EFFECT OF REFLUX TIME IN THE ESTERIFICATION OF KAPOK FIBRE FOR USED COOKING OIL (UCO) TREATMENT

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***Abstract*-In the process of food preparation, used cooking oil (UCO) is produced as a waste. It is an edible oil that classified into vegetable oil which has been used in food making process. One of the applications of UCO is that it can be converted into biodiesel. Nevertheless, it can lead to another problem such as blockages of sewer pipes if being discharged down into kitchen sinks. Thus, a few practical treatments have been conducted to solve the problem such as alkaline-catalyzed transesterification. However, none of the treatments could reduce the environmental impacts as it contains high free fatty acid that has made the reaction not efficient. Hence, the aim of this research is to find the alternative method to reduce the oil content in UCO before discharging into the river by using kapok fibre. Kapok fibre is natural plant fibre that can be renewed. The kapok fibre was investigated for adsorptive removal of oil in UCO. Hydrophobicity of this adsorbent was improved via esterification process in the presence of stearic acid and calcium oxide as catalyst. The effect of reflux time was studied on the esterification of kapok fibre. Both of modified and unmodified kapok fibre were prepared to compare the oil adsorption towards UCO. In the esterification reaction, kapok fibre was mixed stearic acid in the ratio of 1:1, with the percentage catalyst of 10 wt% of kapok fibre mass and refluxing time were tested at 1, 2 and 4 hours, respectively. The experiments were repeated in duplicates. From the results, the average oil removal efficiency produced at 1 and 2 hours were 31.25% and 32.85%, respectively. Meanwhile, the highest oil removal efficiency was obtained at 34.21% by using refluxing time at 4 hours. The unmodified kapok fibre gave the lowest oil removal efficiency compared to modified kapok fibre (MKF) which is at 25.85%.**

***Keywords*-Used cooking oil (UCO), Esterification, Kapok fibre, Reflux time, Oil adsorption**

INTRODUCTION

UCO is used in manufacturing industries such as in the soap production, oil paints and vastly used in the production of biodiesel. Many researches have been done to make a biodiesel from UCO since it is seen as a much cheaper raw material than other edible oil such as soybean oil. It has been said that the generation of used cooking oil is approximately more than 15 million tons from selected countries around the world (César, et. al., 2017). Both animal and vegetable matter can be found in waste cooking oil as it been used in cooking before. However, it is not good enough to be consumed again for human (Gui, et. al., 2008).

However, UCO has drawbacks towards the environment if being discharged down into kitchen sinks. This activity lead to blockages of sewer pipes when the oil solidifies to such a degree where it may lead to water channel problems (Gui, et. al., 2008).

Thus, the wastewater treatment facility turn into the vital part in the UCO disposal system. A few practical treatment advances have been created to solve the problem. For example, in the process of making a biodiesel from UCO, the fatty acids need to be modified to make a shorter carbon chains. The UCO can be converted to biodiesel by using various methods such as catalytic reaction using alkali catalyst, acid catalyst and enzyme or via non-catalytic reaction in supercritical transesterification reaction (Gui, et. al., 2008).

Nevertheless, none of the treatments could reduce the environmental impacts and give a better solution in solving UCO. UCO that has high free fatty acid and water content has made alkaline-catalyzed transesterification reaction not efficient (Gui, et. al., 2008). Hence, the aim of this research is to find the alternative method to reduce the oil content in UCO before discharging into the river by using kapok fibre as adsorbent.

Kapok fibre is one of the natural plant fibre that can be renewed. It also grouped into type of seed fibre because the fibres is collected from seeds or seed cases (Chandramohan, et. al., 2011). Other than having a hydrophobic oleophilic properties, this fibre is a cellulosic fibre with the characteristics of thin cell wall, large lumen and low density (Zheng, et. al., 2015). The features of kapok fibre is homogeneous empty tube shape and is made out of cellulose (35% dry fibre), xylan (22%), and lignin (21.5%) (Hori, et. al., 2000).

