CRYSTALLIZATION-MECHANICAL TECHNIQUE FOR OIL EXTRACTION FROM OIL PALM EMPTY FRUIT BUNCH FIBRE

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Abstract. Oil palm empty fruit bunches fibre (EFB) fibre is a bi-product of palm oil mill. It contains 2 to 7 % of oil residual. The presence of oil residual had reduced the EFB fibre compatibility as filler matrix material. This research investigated the removal of residual oil from EFB fibre using a crystallization-mechanical technique. EFB fibre was crystallized using liquid nitrogen for 1, 3, and 5 minutes and then shaken in a mechanical collector for 5 minutes. All products were characterized and analyzed for oil removal capacity using Fourier transform infrared spectroscopy (FTIR). Images of EFB fibre samples were obtained using scanning electron microscopy (SEM). The results indicated that EFB fibre processed with the crystallization-mechanical technique had an oil content of 1.9890 ± 0.1786%, whereas unprocessed EFB fibre had an oil yield of 2.7126 ± 0.1628%. The dislodged brown powder had an oil yield of 1.3350 ± 0.0585%. FTIR analysis showed that the extracted oil from brown powder had an FTIR spectrum similar to that of crude palm oil. SEM images showed the changes in the EFB fibre's surface pores over the different crystallization times.

Keywords: Liquid nitrogen, crystallization time, oil removal, mechanical collector

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Introduction

Oil palm empty fruit bunch (EFB) is a by-product of palm oil milling that is estimated to constitute 22% of total palm oil production [1]. Malaysia, as the second largest palm oil producer, contributes 38% of the global market [2]. The abundance of EFB gives it the potential to be a sustainable resource for its derived products, since EFB fibre has a selling price of RM400 - RM600 per tonne [3]. However, EFB is known to possess an oil content of between 2 to 7% [4,5] and this oil content has been reported to contribute to reduced compatibility with composite filler [6]. Over time, EFB-derived products, especially in the mattress and cushion industry, emit an unpleasant smell as they degrade. It has been reported that rancidity (i.e. the oxidation of oil) is a key contributor to EFB fibre degradation [7].

In order to utilize EFB potential, oil extraction techniques that are both green and sustainable must be developed. Current oil extraction techniques are incapable of extracting sufficient oil content, despite the use of thermal and/or pressurized operating systems. This failure could be due to oil absorption which is aided by pore capillary mechanisms [4] that hinder the extraction process by reabsorbing the oil. These mechanisms are activated by the applied external energy, especially thermal energy, and by the EFB's porous surface [4].

The application of external energy, namely crystallization, onto the EFB fibre is able to induce molecular movement, which could potentially bend or break molecular bonds, leading to the removal of certain compounds. Whereby for this study, the application crystallization could be capable to break the molecular bonds that bind the EFB fibre and the oil residual. In addition, the removal energy could cause the material's molecular structure to rearrange itself into an organized solid of the same compound. Hence, the crystallization technique, a known separation technique in the chemical industry [8], is applied onto the EFB fibre to remove the oil residual, as produced the cleaned EFB fibre.

In this work, the fundamental theory of crystallization and a morphological understanding of EFB were combined and developed into the crystallization-mechanical technique. This technique aimed to induce internal molecular movement in order to break molecular bonds, especially those that bind oil and EFB compounds.

Materials and Methods

Processed EFB was collected from Taner R&D Palm Oil Mill, Tenom, Sabah, Malaysia. It was cut into lengths of between 8 to 12 cm and weighed to 250 grams, before being submerged into liquid nitrogen for 1, 3, and 5 minutes. The liquid nitrogen was obtained from the UMS Centre of Instrumentation and Science Service. The crystallized EFB fibre was placed into the mechanical collector, shown in Figure 1. The mechanical collector was shaken for 5 minutes, producing two final products, namely, cleaned EFB fibre and brown powder.

10 grams of cleaned EFB fibre and 20 grams of brown powder were placed into a soxhlet extraction chamber where soxhlet extraction was conducted for 4 hours, with n-hexane (AR grade, Merck, 99%) as solvent. The obtained oil-hexane solution was then exposed to rotary vapour for 3 hours, before being placed in an oven for an additional 3 hours to ensure the removal of solvent. The extracted oil yield was calculated based on Eq. 1.

Figure 1. Mechanical Collector.

$$Oil\ Yield, \% = \frac{Weight\ of\ the\ extracted\ oil, g}{Weight\ of\ EFB, g} \times 100\% \quad (1)$$

The extracted oil from brown powder and crude palm oil (CPO) were analysed using FTIR, conducted using a Mettler Toledo unit. SEM images of the surface of both types of EFB fibre were taken with a Carl Zeiss Evo 10 at a magnification of 100X.

