weak due to its reactivity. However, this reactive site may be used for structure modification of oil. Many researchers performed modification *via* epoxidation of unsaturated (C=C) into epoxides and then followed by ring opening reaction epoxides using acid to form estolides or using alcohol to form polyol. This reaction can increase the oxidation stability of oil (Hoang *et al.*, 2015).

Oil modification can also be conducted *via* sulfurization of double bond (C=C) or unsaturated triglyceride (Nagy and Nagy, 2023; Iurii, 2016). Sukirno and Ningsih (2017) studied a simple sulfurization reaction of palm oil (Refined Bleached Deodorized Palm Oil or RBDPO) by reacting the oil with elemental sulfur at an elevated temperature of 150 - 160 °C, stirring at 500 rpm for 3 hours, to produce a sulfurized product as broaching oil. The sulfurized palm oil was proven to have antiwear properties and was suitable for broaching oil.

In another sulfurization study, soybean oil is mercaptanized by adding hydrogen sulfide across double bonds or epoxides of vegetable oils in the presence of UV light (Biresaw *et al.*, 2017). UV-radiation technique (1,000 Watt UV-lamp) was also used to assist in the epoxidation reaction of sunflower oil that was conducted with a mole ratio of 1:0.5:2 for the oil, hydrogen peroxide, and formic acid (Chukwudalu *et al.*, 2024).

Preceding this research, the author carried out the sulfurization of kapok oil by bubbling H_2S gas through kapok oil under UV-254 radiation to produce sulfurized kapok oil at a lower temperature (50°C) than normal sulfurization. H_2S absorbs high energy of UV light, and it causes electron excitation of the molecule to form free radicals H• and HS•. These reactive radicals can attack the C=C of the triglyceride, the most vulnerable site in palm oil, to form the thioether bond C-S-C (Li and Li, 2013).

In this present research, the experimental setup is improved. In the previous study, the H_2S gas flow is one-pass-bubbling through kapok oil in a glass chamber. Now, the H_2S flows *via* recirculated bubbling where the leaving gas is flowed back or recirculated through the oil using a peristaltic pump. With this improvement, sulfurized kapok oil is expected to reach a higher sulfur content or perform better when used as an extreme pressure additive (EP additive). By recirculating bubbling, H_2S gas is released into the environment and avoided while using a reactant, which is also more efficient.

EXPERIMENTAL METHOD

The main reactant was *Ceiba pentandra* seed oil (kapok oil) and H_2S gas generated by heating FeS powder and HCl 0.1 M at 70°C. Kapok oil has a density of 0.904 g/cm^3, a kinematic viscosity of 41.02 cSt, and an iodine value of 100.6 g-I_2/100g. The sulfurization was conducted in a glass chamber (as a photochemical reactor) under UV-254 nm radiation.

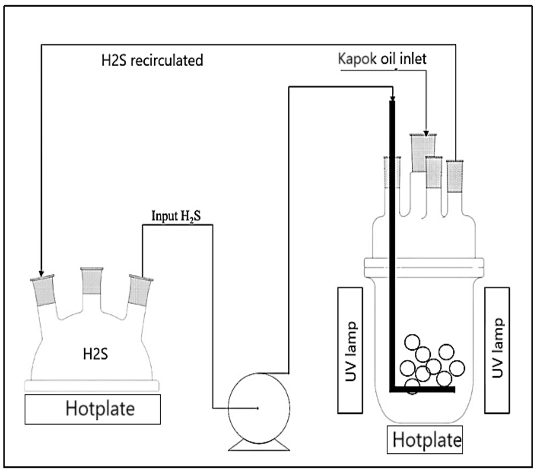

Fig. 1: Diagram of circulated bubbling sulfurization system

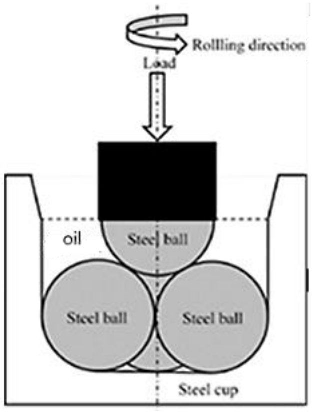

Fig. 2: Diagram of 4-balls wear tester.

