FTIR Analysis on Modified Kapok Fiber via Esterification for Palm Oil Mill Effluent (POME) Treatment

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Abstract—**Palm oil mill effluent is a waste product from the palm oil industry and it was considered as a drawback to the environment. This effluent was highly polluted and many studies have been conducted in order to determine the most economical and environmental friendly scheme for palm oil mill (POME) treatment. The objectives for this research were to modify the kapok fiber using esterification technique and to analyze the unmodified and modified kapok fiber using Fourier Transform Infrared (FTIR) spectroscopy. The kapok fiber was modified by using esterification reaction with the different percentages of catalyst (5% w/w, 10% w/w and 15% w/w). The modified kapok fiber was analyzed by using Fourier Transform Infrared (FTIR) spectroscopy to observe the functional groups presented after modification and the results were compared with the unmodified kapok fiber. Based on the FTIR spectra, the ester group was formed at the range of 1733-1737 cm^{-1} for the esterified kapok fiber for all of the percentages of catalyst. Meanwhile, the alcohol O-H stretching was presented at the region of 3329-3346 cm^{-1} both for unmodified and modified kapok fiber. However, the alcohol O-H stretch in esterified kapok fiber has reduced due to the reaction between the alcohols with stearic acid to form an ester. The best modification was by using the 5% of calcium oxide as the result showed the highest formation of ester which was 90.5%T. In conclusion, it shows that the esterification reaction has successfully modified the characteristic of the unmodified kapok fiber.**

Keywords— Palm Oil Mill Effluent (POME), Esterification, Kapok Fiber, Fourier Transform Infrared (FTIR) Analysis

I. INTRODUCTION

Palm oil industry is being a major industry as it produces raw material for other industrial sector and it is becoming one of the income that contributes to the Malaysian economy. This industry is still in progress as it is undergoing a lot of research and development mainly in Malaysian Palm Oil Board (MPOB) as to make a new product that will be marketing worldwide (Nazatul and Khairul, 2014).

Before getting the crude palm oil product, the fruit needs to undergo a lot of processes or stages such as extraction, sterilization, stripping, digestion, pressing, clarification, purification and vacuum drying. The process of extraction required a huge amount of water. For 1.5 m^3 of water, it is equivalent to 1 t of fresh fruit bunch. Meanwhile, half of the water ends up as palm oil mill effluent (Soh, *et. al.*, 2013).

Palm oil mill effluent (POME) is a viscous brown liquid accumulated with fine suspended solids. It is acidic as the pH number is in between 4 and 5. This effluent is highly polluted wastewater that contaminates the environment directly and indirectly through many ways. Due to the variety of mill operations and seasonal cropping throughout the year, the chemical properties of POME are different (Anwar, *et. al.*, 2014). If the untreated POME is discharged into watercourses, there will be a major problem towards the environment and thus there were many studies to determine the most economical and environmental friendly schemes for POME treatment.

According to Jeremiah, *et. al.,* (2014), there were various effluent treatments which are presently applied by the palm oil industry in Malaysia such as anaerobic or facultative ponds, tank digestion with mechanical aeration, facultative ponds with tank digestion, facultative ponds with decanter and physic-chemical with biological treatment. The ponding system is the most adapted one in Malaysia's palm oil mill. However, it is not an effective effluent treatment as the concentration oil residue in palm oil mill is high than in toxic wastewater. As for anaerobic ponds, the uses of microbial populations are still in progress studies by the researchers.

Nowadays, the technology of oil sorption has been studied among the researchers as one of the techniques to solve the POME problem. It has high possibility and most efficient solution to treat the effluent which involved the mechanism of adsorption by using the natural sorbents. Although different kinds of element such as organic, inorganic mineral and synthetic polymers have been used as the adsorbent agents in previous studies, the natural sorbent is the most economical because the price is cheaper than the non-renewable materials. The representatives of natural sorbent are kapok fiber, cotton fiber, wool fiber, milkweed, sawdust and many other materials that can be found (Jintao, *et. al.*, 2012).

