Effect of Stirring Rate and Freezing Time on the Percentage of Recovery of Residual Oil from Palm Oil Mill Effluent via a Stirred Freeze Crystallizer

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Abstract
In palm oil industries, treating palm oil mill effluent (POME) is still problematic due to both technologies sustainability and management will. In conjunction with the POME problem, increasing the oil extraction rate (OER) is also the most crucial task for these palm oil production community. The most promising method to address these two challenges is by direct recovering of lost oil in the POME. Among the popular separation processes for recovery of residual oil from POME are by using evaporation, adsorption and reverse osmosis as process media generated a good amount of percentage recovery of residual oil from the effluent. However, these methods require high amount of energy and the process itself are complex where it can affect the quality of the residual oil. The goal of this project is to extract and recover the residual oil in POME using an advanced approach called progressive freezing, in order to meet the standard quality discharged of effluent and improve oil extraction rate (OER). In this research, a cylindrical stirred freeze crystallizer was designed and fabricated, where the crystallizer was immersed in a refrigerated water bath for cooling purpose. The effect of stirring rate and freezing time on the percentage of recovery of residual oil was investigated. It was found that higher stirring rate resulted in a lower percentage oil recovery, which translated into low efficiency. On the other hand, higher percentage of oil recovery was monitored as the freezing time is prolong from 20 to 60 minutes. The highest percentage oil recovery of 76.5% was obtained at coolant temperature of 2°C, freezing time of 40 minutes and the stirring rate of 150rpm.

Keywords: Palm oil mill effluent; Oil Recovery; Residual oil; Progressive Freezing; Freeze crystallization

1. Introduction
Palm oil mill effluent (POME) is an unavoidable highly polluting waste produced from the process of Fresh Fruit Bunch (FFB) in palm oil mill. The main products of palm oil mill process are crude palm oil (CPO) and palm kernel (PK). Nowadays, palm oil has grown into an essential agricultural especially in Malaysia, and Indonesia. Figure 1 shows that 86% of the palm oil production had been concurred by both countries. In addition, 42 million tons of palm oil contributes to the global total production of oil and grease every year [1]. Nevertheless, the current increasing world demand for palm oil is set to increase the by-product of palm oil industry which is POME. In the meantime, it lowers the oil extraction rate (OER) of the palm mill where there is high amount of residual oil flowed into the POME pond because of inefficiency of the machines while processing the FFB.

POME is a large quantity liquid wastes which are non-toxic, organic in environment but have an obnoxious odor and extremely contaminated. According to past research, about 50% of water consumption in the palm oil extraction process will be lost as steam while the other half will end up as POME [2]. Increased global demand for palm oil demand has pushed for higher the oil extraction rate (OER), especially from POME. Generally, 0.7% by weight of residual oil had been found in each ton of POME produced by the FFB processing system where to be exact 1 ton of FFB produces 0.75 ton of POME (by-product) and 0.2 ton of CPO (main product) production rate reported [3].
The palm oil industry is aiming for POME pollution reduction in order to develop a greener impression of the company and to accomplish sustainability [3]. This is due to the majority of the palm oil mills especially in Malaysia have approved the ponding operation for effluent treatment. Nevertheless, finding for an efficient technology used for POME treatment is still the major problem in Malaysia. POME from oil palm crushing mills in Thailand consist of high COD and oil in the range of 45000 and 6000 mg/L, accordingly. After the process of oil recovery, more than 70% of COD was significantly showing a decrement and 78% of oil was efficiently recovered from POME. Thus, the recovery of oil from POME shows a possibility to reduce high COD from POME and increase the residual oil recovery rate [4].

Currently, there are several separation methods used in order to obtain res oil from POME such as coagulation, evaporation, reverse osmosis and adsorption method. This is to cut down the environmental loading from oily waste and reducing the processing outlay. However, some of the current conventional oil recovery techniques have several weaknesses such as the methods used requires high amount of energy and high complexity of the process where it can cause a decrement for the productivity. For example, evaporation method is inconvenient for solutions with volatile organic compounds plus it needs great amount of energy to vaporize the water molecule. Thus, research on new technology are required to extract the residual oil from (POME) in order to fulfil the needs of green palm oil production [5].