Results and Discussion

Analysis of Oil Yield for Cleaned EFB Fibre and Brown Powder. It should be noted that most of the oil residue within EFB fibre is located within its spikelets [4] which have a porous surface where oil is absorbed and retained within the pores [4]. Crystallization of the EFB fibre changed this oil into oil crystals which were then dislodged by the mechanical technique. Then, oil extraction with soxhlet yielded the two final products cleaned EFB fibre and brown powder. The extracted oil yield of the final products is as shown in Table 1.

Table 1 shows that the oil yield extracted from the cleaned EFB fibre was less than that of the EFB fibre without crystallization-mechanical processing, indicating successful oil removal. This oil reduction was confirmed by the presence of extracted oil in the brown powder, which increased with crystallization time. These findings suggest the viability of the crystallization-mechanical technique for oil extraction, and the trend presented in Table 1 suggests the possible mechanism of this technique.

Crystallization for 1 minute produced a lower oil yield in both cleaned EFB fibre (0.9680 ± 0.1904%) and brown powder (0.7193 ± 0.0475%) as compared to the final products produced by 3 and 5 minutes of crystallization. This is due to strengthened intermolecular interactions in the latter [9]. Upon crystallization, the kinetic molecular movements within the EFB fibre were slowed, converting internal energy into stored potential energy [10], and strengthening intermolecular interactions. This would increase the strength of molecular bonds [9], which require a significant amount of energy to break. It should be noted that the energy supplied by soxhlet oil extraction is assumed to be similar throughout this research.

Table 1. Extracted Oil Yield for Final Products of Crystallization-Mechanical Technique by Crystallization Time

Crystallization Time, min	Average Extracted Oil Yield, %	
	Cleaned EFB Fibre	Brown Powder
0	2.7127 ± 0.1625	-
1	0.9680 ± 0.1094	0.7193 ± 0.0475
3	2.2123 ± 0.2501	1.2743 ± 0.0164
5	1.9890 ± 0.1786	1.3350 ± 0.0585

However, prolonged exposure to increased molecular interaction within the crystallized EFB fibre would exert a constant load upon the molecular bonds [11]. This constant load, especially on those bonds between the oil and EFB compounds, would create stress or tension [12], which will eventually lead to irreversible deformation [12]. This could strongly induce the rupture of molecular bonds, increasing the brittleness of crystallized EFB fibre [13] and making it fragile.

External disruptive forces applied to the crystallized EFB fibre will not only initiate internal vibrational movement but will also release stored internal energy (potential energy) which could possibly induce the breaking of the molecular bonds. Since the applied energy prompted cracks to propagate into the stress-fatigue molecule bond, the active mechanism is similar to the mechanisms of thermal shock [14] and stress cracking [13]. The active mechanism for this research can be seen in the increase in oil yield for both final products generated with 3 minutes of crystallization time (brown powder, 1.2742 ± 0.0164%, and cleaned EFB fibre, 2.2123 ± 0.2501%).

The rupture of molecule bonds, especially those that bind the oil and EFB compounds, can be seen in the oil yield from the longest crystallization time (5 minutes). Table 1 shows a slight decrease in the oil yield of cleaned EFB fibre (1.9890 ± 0.1786%), but an increase in the oil yield of brown powder (1.3350 ± 0.0585%), as compared to the extracted oil yield for 3 minutes of crystallization. This indicates that oil crystals were dislodged from the crystallized EFB fibre and demonstrates the potential of the crystallization-mechanical technique for oil extraction.

Although Table 1 indicates the presence of oil within brown powder, it is important to further analyse the extracted oil from brown powder, in order to ensure the potential and the workability of the crystallization-mechanical technique. Hence, FTIR analysis was conducted on the extracted oil from brown powder, and its spectra are compared to that of crude palm oil (CPO).

Comparison of Fourier Transform Infrared Spectroscopy (FTIR) Analysis for the Extracted Oil from Brown Powder and Crude Palm Oil. Although the soxhlet technique (with n-hexane as solvent) is considered to be the standard chemical technique for oil extraction from EFB [15], this may not be true for the oil extracted from brown powder. To establish the presence of oil within brown powder, the extracted oil was subjected to FTIR analysis. The FTIR spectra of the extracted oil for all crystallization times (1, 3, and 5 minutes) were compared to the FTIR spectrum of CPO since it has been reported to possess a similar primary chemical composition.