H_2S gas was bubbling through kapok oil (Figure 1), and the leaving gas was recirculated by a peristaltic pump with 6 liters per minute (Pudi *et al.*, 2022). FTIR analysis was used to identify the functional groups of the product. The sulfur content of the sulfurized kapok oil was measured using ICP. The anti-wear performance of the sulfurized kapok oil was conducted by using a 4-ball wear tester as shown in Figure 2, to test several samples prepared by mixing mineral oil (MO) with sulfurized kapok oil of various concentrations (2%, 6%, and 10%). The MO was Pertamina paraffinic oil 90 with viscosity@100°C 6.7 – 7.6 cSt. Other characterizations were copper strip corrosion test ASTM D130 and viscosity and density measurements (Dongare and Gite, 2014).

RESULTS AND DISCUSSIONS

The sulfurization process of kapok oil's glycerides is characterized by attacking their unsaturated fatty acid, especially the weakest C=C bonds of polyunsaturated, and forming new bonds C-S and S-S, as illustrated in Figure 3 (Silverstein *et al.*, 2005). Since the reaction is endothermic, it needs energy for the reaction to proceed, and it can be supplied *via* heating or UV radiation. FTIR analysis is usually used for functional group identification to determine whether the reactions have occurred.

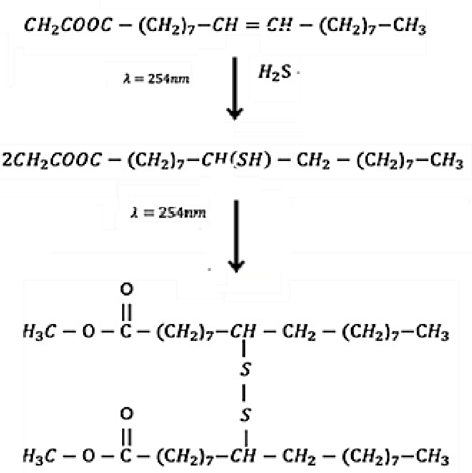

Fig. 3: Description of typical sulfurization reaction of double bond C=C

The FTIR spectrum of kapok oil before sulfurization is shown in Figure 4, while the FTIR spectrum of sulfurized kapok oil is in Figure 5. By comparing this 2 FTIR spectrum, we can recognize the appearance of a new peak at 581 cm^{-1} (stretching vibration of C-S bond) in Figure 5 and the disappearance of the peak at 3,007 cm^{-1} (stretching vibration of C=C bond), which initially exists in the spectrum of kapok oil in Figure 4.

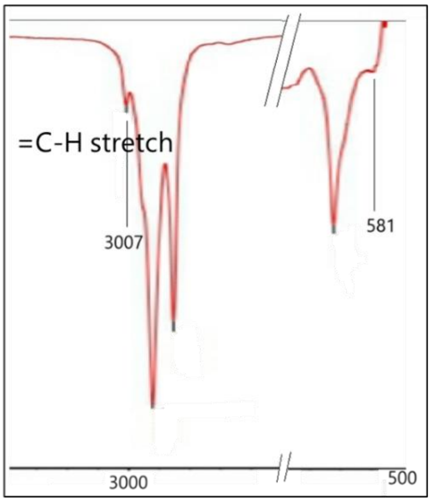

Fig. 4: FTIR peak of kapok seed oil before sulfurization

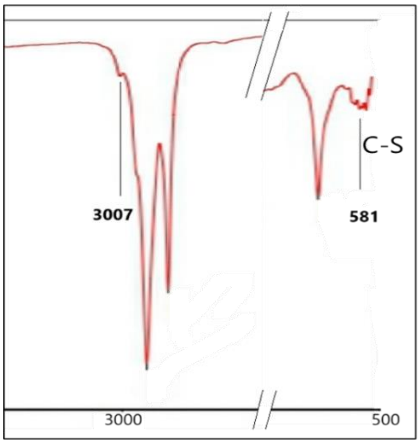

Fig. 5: FTIR peak of sulfurized kapok seed oil

This evidence proves that sulfurization reaction under UV-254 radiation has happened. The UV 254 nm, with photon's energy around 4.88 eV, is strong enough to break the C=C bond (more specifically, the pi bond of the C=C) and also able to provide energy needed for the formation of the S-S bond (266 kJ/mol), C-S bond (272 kJ/mol) and S-H bond (347 kJ/mol) (Ivlev *et al.*, 1973).

Unfortunately, not all expected vibration peaks appear in the FTIR spectrum. The S-S bond, which is expected to appear around 400 – 500 cm^{-1}, is very difficult to be identified (Silverstein *et al.*, 2005). The C-O bond that should appeared at 1098 cm^{-1} and the S=O bond that should appeared at 966 cm^{-1} are weak and difficult to identify in the FTIR spectrum, though they have very strong dipole moment.