Furthermore, this research will initiate a new oil recovery method from POME which has never been probe especially in Malaysia and improving OER by recovering oil from POME. This is very necessary to be done in order to explore a new alternative that can replace current existing methods through promoting a more convenient and more efficient method. The comparison between conventional methods and proposed methods had been shown in Table 1 based on previous research. Based on the Table 1, PFC can be a better method to concentrate solutions that could replace the conventional methods since it has a lot of advantages compared to others. Even though the productivity of PFC has been found to be lower than other techniques, various studies are currently be operated to intensify the performance of the PFC. Nevertheless, there is no systemized analysis that had been reported in term of evaluating the mechanism of concentration and separation in PFC.

| Techniques | Advantages | Disadvantage | References |
|------------|------------|--------------|------------|

![World palm oil production in 2017](image-url)
AdSORption  
Eco-friendly, low production expenditure, easy process and have high efficiency.  
The used of adsorbent are hard to be disposed. Therefore, a post treatment on the adsorbent is needed since it causes danger to the environment and increase expenditure.  
[6]

Evaporacion  
The process is simple, high efficiency and environmentally friendly.  
High temperature involved in evaporation is bad since it could damage the vital composition in the solution such as aroma, flavour and nutrition. Therefore, it is not advisable for solutions with volatile organic compound which may cause hazards and dangers. Plus, the energy requirement is high.  
[7], [8]

Reverse osmosis  
Excellent efficiency of oil and grease removal, low labour cost and required a small area.  
High maintenance cost is absolutely needed not only for maintaining and replacing the membrane but also for attaining osmotic pressure required for the process. High pressure is required, fouling and short life expectancy.  
[9]

Progressive Freezing Concentration  
The system is simple, environmentally friendly, low maintenance and operating cost, low temperature, less unit operations needed and green technology.  
The productivity of PFC has been found to be lower compared to other method.  
[8]

Besides, it also can give opportunity for people inside or outside Malaysia to recognize the new method as a new effective oil recovery process, either through publication, conference or demonstration. It is a must to ensure that the entire procedure is safe, easy to operate and environmentally friendly since we are handling with the polluting waste, even though the need is to find a lowest cost process method is favored. Knowledge in this study, could be a reference to other related courses.

In this project report, progressive freezing (PF) has been introduced to replace the conventional residual oil recovery methods. Basically, PF is a method used to freeze one component into a layer of plain crystal and afterwards separating the frozen fragment from the mother solution. By using PF, it could maintain the thermally sensitive materials in the product because it used low temperature and energy in the process involved as compared to evaporation [10]. By introducing the progressive freezing
method for residual oil recovery from POME, it should be able to extract high amount of oil from POME since the separation occurs depends on the change of melting or freezing points. In this research, the impact of stirring rate and freezing time on the performance of PFC in recovering the residual oil was evaluated. The freezing time and stirring rate were varied from 20min to 60min and 150rpm to 350rpm. The performance of the progressive freezing was analyzed by testing the oil and grease value before and after the freezing process.

2. Methodology

2.1 Materials
POME samples are collected from a mixed raw effluent (MRE) pond at FELCRA Nasaruddin palm oil mill in Perak, Malaysia. The sample consist of sludge, water and the escaped oil because of inefficiency of the machine used. The sample is then stored in the freezer room to prevent from disintegration, deterioration and variation to the free fatty acid (FFA) composition. Pre-treatment to remove the solid sludge from the liquid sample had been done by doing sedimentation process. After the sludge removed, the sample was tested for the initial oil and grease value. Besides, 50:50 volume ratio of ethylene glycol and water was used as the coolant for the freezing process.

2.2 Experimental Setup
Figure 2 shows the experimental apparatus for the PF process, which consists of a retort stand, a digital stirrer, a cylindrical freeze crystallizer, and a refrigerated water bath. The cylindrical freeze crystallizer is the primary equipment of this system which functions to allow crystallization to take place. The temperature of the freezing process was controlled according to the desired reading of the coolant temperature. The retort stand was utilized to seize the crystallize during the time it was submerged in the water bath. Next, digital stirrer was put up to agitate the sample inside the crystallizer in order to provide a well-mixed solution. Last but not least, oil and grease analyzer and pH meter are used at the end of the experiment to measure the value oil and grease and pH of the samples before and after the freezing process.
2.3 Experimental Procedure

The experimental procedure was initiated by preparing the palm oil mill effluent (POME) sample which had been stored in the cold room beforehand. The cylindrical freeze crystallizer was attached to the retort stand and was then immersed into the refrigerated water bath. As the desired stirring rate reached, 500 mL of POME sample was poured into the cylindrical freeze crystallizer to let the crystallization process to happen. The coolant temperature was then kept constant at 6°C.