The FTIR spectra in Figure 2 show that all samples had absorption peaks at 2931 and 2852 cm^{-1}, within the C-H olefinic stretching region (3050 to 2800 cm^{-1}) [16]. These absorption peaks could also indicate the presence of sp3 hybridization in C-H band within the hydroxyl group. C-H movement could also be identified in the absorption peaks of 1462 cm^{-1} (rocking vibration) and 724 cm^{-1} (bending vibration) [17]. Figure 2 shows an intense absorption peak at 1745 cm^{-1}, indicating the C=O functional group within all samples. It has been reported that this absorption peak falls within the stretching of C=O within the ester compound [16]. The carbonyl (C-O) compound group can be detected within all samples, corresponding to the absorption peak of 1159 cm^{-1}.

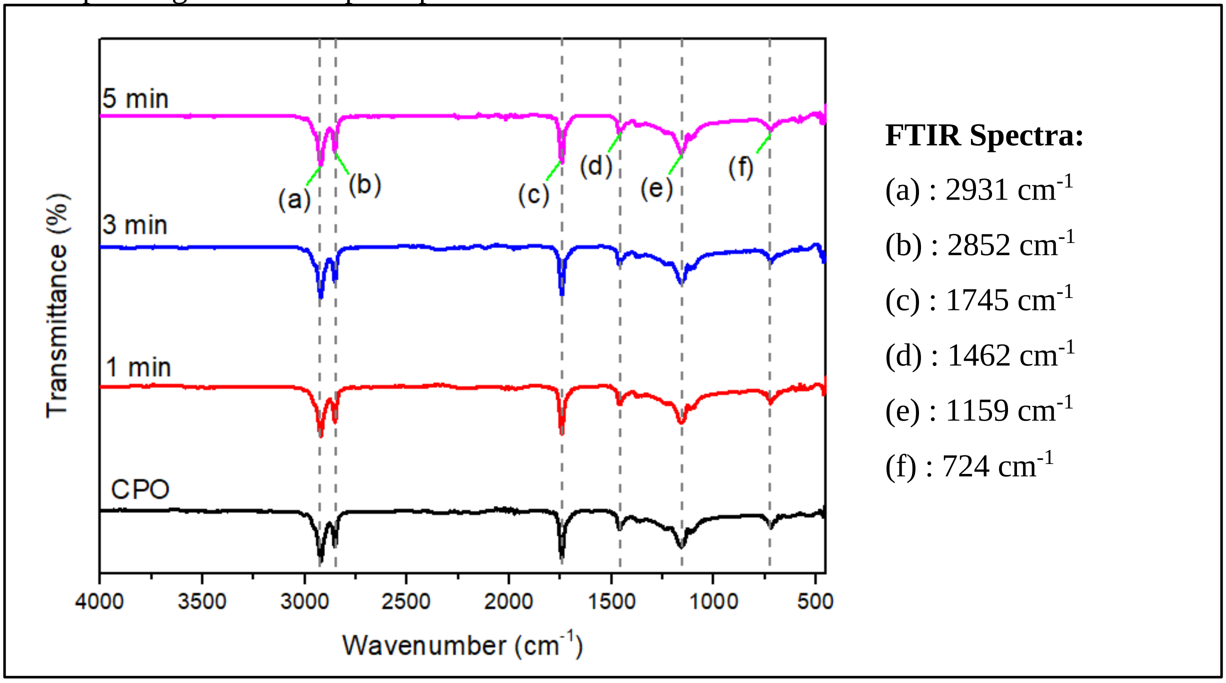


Figure 2. FTIR Spectrums of The Extracted Oil from Brown Powder and Crude Palm Oil (CPO).

From Figure 2, it can be seen that all samples of the extracted oil from brown powder were similar to CPO, with the main functional groups consisting of C-H, C=O, and C-O bands. This similarity established the presence of oil within the brown powder, further indicating the dislodgement of oil from crystallized EFB.

Scanning Electron Microscopy Images of EFB Fibre and Cleaned EFB Fibre. Although the findings just presented demonstrate the potential of the crystallization-mechanical technique for oil extraction from EFB fibre, this method may not be able to completely extract residual oil. However, its lack of chemicals and fairly easy execution process suggest that that the crystallization-mechanical technique could possibly serve as the pre-treatment technique for any composite filler matrix application. To investigate this, morphology analysis was conducted using scanning electron microscopy (SEM). Images of all samples analysed are shown in Figure 3.

