Modification of Kapok Fibers via Esterification for POME Treatment

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***Abstract*— Kapok fibers, the native of Central America is a good oil absorbent and low in cost. Adsorptive of oil in kapok fibers. The purpose of this study is to modified kapok fibers by esterification. The esterified kapok fibers were then test for POME treatment. Kapok fiber is one of natural fibers that have good hydrophobicity and buoyancy and is suitable for POME treatment specifically in term of oil adsorption. However due to increase its hydrophobicity, kapok fibers need to be modified. Based on the literature search, esterification of natural fibers can increase its ability to adsorb oil. Thus, in this research, the kapok fibers were esterified and oil removal test was conducted in order to see the effect of esterification of kapok fibers on its effectiveness to reduce the oil from POME. The esterification of kapok fibers were conducted at ration of kapok fibers to stearic acid by 1:1, 4:1 and 7:1. Effectiveness of kapok fibers to remove oil increase by 30 % after esterification. The oil and grease test shows that ratio kapok fibers to stearic acid by 4:1 gives 98.03 % of oil removal compared to 1:1 and 7:1 but it has very low different in percentage with 1:1. Water quality test such as BOD,COD,TSS and pH also conducted and shows that esterified kapok fibers gives better quality to POME. It decrease BOD by 76.90%, COD 67.84%, TSS 60.09 % and pH 21.21 %. The oil removal efficiency of kapok fibers successfully increased by esterification also help in increasing the quality of POME**

Keywords*— Esterification,kapok fibers, oil removal,stearic acid,water quality

I. Introduction

Palm oil industry has been an important industry of agricultural sector in the world. Indonesia followed by Malaysia are two leading country of palm oil industry. This industry gives big impact in Malaysia's economy growth. Currently, the palm oil tree occupies largest portion of farmer land in Malaysia [9]. Palm oil tree planted area in 2014 is 5.39 million hectares and increase by 4.6 percent to 5.64 million hectares in 2015 [7]. However, palm oil industry also gives a big environmental impact because of its huge waste generation. Empty fruit bunches (EFB), palm oil mill effluents (POME), mesocarp fibers and shells are types of waste generated by palm oil mills. Among all wastes generated by palm oil mills, POME can be classifying as most hazardous waste.

POME is highly contaminant. It contains very high BOD, COD, TSS, oil and grease. It is the most significant water pollution if not treated well. There are many researches had been done to treat POME. However, the research conducted did not overcome this problem. This research is conducted to find a better and cheaper way to treat POME by oil adsorption. In this research, the kapok fiber is used as oil adsorption medium of POME. In order to increase its hydrophobicity, kapok fibers need to be modified. Esterification of kapok fibers is done in this research to increase the hydrophobicity of kapok fibers together to increase its capability to adsorb oil from POME. Ongom, Ambual and Punti river near Keningau and Mural village are among that experience the impact of released POME into the rivers [14]. Oil and dirt from a palm oil mill near the village has polluted the villagers' water resources. This is a big issue that should be look at seriously. Due to the large tons generated at a time, POME being the most expensive and difficult to manage waste. That is the reason many palm oil mills' management unit decides just to discharge POME into rivers or water system.

There are many treatments system developed to treat POME such as ponding system, anaerobic digester and land application system. Because of high biological content in POME, usually POME will be treated in biological treatment system. Anaerobic digester is an example of biological treatment system of POME. Together with its ability to treat POME, this system will produce methane as by product which can contribute to global warming. For ponding system and land application system, high cost and land needed always make people think twice to use the system. For sustainability purpose, POME issues must be solved. If not, our waste resources will be worst polluted and affect our next generation.

This research is conducted to treat POME by using kapok fibers. Kapok fibers are chosen among natural fibers to treat POME because of its good adsorption. However, due to a several weaknesses of natural fibers such as low hydrophobicity and low buoyancy, modification needs to be conduct. In this research, the kapok fibers are modified via esterification to increase its hydrophobicity in which at the same time increases its capacity to adsorb oil.