Kapok fibre is significantly hydrophobic. Thus it does not adsorb water and not get wet in water. In an oil absorptivity test using machine oil, it showed that the machine oil colored by a dye suspended in water was directly absorbed by the kapok fibres, contradict to water which did not absorbed by the fibre. Kapok fibre extracted with diethylether followed by alcohol-benzene gave the same conclusion as the original data which is capacity of oil absorbance of any samples was 40g/g of fibre (Hori, et. al., 2000).

Modification is commonly done on the surface of the fibres such as chemical treatment and physical treatment. Physical treatment comprises of two method such as ultrasonic treatment and radiation treatment. Meanwhile, for chemical treatment it is divided into several methods such as alkali treatment, acid treatment, solvent treatment, oxidation treatment, esterification and acetyle treatment (Zheng, et. al., 2015). Among those treatments on natural fibres, esterification method is used in chemical modifications as it can increase the efficiency of oil removal of natural fibres (Wahi, et. al., 2013).

In this research, esterification method is used in treating the kapok fibre in order to increase the hydrophobicity of the kapok fibre thus increase the oil absorptivity. The reaction was performed with the presence of stearic acid, (SA) and calcium oxide, CaO as catalyst. The CaO is used as a base to deprotonate the abundance of hydroxyl group available in the kapok fibre. The alkoxy group formed subsequently reacted with stearic acid to formed modified kapok fibre (MKF). The effect of reflux time was studied on the esterification of kapok fibre. The treated kapok fibre (modified) and untreated kapok fibre (unmodified) were prepared to compare the oil adsorption towards UCO. The experiment was repeated in duplicates.

METHODOLOGY

Materials

Kapok fibre was purchased from the supplier. The raw UCO was collected from Dataran Cendekiawan, UiTM Shah Alam. The chemicals used in this study were stearic acid, ethyl acetate, n-hexane, hydrochloric acid, calcium oxide catalyst and anhydrous sodium sulphate (Merck). All chemicals were of reagent grade.

Esterification of kapok fibre

1 g of kapok fibre was placed in 500 mL round bottom flask containing 100 mL ethyl acetate. Stearic acid was added according to

required ratio of kapok fibre to stearic acid by 1:1. The catalyst, CaO was added at 10 wt% of kapok fibre mass to the mixture. The mixture was well mixed before immersed in water bath and heated at 85°C and 150 rpm. The reflux time were ranged at 1 hour, 2 hours and 4 hours. Next, the mixture was filtered and washed with ethyl acetate to remove unreacted stearic acid. The kapok fibre was then oven dried at 70°C for 15 minutes and cooled at room temperature prior to use.

Oil adsorption test in UCO

Batch adsorption study was conducted using modified kapok fibre, MKF (0.35 g), on raw UCO (50 mL) at room temperature. The MKF-UCO mixture together with 50 ml tap water was stirred for 10 minutes on a magnetic stirred before being filtered. The mixture was stirred at 150 rpm. Then, the filtrate was analysed for oil content.

The determination of oil content in UCO was conducted by n-hexane solvent extraction method. 100 mL sample was transferred to separatory funnel. About 9 drops of 1:1 HCl:water was added to obtain UCO of pH ≤2 prior to addition of hexane (3 mL). The separatory funnel was vigorously shaken for 2 min and left for 10 min to form two layers. The oil layer was collected onto gravity filtration apparatus and dried over $NaSO_4$ anhydrous. The hexane in oil was removed by using rotary evaporator. Next, oil sample was oven dried at 103˚C for 15 min, cooled to room temperature and weighed. The measured weight was taken as oil and grease content value. The oil removal efficiency was determined by using the equation below:

$$\text{Oil removal efficiency (\%)} = \left[\frac{C_o - C}{C_o}\right] \text{ x } 100\text{---(1)}$$

where Co and C are the initial oil concentration in UCO and the oil concentration in the filtrate, respectively.

RESULT AND DISCUSSION

Effect of reflux time on the modified kapok fibre (MKF)

The function of calcium oxide used throughout the experiment is to deprotonate the abundance hydroxyl group available in the kapok fibre (Wahi, et. al., 2013). In the esterification reaction, the hydrophobicity of the kapok fibre was increased as the oil removal efficiency shows higher on the modified kapok fibre.