Kapok fiber is a natural sorbent material and environmental-friendly cellulosic fiber as it does not consist of pesticides or chemicals. This fiber is also a heat and sound insulation material, lightweight and a good filling material (Ying, *et. al.,* 2014). Kapok fiber derives from silk-cotton tree is effective as a natural sorbent because it shows high oil sorption capacity depending on its big hollow lumen and the hydrophobic –oleophilic surface (Jintao, *et. al.*, 2012).

Since many investigators only concentrate their research about total removal of COD, production of methane and are not interested in studying the effectiveness of the oil matters adsorption by using esterification method thus, the research has not been done on the esterification of different natural fibers (e.g. kapok fiber) that has the possibility to reduce the pollutant components in POME treatment problem. From this study, the functional groups of modified kapok fiber will be obtained through FTIR analysis and the results will be compared with unmodified kapok fiber. Consequently, the benefits and the advantageous of esterification method by using natural fiber for POME treatment will then be introduced widely where it can reduce the waste generated in palm oil mill industry through adsorption. Therefore, this study is being conducted to acknowledge the treatment of POME with modified kapok fiber as the subject.

Periodic research has been carried out to find the right and suitable solution for POME treatment and management system.

Although many studies have been done to overcome the POME problem using the kapok fiber, there is still no research conducted by using the modified kapok fiber via esterification as an alternative way to treat POME. It is believed that by using the Fourier Transform Infrared (FTIR) spectroscopy, the functional group in the unmodified and modified kapok fiber can be analyzed and compared. Hence, the objectives of the research were to modify the kapok fiber using esterification method and to analyze the unmodified and modified kapok fiber by using Fourier Transform Infrared (FTIR) spectroscopy.

II. METHODOLOGY

A. Preparation of kapok fiber

The kapok fiber was esterified with stearic acid in a ratio of 1:1. The catalyst used was calcium oxide (CaO) at three different percentages, namely; 5% w/w, 10% w/w and 15% w/w, respectively. The esterification process was taken place in a reflux condenser in 5 hours of reaction time (Wahi, *et. al.,* 2014). Each sample was run in duplicates.

B. FTIR analysis on unmodified and modified kapok fiber

Fourier transform infrared (FTIR) spectroscopy was used as to determine the functional group in a sample. Generally, the result of FTIR analysis was showed in graph and the wave number of each functional group was labeled where the peaks of the graph were located. A range of wave number was in specific for one functional group. The modified kapok fiber was analyzed by using Fourier Transform Infrared (FTIR) spectroscopy to observe the functional groups present before and after modification. The results obtained were compared with the unmodified kapok fiber for further analysis.

III. RESULTS AND DISCUSSION

Chemical modification via esterification process was performed and FTIR analysis was done to analyze the functional groups present in kapok fiber. The raw kapok fiber was modified with stearic acid and the solvent used was ethyl acetate. The samples of esterified kapok fiber collected were based on the difference in percentage of calcium oxide, CaO (5% w/w, 10% w/w and 15% w/w) that functioned as the catalyst in performing the esterification process. For each percentage of calcium oxide, the experiment is run twice as to reduce the probability of errors during the experiment and to obtain the precise results from the averages of the modified samples shown by the FTIR spectra.

A. FTIR analysis on the unmodified kapok fiber

Unmodified kapok fiber is the raw material used before the esterification process was performed and it is an adsorbent that is currently in research. The purpose of undergoing the FTIR analysis towards the unmodified kapok fiber was to figure out the functional group presents in the adsorbent before the esterification process. The results of the FTIR analysis will be the parameters to compare with the FTIR spectra of the modified kapok fiber.