The process was stopped after certain specified period. Later, the crystallizer was taken out from the water bath and liquid mixture was transferred into a sample bottle for characterization purpose. The oil and grease value of the sample is then measured using a TOG analyzer. The experimental process was repeated at different stirring rate and freezing time.

3. Results and Discussions

3.1 Effect of Stirring Rate

The stirring rate of the digital stirrer used in this study was varied from 150 to 350 rpm. The other two parameters, which are freezing time and coolant temperature were kept constant at 40 minutes and 6°C, respectively. According to previous literature, the higher the stirring rate, the lower the final oil and grease value of the sample, indicating the higher percentage oil recovery [11]. Theoretically, higher stirring rate promotes heat transfer from the sample to the coolant, which eventually will enhance the planar growth of ice crystal from the cooling wall by keeping contaminants away from ice-liquid interface. Therefore, stirring rate played a significant part in providing a low concentration of the oil in liquid phase.

Table 2 shows the percentage recovery of oil and grease from the POME samples at different stirring rate. As the stirring rate is increased from 150 rpm to 300 rpm, the oil and grease value also increased. However, as the stirring rate is further heightened to 350 rpm, the oil and grease value drop a little. In addition, it can be observed that the percentage recovery of oil reached the highest of 59% at the lowest stirring rate of 150 rpm. This is because, the solid oil started to break apart and scatter at stirring rate of 200 rpm and above which produced high amount of small particles floated at the surface of the water. Therefore, the solid oil in the crystallizer has started to become less concentrated and could possibly be dissolved back upon mixing at higher rate. Furthermore, stirring rate from 150 rpm to 250 rpm managed to reduce the oil and grease value of the POME below the Malaysia Department of Environment (DOE) standard (50 mg/L).

| Stirring Rate (rpm) | Initial oil and grease value (mg/L) | Final oil and grease value (mg/L) | DOE Standard (mg/L) | % Recovery |
|---------------------|-----------------------------------|-----------------------------------|---------------------|------------|
| 150                 | 35.6                              | 35.6                              | 50                  | 59         |
| 200                 | 44.8                              | 47.3                              |                     | 47.3       |
| 250                 | 49.7                              | 50                                | 41.5                |            |
| 300                 | 53.9                              | 36.6                              |                     |            |
| 350                 | 52.5                              | 38.2                              |                     |            |
3.2 Effect of Freezing Time

In order to investigate the effect of freezing time on the effectiveness of the PF process, the freezing time was manipulated from 20 to 60 minutes. The temperature of coolant and stirring rate were fixed at 6°C and 150 rpm. The percentage recovery of oil and grease is tabulated in Table 3.

| Freezing Time (min) | Initial oil and grease value (mg/L) | Final oil and grease value (mg/L) | DOE Standard (mg/L) | % Recovery |
|---------------------|------------------------------------|----------------------------------|---------------------|------------|
| 20                  | 36.6                               | 56.9                             |                     |            |
| 30                  | 34.2                               | 59.7                             |                     |            |
| 40                  | 31.8                               | 62.6                             | 50                  |            |
| 50                  | 28.1                               | 66.9                             |                     |            |
| 60                  | 27.3                               | 67.9                             |                     |            |

Theoretically, a longer freezing time will result in a lower oil and grease in the unfrozen POME sample, portraying a good efficiency of the PF process [12]. However, increasing the freezing time would lead to a highly saturated solution with oil, thus enhancing the inclusion of oil in the formed solid. Hence, by achieving a suitable duration or freezing time, it can result in a high purity of the liquid component.

From Table 3, it can be observed that the oil and grease left in the sample shows a decreasing trend from 20 to 60 minutes of freezing time. The highest oil recovery of 67.9% was recorded at 60 minutes. Since the limit discharge by Malaysia DOE is 50 mg/L, all tested freezing time managed to remove the oil and grease from POME below this standard.

4. Conclusion

A simple and convenient method called progressive freezing (PF) had been chosen for this project to recover the residual oil from palm oil mill effluent (POME). In this study, the performance of PF process was represented by the percentage recovery of oil and grease from the POME and was evaluated at different freezing time and stirring rate. The results show that lower stirring rate and higher freezing time resulted in higher percentage of recovery of residual oil from the POME. Based on the results, the highest percentage oil recovery is 67.9% at the coolant temperature of 6°C, freezing time of 60 minutes and the stirring rate of 150 rpm.

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