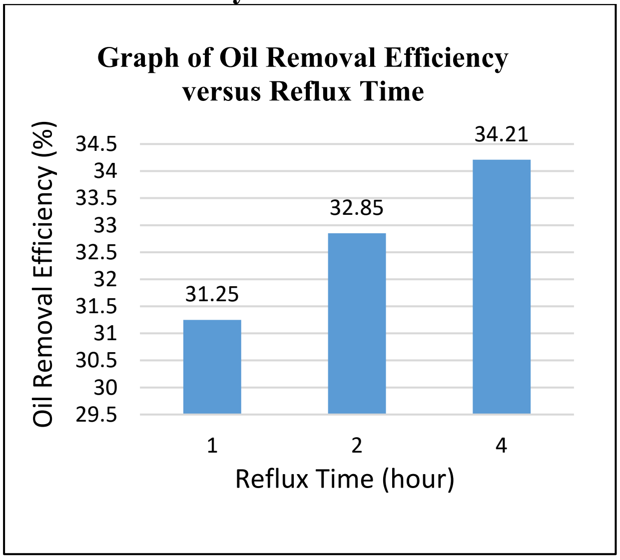
The oil removal efficiency of MKF at 1 hours refluxing time was 30.16% (Run 2) and 32.34% (Run 3). At 2 hours of refluxing time, the oil removal efficiency was 32.34% (Run 4) and 32.98% (Run 5), respectively. Meanwhile, the maximum oil removal efficiency of MKF was at 4 hours of refluxing time which gave 33.44% (Run 6) and highest at 34.96% (Run 7). Wahi, et. al., (2013) has reported that long refluxing time allowed exposure of internal surfaces of kapok fibre, which in turn increased ester formation sites.

In contrast, the unmodified kapok fibre gave the lowest oil removal efficiency compared to modified kapok fibre which is at 25.85%. Table 1 shows oil removal efficiency of kapok fibre when being tested with different reflux time.

Table 1: Oil removal efficiency of kapok fibre when being tested with different reflux time

Run Order	Reflux Time (hours)	Oil Removal Efficiecy (%)
1	Unmodified	25.85
2	1	30.16
3	1	32.34
4	2	32.72
5	2	32.98
6	4	33.44
7	4	34.96

Figure 1: Graph of the average oil removal efficiency versus reflux time



The esterification reaction at prolong hours in reflux time resulted in modification surface topography of kapok fibre due to removal of fibre's wax and cuticles (Banerjee, et. al., 2006). The time were ranged from 1, 2 and 4 hours and experiment was duplicated to get the average of oil removal efficiency (Figure 1). At the reflux time of 1 hour, the average oil removal efficiency was 31.25% and increased at 2 hours reflux time (32.85%). Thus, the maximum oil removal efficiency was obtained at 34.21% by using refluxing time at 4 hours.

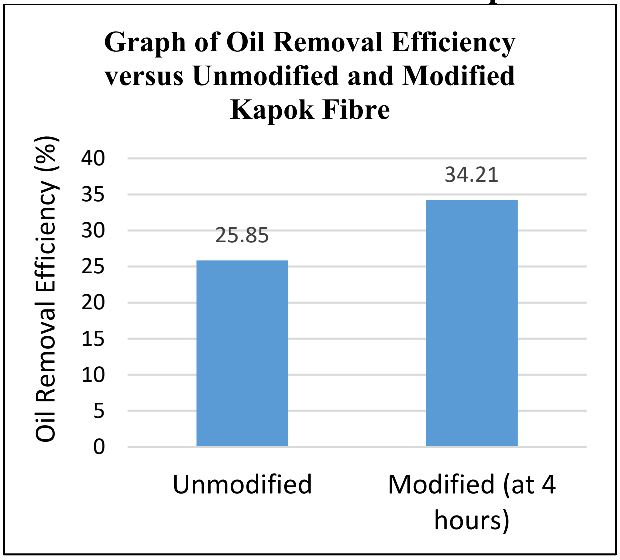
Comparison of oil removal efficiency between modified and unmodified kapok fibre

The modified kapok fibre at 4 hours refluxing time was compared to the unmodified kapok in terms of oil removal efficiency. Based on Figure 2, the modified kapok fibre (MKF) showed the highest oil removal efficiency (34.21%) as compared to the unmodified kapok fibre which was at 25.85%. According to Ali, et. al., (2012), most of natural fibres have low hydrophobicity and low buoyancy. Thus, they are only suitable for oil removal in the absence of water. Hence, the chemical modifications is needed to increase the oil removal efficiency of natural fibres such as esterification reaction (Ren, et. al., 2007).