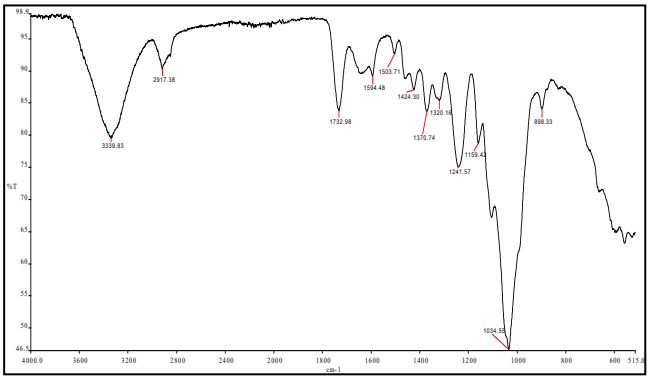

Figure 1(a): FTIR spectrum of unmodified kapok fiber at first run. *Note*: %T = % Transmittance

From Figure 1(a), the peak at region of 3339.83 cm^{-1} implied the alcohol O-H stretch which was the main functional group that involved in the esterification process. On the other hand, the peak at 2917.38 cm^{-1} indicates the alkyl C-H stretch in the raw kapok fiber. The presence of peak 1732.98 cm^{-1} in unmodified kapok fiber corresponding to the C=O stretching of carbonyl group. The highest peak was at region 1034.55 cm^{-1} which implied the C-O stretching vibration of cellulose backbone. According to Yian, *et. al.,* (2015), the kapok fiber is highly composed of cellulose which is about 35% to 64% and this is proven by the highest peak shown from the FTIR spectrum shown above.

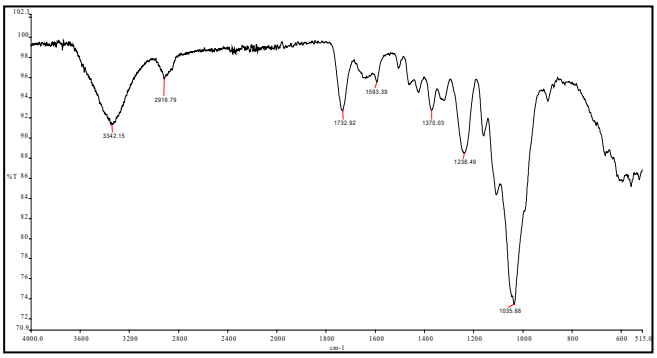

Figure 1(b): FTIR spectrum of unmodified kapok fiber at second run. *Note*: %T = % Transmittance

From Figure 1(b), the FTIR spectrum showed the similar trend as in Figure 1(a). The alcohol O-H stretch was the main functional group that involved in the esterification process and it was represented by the peak at 3342.15 cm^{-1}. On the other hand, the presence of alkyl C-H stretch in the raw kapok fiber can be referred to the peak at 2916.79 cm^{-1}. The peak formed at 1732.92 cm^{-1} in unmodified kapok fiber corresponding to the C=O stretching of carbonyl group. The highest peak was at region 1035.88 cm^{-1} which indicated the C-O stretching vibration of cellulose backbone.

Those two different groups of C-O and C=O have been highlighted in previous study which discussed about the esterification of *Metroxylon sagu* bark as an adsorbent to remove emulsified oil. It was an important functional group to analyze as it was needed in the estimation on the degree of esterification. The average intensity ratio was calculated for each of the parameters involved in the study to strengthen their results and findings about the potential of *Metroxylon sagu* bark or sago to remove emulsified oil (Wahi, *et. al.,* 2014). Therefore, the unmodified kapok fiber was used for further modification to perform the esterification process as the alcohol O-H group was shown in the FTIR spectra.

B. Effect of 5% calcium oxide on FTIR spectra of modified kapok fiber

The kapok fiber was modified by using the esterification process. The percentage difference of the catalyst added was investigated in order to study the effect towards the formation of ester in the modified kapok fiber. The powdered catalyst used was calcium oxide which was chosen based on the method performed by Wahi, *et. al.,* (2014).