Visual Appearance of Sulfurized Kapok Oils and Sulphur Content

The color of the sulfurized kapok oil is light brown. Its color gets darkened with time of the sulfurization process.

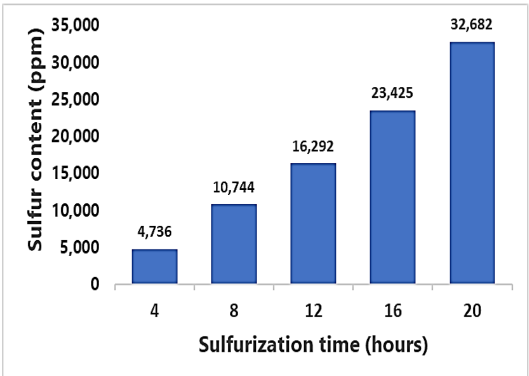

Fig. 6: Sulphur content of sulfurized kapok oil *vs* sulfurization time

The sulfur content of sulfurized kapok oils increases almost linearly with the time of the sulfurization process, as shown in Figure 6, where it is initially zero ppm and reaches 32,682 ppm after 20 hours of sulfurization.

The longer the radiation time, the more the reactants (C=C and H_2S) are excited to reach the activated energy of the sulfurization reaction (Houda *et al.*, 2018). The more H_2S molecules could attach to C=C (unsaturated fatty acid), the more the products (thioether C-S-C) were accumulated (Biresaw *et al.*, 2017). In the experiment (non-recirculation sulfurization system), the product only reached a sulfur content of 19,875 ppm after 20 hours of bubbling time.

Viscosity and Density Measurement

Figures 7 and 8 show the viscosity and density measurements on ASTM D-455 and DMA 4100M. The viscosity and density of the sulfurized kapok oil increase with the sulfurization process (Sharma and Sachan, 2019).

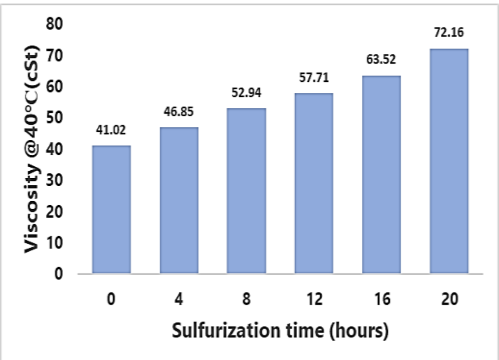

Fig. 7: Viscosity of sulfurized kapok oil

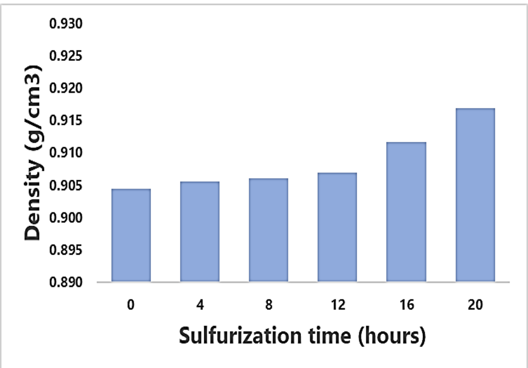

Fig. 8: Density of sulfurized kapok oil

After 20 hours of sulfurization, the density reaches 0.91 g/cm^3, and the viscosity reaches 72 cSt. The attachment of the sulfur atom *via* the polyunsaturated glyceride structure increases its molecular weight and polarity. Therefore, the van der Waals attraction dipole attraction force increases viscosity and density (Petlyuk and Wilczura-Wachnik, 2017).

Performance Test of Sulfurized Kapok Oils

The sulfurized kapok oil containing sulfur 32,682 ppm is used as EP additives to be mixed with mineral oil (MO) SAE-30. Several samples are prepared, including mineral oil (MO), MO +10% kapok oil, MO+2%, 6%, and 10% sulfurized kapok oil. The performance of sulfurized kapok oil as EP additive for mineral oil was assessed using a 4-ball wear tester, with the results shown in Figure 10.