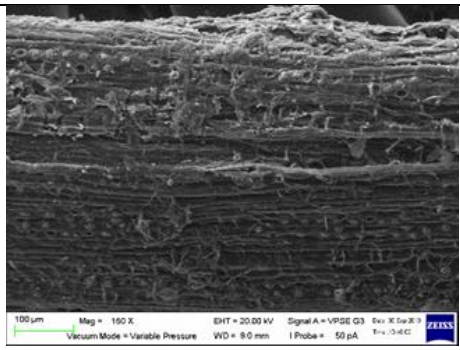
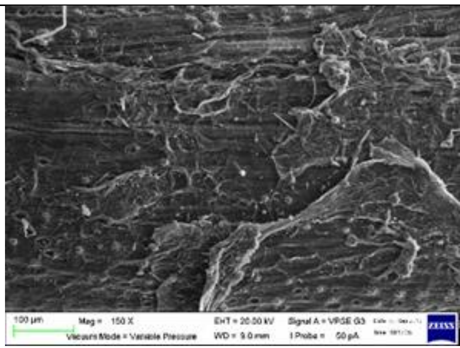
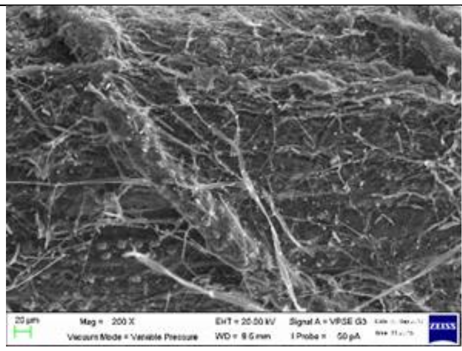
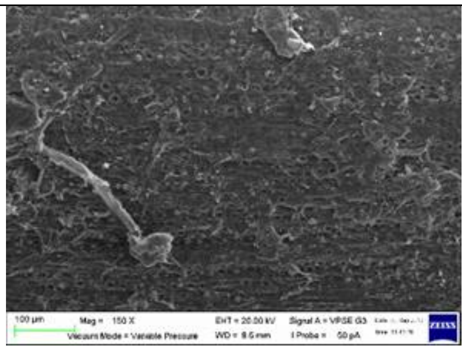
Crystallization Time, min	**EFB Fibre**
0	
1	
3	
5	

Figure 3. SEM Images of EFB Fibre and Cleaned EFB.

The first SEM image in Figure 3 is of the EFB fibre which was not subjected to the crystallization-mechanical technique. This sample is clearly similar, in terms of the number of clogged and unclogged pores, to the cleaned sample with the shortest crystallization time (1 minute). As seen in the SEM images of the cleaned EFB fibre generated with 3 and 5 minutes of crystallization, the number of clogged pores increased with prolonged exposure to liquid nitrogen as crystallization medium. These visible changes correlated with the highest oil yield results found in Table 1.

It has been reported that most of the EFB residual oil is located within the porous surface of EFB fibre [4]. Our findings not only verified the location of the residual oil within EFB, but also further indicated that 3 minutes of crystallization with crystallization-mechanical technique is able to extract the greatest oil yield from the cleaned EFB fibre. Table 1 also shows a reduction in oil yield with the longest crystallization time (5 minutes). This corresponds to the greatest number of unclogged pores visible in its SEM image, further indicating the possible dislodgement of oil crystal from the crystallized EFB fibre.

It is worthwhile to note here that EFB fibre does contain moisture which is also subject to changes in its crystal lattice. Upon crystallization, the crystal lattice of the moisture will expand as it rearranges itself to form a hexagonal structure [18]. This movement could possibly push the residual oil out from the pores, as indicated by the visible increase of clogged pores in the cleaned EFB fibre generated by 3 minutes of crystallization.

The movement of residual oil could exert stress on the molecular bonds, especially those binding the oil and EFB compounds. Hence, it may have accelerated the rupture or the breakage of the molecular bonds within the EFB fibre, thereby increasing the brittle properties of crystallized EFB and the dislodgement of oil crystal. The final result would be an increased number of unclogged pores on the EFB fibre surface, which are known to be highly desirable in composite-matrix filler applications.

Conclusion

This study demonstrated the potential of a new crystallization-mechanical technique for oil extraction from EFB fibre. The technique developed here proved able to dislodge oil crystals from crystallized EFB fibre. The crystallization-mechanical technique (using five minutes of crystallization time) was able to reduce oil yield by 26.67% compared to unprocessed EFB fibre (oil yields of 1.9890 ± 0.1786% and 2.7126 ± 0.1628%, respectively). The dislodged oil crystals from the crystallized EFB fibre were found within the brown powder, as evidenced by the oil yield of brown powder (1.3350 ± 0.0585%). In addition to oil extraction, the crystallization-mechanical technique is also able to produce a rough and porous surface on the EFB fibre, making this technique suitable for pre-treatment, especially in composite filler matrix applications.

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Author Contributions

All authors were involved in the study, Kessnia Ira Ng led the cystallization-mechanical technique for oil extraction from oil palm empty fruit bunch, data analysis and manuscript writing; Coswald Stephen Sipaut @ Mohd Nasri is the principal investigator and is responsible for the overall direction of the project.

Disclosure of Conflict of Interest

The authors have no disclosures to declare.

Compliance with Ethical Standards

The work is compliant with ethical standards.

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