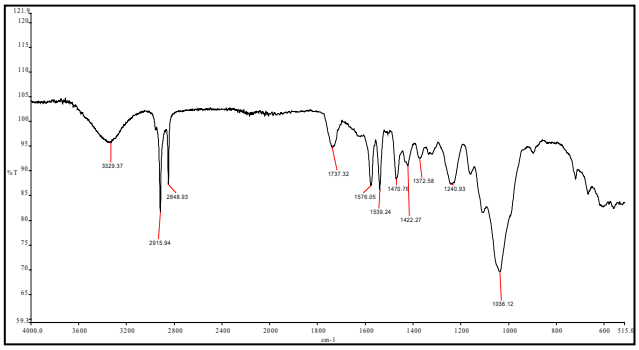

Figure 2(a): FTIR spectrum of modified kapok fiber at first run with 5% of calcium oxide. *Note:* %T = % Transmittance

The FTIR spectrum from Figure 2(a) depicted the changes of functional groups of kapok fiber after modification through esterification process. The presence of peak at 1737.32 cm^{-1} in modified kapok fiber was attributed to the formation of ester. According to Wahi, *et. al.,* (2014), the region at 1735 cm^{-1} was the region where the ester will be formed throughout the esterification process. Although it was not the exact peak like in the previous study, it was included in the ester group as the peak was the nearest to the range. Meanwhile, the carboxylic acid O-H stretch was shown in the FTIR spectrum at peak 2848.93 cm^{-1} for esterified kapok fiber as there was unreacted stearic acid left in the samples after the experiment conducted.

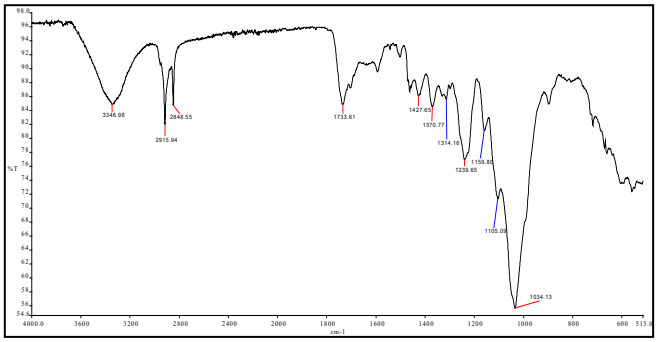

Figure 2(b): FTIR spectra of modified kapok fiber at second run with 5% of calcium oxide. *Note:* %T = % Transmittance

The FTIR spectrum from Figure 2(b) implied the same trend to the first run as in Figure 2(a). The peak of 1733.61 cm^{-1} in esterified kapok fiber was due to the ester group and it was one of the main different shown in the FTIR analysis after modification through esterification process. Furthermore, the presence of peak at 2848.93 cm^{-1} depicted the carboxylic acid O-H stretch formed in the modified kapok fiber. This functional group was present due to the unreacted stearic acid left in the samples. However, the ester group that was formed due to the reaction of alcohol with stearic acid affected the alcohol O-H stretching. The peak was decreasing after the kapok fiber has been modified via esterification process and it was referred to the peak of 3336.20 cm^{-1}.

C. Effect of 10% calcium oxide on FTIR spectra of modified kapok fiber

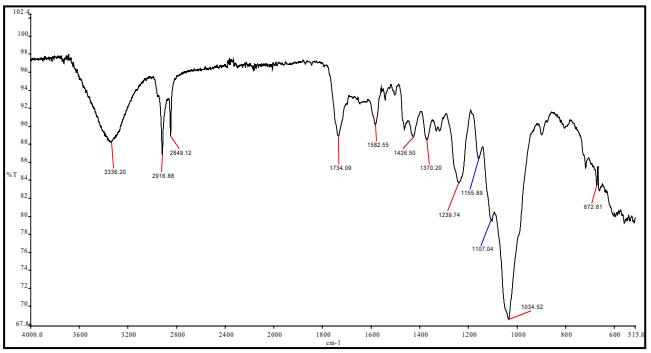

Figure 3(a): FTIR spectra of modified kapok fiber at first run with 10% of calcium oxide. *Note:* %T = % Transmittance