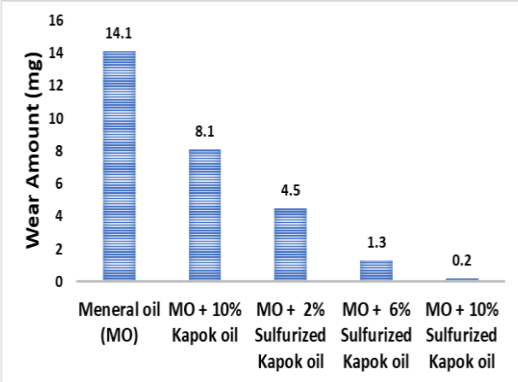

Fig. 9: Antiwear performance of mineral oil containing sulfurized kapok oil

The mineral oil (MO) without additive shows the highest wear amount, followed by sample MO +10% kapok oil. The fact that kapok oil shows antiwear ability is not surprising because kapok oil has an esters group that can adhere to metal surfaces better than mineral oil (Masripan *et al.*, 2023). Then, as expected, the antiwear performance of sample MO+10% sulfurized kapok oil gives the lowest amount of wear. Even the sample MO+2% sulfurized kapok oil performs better than the sample MO+10% kapok oil (Sharma and Sachan, 2019).

The sample (MO + additive 10% sulfurized kapok oil) showed a wear reduction of up to 98%. The sample (sulfur content of 3,268 ppm) is comparable to formulated lubricants, which usually contain 3% ZDDP or equal to the sulfur content of 3,393 ppm (Kiw and Schaeffer, 2022; Shubhamita *et al.*, 2019).

The superior antiwear performance of the sulfurized kapok is attributed to the existence of a sulfur functional group, which, under extreme load and friction, can tribochemically react with the surface to form a protective layer. The layer can prevent direct contact between the surface. From the effectiveness of the protection, we can call the sulfurized as an EP additive (Nagy *et al.*, 2023; Bhattacharjee *et al.*, 2020).

Anti Corrosion Test

The sulfur element is very corrosive and should never be used as an EP additive. Though sulfur-containing compounds (bonded sulfur), such as sulfurized kapok oil, are considered far less corrosive and can be used as EP additives, it is important to measure their corrosivity. One of the tests is conducted *via* the copper strip corrosion method ASTM D130-19. The samples prepared are mineral oil mixed with sulfurized kapok oil at various compositions (2%, 6%, and 10%). In this method, a strip of copper is dipped in the sample and heated at 100°C for 3 hours and the copper strip is cleaned, and its color change is assessed based on reference color. The results are shown in Table 1; all samples, 2%, 6%, and 10%, show corrosion level 1a, which means the copper strip shows light yellow, without significant corrosion. It can be interpreted that the sulfurized kapok oil contains bonded sulfur (not free sulfur. Therefore, if it is used for lubricant formulation, it will not damage the engine.

One Pass Bubbling *vs* Recirculated Bubbling Sulfurization Efficiency

The efficiency of using H_2S in the 2 methods is compared, based on 20 hours of bubbling sulfurization. When using the recirculated bubbling sulfurization method, the reactant consumed during H_2S generation was 120 ml HCl and 20 g FeS, and the product obtained was the kapok oil with a sulfur content of 32,682 ppm.

When using the one-pass bubbling sulfurization method (the previous experimental), it took 3 times recharge, which means that the reactant needed for generating H_2S was 3 times the above amount; it provides sulfur content of 19,875 ppm. Thus, the efficiency usage of a reactant increases by about 490%, based on the products obtained.

Table 1. Copper strip corrosion mineral oil containing sulfurized kapok oil

Sample	Corrosion Level
MO + 2 % Sulfurized kapok oil	1a
MO + 6 % Sulfurized kapok oil	1a
MO +10 % Sulfurized kapok oil	1a

(MO=Mineral oil).

CONCLUSION

From the study of sulfurization at temperature *via* H_2S bubbling through Kapok oil under UV-light radiation, some conclusions can be deduced as follows:

1. The sulfurized kapok oil obtained by this low-temperature sulfurization technique has been confirmed to have a sulfur bond (C-S), shown in its FTIR spectrum. The sulfurized kapok oil reached a sulfur content of 19,875 ppm after 20 hours of sulfurization using one-pass-bubbling (previous method). The sulfur content increased to 32,682 ppm after 20 hours of sulfurization using recirculated bubbling (current method).
2. The sulfurized kapok oil is an effective EP additive for mineral oil. Using the 4-ball wear test (load, 62kgf, and 1,760 rpm), the sample (MO + additive 10% sulfurized kapok oil) showed a wear reduction of up

to 98%. The sample with a sulfur content of 3,268 ppm is comparable to a lubricant containing 3% ZDDP additive or a sulfur content of 3,393 ppm.

3. The copper corrosion test found that the sample (MO + 10% sulfurized) showed a corrosion level 1a, which means it is fine or normal.

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