POME contains high amount of organic matter, biochemical oxygen demand (BOD), chemical oxygen demand (COD), oil and grease, and total solid. Due to the huge amount of POME produced during oil extraction process, it requires a serious attention. Palm oil mills have a big responsibility to face it in term of environmental protection, economic viability and sustainability development [13]. As it is expensive and high maintenance, usually the palm oil mill take for granted on it and choose to just dispose it into the river. The crucial part is to meet Department of Environment standard to dispose wastewater into river. This research is done to treat POME using renewable, eco- friendly and cheap treatment so that all palm oil mills afford to handle POME wisely. The type of treatment is chemical treatment via esterification. Natural fiber is the medium of the treatment. Among natural fibers, kapok fibers are chosen because of it has better hydrophilic-oleophilic properties than other natural fibers. However, the natural fibers have low hydrophobicity and low buoyancy. Hence, it needs to be modified. Modification of kapok fibers using esterification method can increase its hydrophobicity and efficiency to adsorb oil.

Natural fibers are one of the important oil sorbent [4]. Some of it has better ability to remove oil than synthetic fibers. (comparison with types synthetic fibers) Biodegradable and chemical free are other advantages of natural fibers compared to synthetic fibers [4].

Kapok, barley straw, wool, rice husk, sugarcane bagasse and sawdust are some types of natural fibers use in oil sorbent. These natural fibers contain cellulose and lignin that responsible for oil sorbent.

Kapok, or its scientific name Ceiba Pentrandra also called as java tree, ceiba and java kapok native to Central America but now it is widely spread to rain forest. It grows in most of Asean country such as Malaysia, Thailand and Indonesia. It is yellowish-brown single cell plant hairs that enclosed to seed of kapok trees. As it is cheap and easy to get, kapok fibers are widely used in many conventional uses such as stuffing for bedding, upholstery, life preserve, water safety equipment, sound and heat insulator, warmth retention properties and water absorption reduction materials.

Kapok fiber consists of 64% cellulose, 13% lignin and 23% pentosane on weight basis. Optical microscopy and SEM observation found that kapok fibers show a cylindrical shape, a surface without texture and thickening grains at the ends [8]. Kapok fibers also have excellent hydrophobicity, huge lumen, good buoyancy and low density. Its hollow lumen and waxy surface gives kapok fibers hydrophobic-oleophilic properties [1]. Due to its good properties, kapok fibers have received a great attention as a natural sorbent of oil and as water-oil separation material [1], [2], [9]. 1g of kapok fibers could absorb 40g of crude oil. [9] Besides excellent oil sorbent, kapok also a good COD and turbidity removing material. [1] This gives an added value to kapok fiber so that it also can be used in waste water treatment.

To increase the efficiency of kapok fibers ability in oil removal, physical and chemical modification need to be done. Several physical and chemical modification of kapok fiber [1] The physical modifications are consisting of ultrasonic treatment and radiation treatment. On the other hand, the chemical modifications are consisting of alkali/acid treatment, solvent treatment, oxidation treatment and acetylation treatment [1]

Previously, research has been done on esterification of natural fibers using acetic anhydride, but it produces acetic acid as by product that cause residual smell and metal fastener corrosion. The alternative is using fatty acid such as stearic acid that produce water as by-product [4]. Esterification is one of famous chemical treatment to increase oil efficiency of kapok fibers [4] It increases the hydrophobicity of kapok fibers to enhance the oil removal capacity. Thus, in this research, it is proposed to use chemical treatment, i.e. the modification process to treat the kapok fibers.

II. METHODOLOGY

A. *Materials*

Kapok fibers was ground into short shapes. The sample was kept for further usage. POME is collected from FGV plant, Sungai Tengi. Calcium oxide, CaO, ethyl acetate, stearic acid and silicon oil.