The FTIR spectrum from Figure 3(a) corresponded to the changes of functional groups of kapok fiber after modification through esterification process. The peak of 1734.09 cm^{-1} in esterified kapok fiber was due to the ester group that was formed. Based on Wahi, *et. al.,* (2014), the formation of ester was at 1735 cm^{-1} after the kapok fiber performed the esterification process. The peak was included in the ester group as the peak was the nearest to the range even though it was not in the exact region as referred in the previous study.

Meanwhile, the carboxylic acid O-H stretch was shown at peak 2849.12 cm^{-1} in the FTIR spectrum for esterified kapok fiber as there was unreacted stearic acid left in the samples after the experiment conducted. On the other hand, the alcohol O-H stretching was reduced after the kapok fiber has been modified via esterification process and this result was shown at the peak 3336.20 cm^{-1}. This is due to the formation of ester group from the reaction of alcohol with stearic acid.

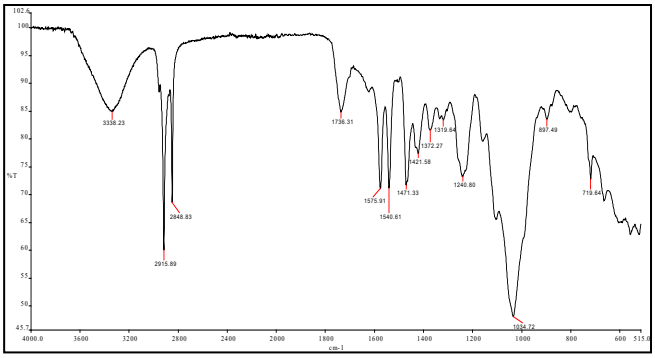

Figure 3(b): FTIR spectra of modified kapok fiber at second run with 10% of calcium oxide. *Note:* %T = % Transmittance

From Figure 3(b), the FTIR spectrum indicated a similar trend to the first run as in Figure 3(a). The presence of peak at range 1736.31 cm^{-1} in the FTIR analysis was attributed to the formation of ester in esterified kapok fiber. Meanwhile, the peak at 2848.93 cm^{-1} depicted the carboxylic acid O-H stretch as it was shown in the FTIR spectrum. This functional group was there because of the non-reacted stearic acid that has been left behind throughout the process. Moreover, the peak at 3346.96 cm^{-1} was corresponded to the alcohol O-H stretching and it was decreasing after the kapok fiber has been esterified. This was the effect from the reaction of alcohol with stearic acid to form ester.

D. Effect of 15% calcium oxide on FTIR spectra of modified kapok fiber

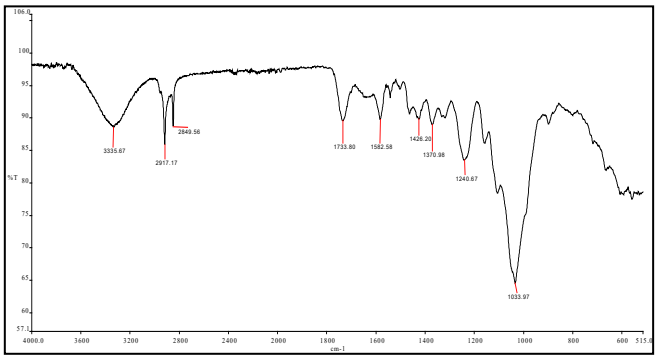

Figure 4(a): FTIR spectra of modified kapok fiber at first run with 15% of calcium oxide. *Note:* %T = % Transmittance

Based on Figure 4(a), the FTIR spectrum indicated the differentiation of functional groups in kapok fiber after been into a modification via esterification process as to improve the quality of the adsorbent. The formation of ester was found by the peak at range 1733.80 cm^{-1} and by referring to Wahi, *et. al.,* (2014), this was the region where the ester will be formed throughout the esterification process. However, there was unreacted stearic acid left in the samples after the experiment conducted and it was shown by the peak at 2849.56 cm^{-1} that corresponded to the carboxylic acid O-H stretch. On the other hand, the alcohol O-H stretching at 3335.67 cm^{-1} was decreasing after the kapok fiber has been esterified. The result occurred because of the ester group that has formed after the alcohol group reacted with stearic acid through the process of esterification.