In addition, the high oil removal efficiency of MKF compared to unmodified kapok fibre was due to several reasons. Ibrahim, et. al., (2009) reported that the modification happened allowed MKF surface to be rough and exposed internal structures thus increased the oil entrapment sites. Besides, the relatively higher of oil removal efficiency was because the site for oil entrapment in both MKF and unmodified kapok fibre were different. During the oil removal from UCO, oil was physically attached to the unmodified kapok fibre surface. On the other hand, the oil which attached to the MKF surface is due to the hydrophobic tails. The hydrophobic tails was available after substitution of the –OH groups in the MKF with hydrophobic groups in stearic acid. (Wahi, et. al., 2013).

In the esterification, CaO is used as catalyst to enabled excellent deprotonation of hydroxyl group in kapok fibre. Hence, more reactions happened between stearic acid and kapok fibre which in turn increased ester formation sites on MKF. The MKF is more preferrable than unmodified kapok fibre because the esterification on fibre could cause the formation of pore channels (Ibrahim, et. al., 2009). Thus, the MKF exhibits better potential as an adsorbent for removing oil from UCO compared to the unmodified kapok fibre.

Figure 2: Graph of oil removal efficiency versus unmodified and modified kapok fibre



CONCLUSIONS

In conclusion, kapok fibre has been successfully utilised for the oil removal in UCO. The modification through esterification reaction has successfully increased the hydrophobicity of kapok fibre. Modified kapok fibre gave the highest oil removal efficiency in UCO with the percentage of 34.21% compared to the unmodified kapok fibre with the percentage of 25.85%. The maximum of oil removal efficiency was obtained at 4 hours refluxing time (34.21%).

REFERENCES

1) Gui, M. M., Lee, K. T., & Bhatia, S. (2008). Feasibility of edible oil vs. non-edible oil vs. waste edible oil as biodiesel feedstock. *Energy, 33*(11), 1646-1653.

2) César, A. d. S., Werderits, D. E., de Oliveira Saraiva, G. L., & Guabiroba, R. C. d. S. (2017). The potential of waste cooking oil as supply for the Brazilian biodiesel chain. *Renewable and Sustainable Energy Reviews, 72*(Supplement C), 246-253.

3) Chandramohan, D., & Marimuthu, K. (2011). A review on natural fibers. *International Journal of Research and Reviews in Applied Sciences, 8*(2), 194-206.

4) Zheng, Y., Wang, J., Zhu, Y., & Wang, A. (2015). Research and application of kapok fiber as an absorbing material: a mini review. *Journal of Environmental Sciences, 27*, 21-32.

5) Hori, K., Flavier, M. E., Kuga, S., Lam, T. B. T., & Iiyama, K. (2000). Excellent oil absorbent kapok [Ceiba pentandra (L.) Gaertn.] fiber: fiber structure, chemical characteristics, and application. *Journal of Wood Science, 46*(5), 401-404.

6) Wahi, R., Chuah, L. A., Choong, T. S. Y., Ngaini, Z., & Nourouzi, M. M. (2013). Oil removal from aqueous state by natural fibrous sorbent: an overview. *Separation and Purification Technology, 113*, 51-63.

7) Ren, J., Sun, R., Liu, C., Cao, Z., & Luo, W. (2007). Acetylation of wheat straw hemicelluloses in ionic liquid using iodine as a catalyst. *Carbohydrate Polymers, 70*(4), 406-414.

8) Ibrahim, S., Ang, H.-M., & Wang, S. (2009). Removal of emulsified food and mineral oils from wastewater using surfactant modified barley straw. *Bioresource Technology*, 100(23), 5744-5749.