B. *BOD, COD , TSS and pH test*

C. *Esterification of Kapok Fibers*

Kapok fibers in a quantity of 5 g were placed in 500 mL round bottom flask containing 100 mL ethyl acetate. Stearic acid (SA) was added according to required kapok fibers:SA ratios, i.e. 1:1, 4:1, and 7:1. CaO of 5 % of kapok fibers mass was added to the mixture as catalyst. The flask was immersed in oil bath and heated at reflux for the required times (5 h). The mixture was then filtered, washed with ethyl acetate to remove unreacted stearic acid, and cooled to room temperature prior to use. (Rafeah et. al., 2013).

D. *Oil removal test for unmodified kapok fibers and esterified kapok fibers*

0.35 g kapok fibers and 20 mL of POME were used to undergo this test. The mixture of esterified kapok fibers and POME is stirred for 30 minutes before being filtered. Oil removal test of esterified kapok fibers was conducted using n-hexane solvent extraction method. 20 mL of filtered sample was added to separatory funnel. Before 3 mL of hexane was added, the sample's pH must be lower than 2, so that 9 drops of HCl-water mixture was added to the sample. Then, the separatory funnel was vigorously shaken for 2 minutes, and left for 10 minutes to form two layers. The organic-oil layer was collected using gravity filtration apparatus, and dried. Hexane content in the oil sample was removed using rotary evaporator. The oil sample was dried in oven at 103oC for 15 minutes. The oil content removal efficiency was measured by using equation (2) below:-

$$\text{Oil removal efficiency} = \frac{C_o - C}{C_o} \times 100 \qquad (2)$$

The steps are repeated using unmodified kapok fibers to compare the efficiency of oil removal between the esterified kapok fibers and unmodified kapok fibers. (Rafeah et. al., 2013).

III. RESULTS AND DISCUSSION

A. *Esterification of Kapok Fibers*

Chemical modification of kapok fibers via esterification is done to increase its hydrophobicity. This modification is performed by the presence of stearic acid and calcium oxide. Calcium oxide act as catalyst to deprotonated the abundance hydroxyl group available in kapok fibers (Wahi et. al, 2016). Abundance of calcium oxide in stearic acid formed alkoxyl group the reacted with kapok fibers to produce esterified kapok fibers. Oil content test shows that esterification of kapok fibers successfully increase its ability to remove oil compared to raw kapok fibers.

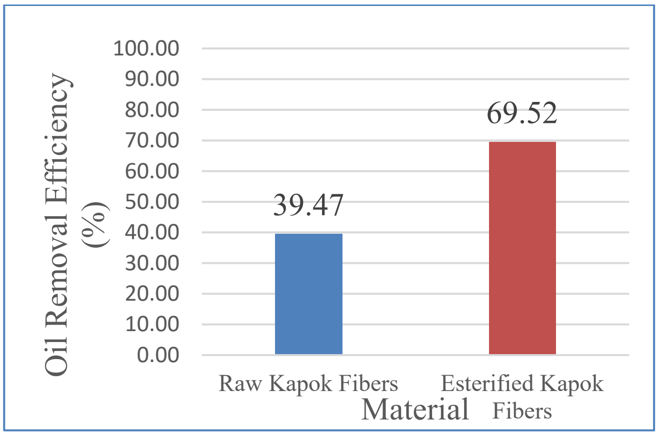

Fig. 1 Percent oil removal comparison between raw and esterified kapok fibers

Table 4.1 shows data of removed oil from POME treated with raw kapok fibers and esterified kapok fibers. Raw kapok fibers removed 39.47 % of oil from POME while esterified kapok fibers removed 69.52 % of oil from POME. In this research, ratio of kapok fibers to stearic acid ratio is variable to examine different stearic acid effect on esterification of kapok fibers. The amount of calcium oxide is fixed to 5% of kapok fibers and the reflux time is 4 hr due to shortage of chemical and experiment time.