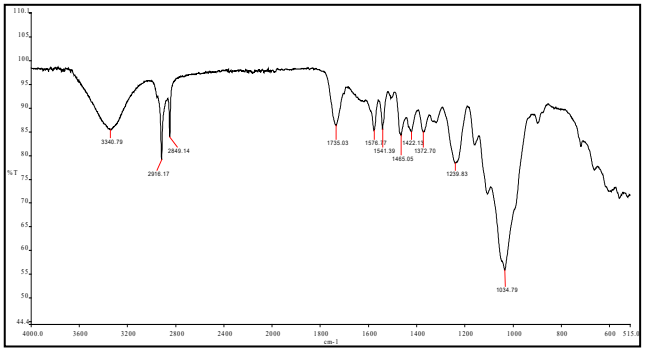

Figure 4(b): FTIR spectra of modified kapok fiber at first run with 10% of calcium oxide. *Note:* %T = % Transmittance

The FTIR spectrum from Figure 4(b) depicted the similar trend to the first run as shown in the Figure 4(a). The formation of ester that occurred at peak 1735.03 cm^{-1} was due to the modification through esterification process. It was the exact peak value based on Wahi, *et. al.,* (2014) as this was the region where the formation of ester occurred via the esterification process. Moreover, the carboxylic acid O-H stretch was shown at region 2849.14 cm^{-1} in the FTIR spectrum for esterified kapok fiber. This was due to the unreacted stearic acid left in the samples.

Meanwhile, the alcohol O-H stretching has reduced after the esterification of kapok fiber and it was shown at peak 3340.79 cm^{-1}. This is because of the formation of ester group that happened due to the reaction of alcohol with stearic acid. Therefore, the modified kapok fiber is proven to achieve the esterification process as the formation of ester has been shown in the FTIR spectra. Among the three different percentage of calcium oxide as shown in Figure 4.2, 4.3 and 4.4, the best modification was the modified kapok fiber by using the 5% of calcium oxide as the catalyst added into the esterification process.

E. Comparison of the percentage of catalyst added towards the formation of ester in modified kapok fiber

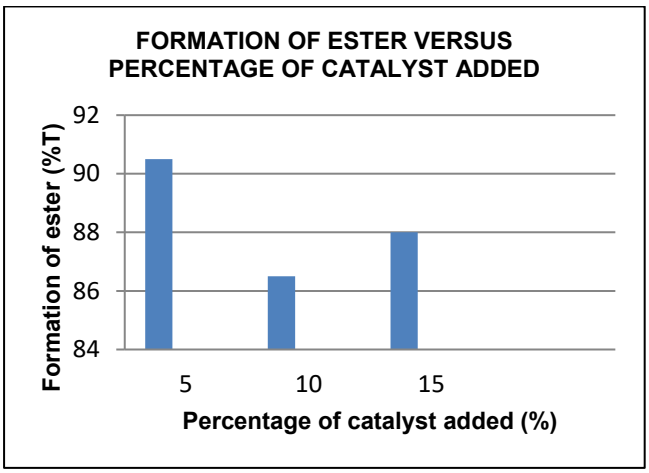

Figure 5: The bar chart of the formation of ester in FTIR spectrum against the percentage difference of catalyst added in the modified kapok fiber

The best modified kapok fiber has been selected based on the highest formation of ester. This can be referred to the Figure 5 which showed the bar chart that represented the formation of ester with different percentage of catalyst added to the modified kapok fiber. The highest formation of ester was by using the 5% of catalyst added, followed by using the 15% of catalyst added and the lowest was by using the 10% of catalyst added in the esterification process. In conclusion, the best modification was by using the 5% of catalyst added.

F. Comparison between the unmodified kapok fiber with modified kapok fiber

The functional groups present in the kapok fiber before and after modified via esterification process were used as the main parameter to compare the adsorbent. From the Figure 6(a), the peak of 3342.15 cm^{-1} indicated the presence of alcohol O-H stretch and confirmed that the unmodified kapok fiber has the main component for the esterification process to occur.

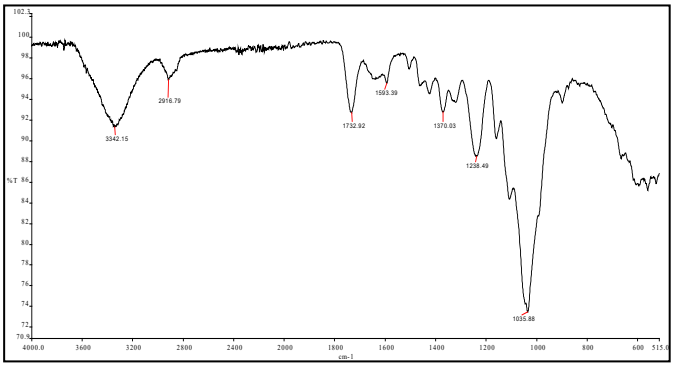

Figure 6(a): FTIR spectrum of unmodified kapok fiber. *Note*: %T = % Transmittance

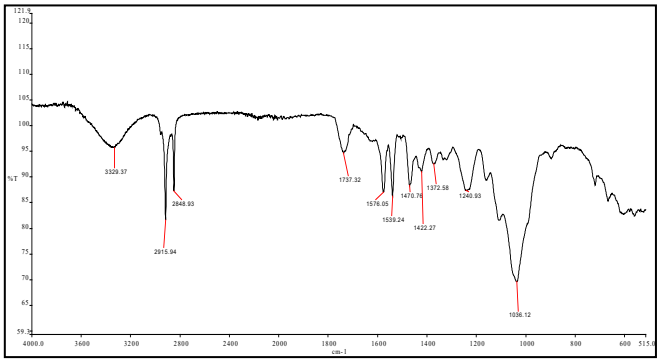

Figure 6(b): FTIR spectrum of modified kapok fiber by using the 5% of calcium oxide. *Note*: %T = % Transmittance

The modification through esterification process was successful because the ester group was formed in all the samples of modified kapok fiber. Based on the experiment performed, the FTIR spectra from the modified kapok fiber showed the formation of ester at range of 1733-1737 cm^{-1}. From Figure 6(b), it was the highest formation of ester by using the 5% of calcium oxide as catalyst added. The alcohol O-H stretch presented in the modified kapok fiber was lower than the unmodified kapok fiber. This was due to the esterification process that has taken place between the alcohol and stearic acid to form an ester. Therefore, the FTIR analysis on unmodified and modified kapok fiber was completely done and it showed that the characteristic of unmodified kapok fiber was successfully modified via esterification process.

IV. Conclusion

The FTIR analysis on unmodified and modified kapok fiber has been successfully done. The esterification reaction was done on the kapok fiber in order to modify the characteristic of kapok fiber. The ester group has been shown at the peak range of 1733-1737 cm^{-1} for the esterified kapok fiber. On the other hand, the alcohol O-H stretching has been presented at the peak region of 3329-3346 cm^{-1} for unmodified and modified kapok fiber. The highest formation of ester was achieved by using the 5% of calcium oxide, followed by using the 15% of calcium oxide and the lowest was by using the 10% of calcium oxide in the esterification process. Therefore, the best modification was by using the 5% of calcium oxide because the result showed the highest formation of ester. In conclusion, the characteristic of the raw kapok fiber has been successfully modified by the esterification reaction.

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