B. Effect of Stearic Acid

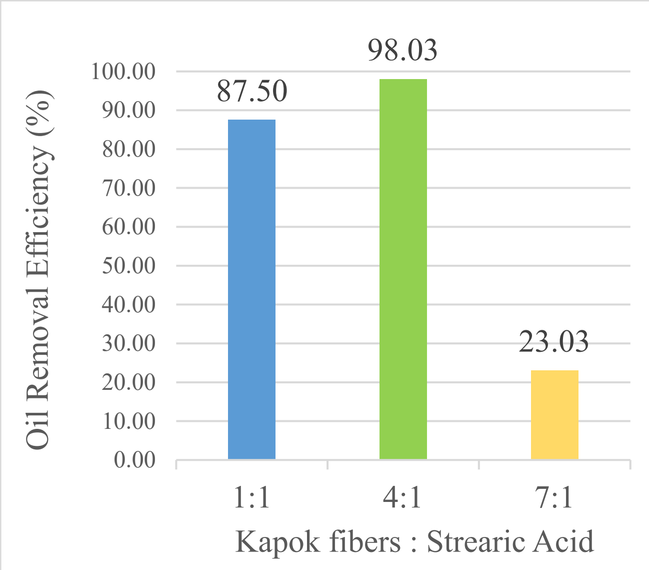

Fig. 2 Percentage of oil removal vs kapok fibers to stearic acid ratio

Figure 2 shows the result of esterification of kapok fibers with different kapok fibers: stearic acid. The kapok fibers: stearic acid ratio of 4:1 shows highest capacity to remove oil

C. Water Quality of POME

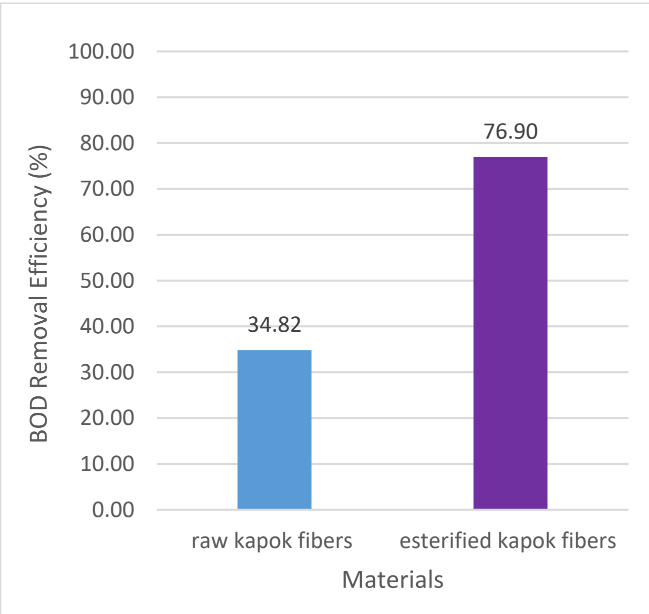

Fig 3. BOD removal efficiency (%) vs Materials

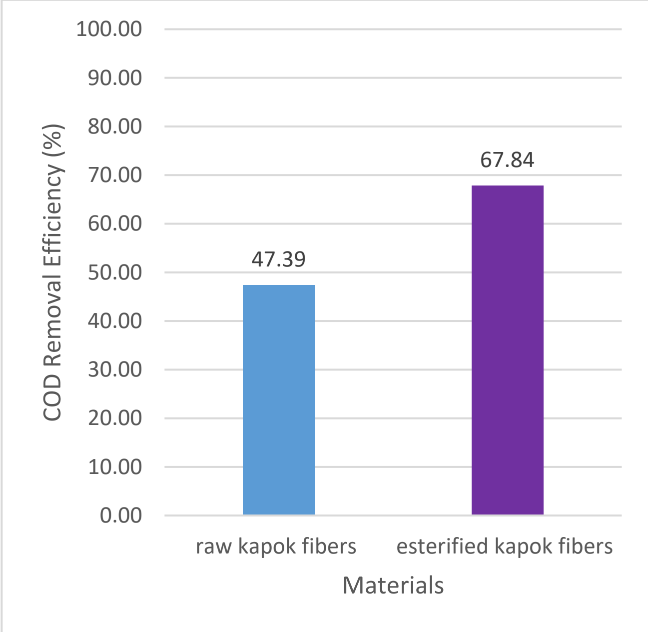

Fig 4. COD removal efficiency (%) vs Materials

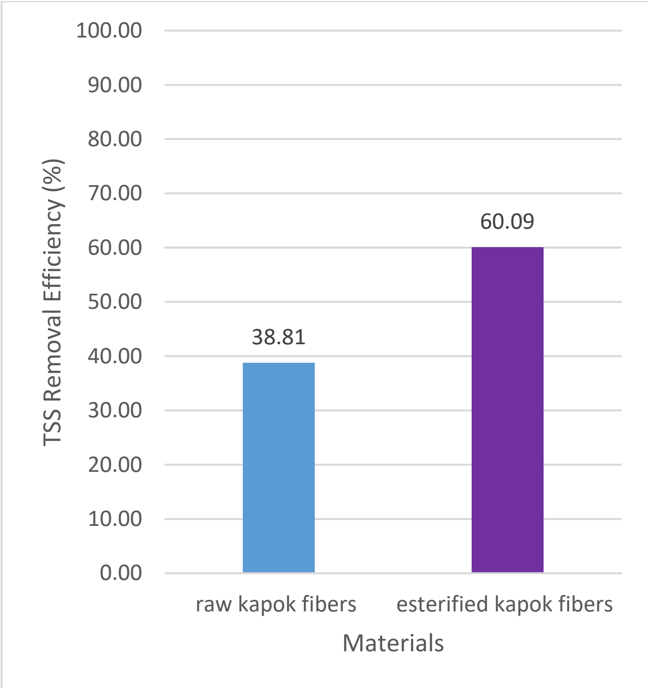

Fig 5. TSS removal efficiency (%) vs Materials

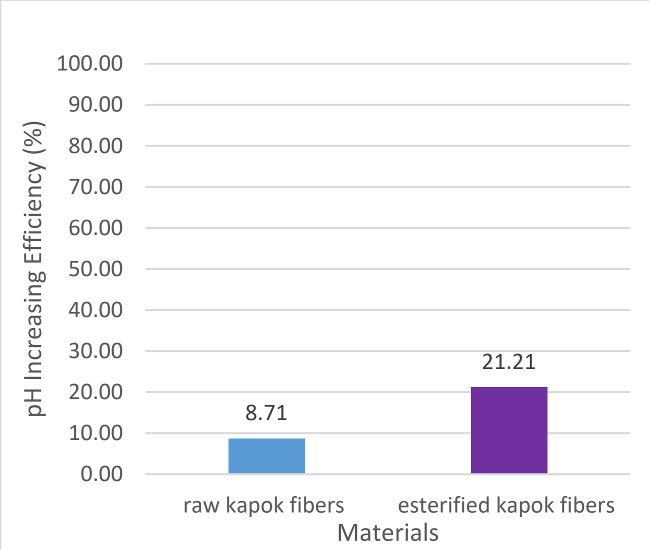

Fig 6. pH increasing efficiency (%) vs Materials

Figure 6 shows that raw kapok fibers increase POME's pH by 8.71 % while esterified kapok fibers increase 21.21 % of POME's pH. This indicates that treatment by kapok fibers can help to neutralize POME and esterified kapok fibers has better efficiency to neutralized POME than raw kapok fibers.

IV. Conclusion

In summary, kapok fibers has successfully modify to increase it hydrophobicity and increase its oil removal efficiency. Oil removal efficiency of kapok fibers increase by 30 % after esterification. Ratio kapok fibers to stearic acid by 4:1 gives highest oil adsoption quality. Future works include variability of CaO as catalyst and reflux time.

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