Recovery of Oil from Waste Palm Kernel Cake by Sub-Critical Water

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Abstract

Palm kernel cake is one of the wastes produced by palm kernel oil mill. Malaysia as one of the largest oil producers in the world produces a large number of waste palm kernel cake annually and mostly treated as animal feed while it still contains valuable oil residue. This study presents the application of sub-critical water as an environmental friendly medium for recovery of oil from waste palm kernel cake. Experiments were conducted in batch reactors with sub-critical water at temperature ranging from 180°C to 280°C for 5 minutes. Highest oil yield of 52.9 mg-oil/g-dry waste palm kernel cake was obtained at reaction temperature of 240°C. This amount is 54.4% of the amount of oil extracted via Soxhlet method with hexane. The extraction of oil using sub-critical water at temperature below 240°C has correlation coefficient of 0.97 to dielectric constant of water. Solid waste also can be reduced by sub-critical water treatment as the yield of solid residue decreased with increasing temperature until 0.1g-solid residue/g-dry waste palm kernel cake at 280°C. This study provides the benefits of sub-critical water as oil extraction method and treatment medium for waste palm kernel cake without using harmful solvent.

Keywords: Biomass; Oil recovery; Palm kernel cake; Sub-critical water

INTRODUCTION

Malaysia is one of the main countries producing palm oil in the world. It has been reported that Malaysia produces 20 million tonnes of crude palm oil and 2.5 million tonnes of waste palm kernel cake in 2015 [1], [2]. This process of oil extraction leaves behind various residues such as leaves, tree trunks, decanter cake, fruit bunches, mill sludge and fibers, shells and palm kernel cake [3], [4]. Since there is a large amount of waste palm kernel cake produced in oil palm mills, there is a need to recover and utilize these wastes.

Palm kernel cake is one of the solid residues that are produced after the extraction of oil from palm kernel process [5], [6]. Currently, palm kernel cake is majorly commercialized as ingredients of beef and dairy feed [7], [8]. In Malaysia, oil from palm kernel is typically extracted using mechanical screw pressing and thus generate a byproduct called waste palm kernel cake. Although this method is considered as effective, it will leave residual oil of 4% to 10% in the palm kernel cake [9], [10]. Thus, it is worth to recover oil and add value to the waste palm kernel cake.

There are various methods to recover residual oil. Pyrolysis, hydrolysis and supercritical liquefaction are a few of methods to recover oil [11]–[13]. Nevertheless, some of the methods require the usage of organic solvent which is not suitable for food processing. In addition, it also may contribute to environmental issues. Therefore, alternative environmental friendly method is needed for recovery of oil.

Dielectric constant is the ratio of permittivity of a substance to a free space. Figure 1 shows the dielectric constant of water as a function of temperature. The dielectric constant of water at room temperature, 25⁰C, is 78.4. Amazingly, it becomes 28.5 at temperature of 240⁰C where it is near to the dielectric constant of ethanol at room temperature [14]. Since ethanol is known as a good solvent extraction, having water of dielectric constant closer to ethanol will probably makes the water to behave like ethanol.

Figure 1: Dielectric constant of water at various temperatures. Data was obtained from International Steam Tables: Properties of Water and Steam Based on the Industrial Formulation [27].

Sub-critical water is defined as liquid water that lies in between the temperature of its boiling point and its critical temperature [15]. Sub-critical water treatment is an extraction
technique where the water is used at elevated temperature in between 100°C to 374°C at a pressure that is high enough to maintain the liquid state [16], [17]. Sub-critical water treatment has been studied for good extraction and hydrolysis [14], [18]. When compared to supercritical fluids, sub-critical water requires lower equipment cost because of its lower operating pressure and temperature; and it is non-corrosive [19], [20]. It is also cleaner, faster and cheaper when compared to the conventional methods [21]. However, the sub-critical water treatment temperature is one of the most important parameters affecting extraction efficiencies. When temperature rises, the dielectric constant will drop almost similar to some solvents such as ethanol at room temperature [17], [22].

The objectives throughout this research are to extract oil from waste palm kernel cake, to compare the extraction efficiency to Soxhlet method, to determine the relationship of sub-critical water reaction with dielectric constant and to study the amount of solid residue left after the sub-critical water treatment.

MATERIALS AND METHOD

Materials

Waste palm kernel cake was collected from one of distributors located in Selangor, Malaysia. The heating bath used throughout the research was molten salts made of industrial grade sodium nitrate, and industrial grade potassium nitrate with ratio 1:1. The ultra-pure water used in this research was prepared in-house by Milli-Q with purity of less than 0.1 μS.

Drying of sample

Prior to the sub-critical water extraction, moisture content of the waste palm kernel cake was calculated by a cumulative dry method of the palm kernel cake. Three samples of palm kernel cake were placed in separated beakers with each sample weight of about 5 g of waste palm kernel cake from the same batch. It was then dried at 80°C and was weighed for every 1 hour, then followed by every 24 hours until the weight becomes constant.

Conventional extraction with the Soxhlet apparatus

Sample was loaded into a thimble and placed into a distillation arm equipped with a condenser. The Soxhlet extraction was conducted for 8 hours by using hexane as the solvent in a round-bottomed flask. After the hexane was recovered sufficiently, the remaining solvent and oil mixture was left in the fume hood until the solvent was completely removed.

Sub-critical water extraction

In this study, a batch laboratory-scale reactor was used for the sub-critical water extraction as in Figure 2. The reactor was a stainless steel tube with volume of approximately 6.64 cm³ comes with Swagelok fittings.

Kurnin et al. [14] and Pourali et al. [23] have shown good oil extraction via sub-critical water extraction using sample to water ratio of 1:5 and 1:6 respectively. Since Kurnin et al. were using palm fruit bunch which is also one of palm wastes, sample to water ratio of 1:5 was preferable. Thus, accurate weight of 1 g of waste palm kernel cake and 5 mL of Milli-Q water were charged into the reactor. Air was then drawn out by purging argon gas into the reactor tube.

Then, the reactor was capped tightly. The reactor was then immersed in a preheated salt bath at the temperature range of 180°C to 280°C for 5 minutes. Figure 3 shows the diagram of the salt bath used. In this research, the 5 minutes residence time includes the heat-up time. The reactor and salt bath was continuously shaken in order to speed up the heating-up rate to a steady state condition in a very short time of about 25 seconds [23]. Once reached the reaction time, the reactor was quickly quenched into tap water at room temperature to stop the reaction.

The content of the reactor was then transferred into a test tube before it was centrifuged. Photograph of products were taken after the centrifugation. An appropriate amount of distilled water was added to the reactor. It was then shook vigorously to clean the inner wall of the reactor and transferred into the same test tube. This procedure was repeated until aqueous solution in the reactor becomes colorless. The test tube was then centrifuged and a suitable amount of hexane was added and shook gently without touching the solid, to only recover oil that has been extracted into the supernatant. The reactor was also added with hexane to recover oil which sticks on the reactor wall and poured into the test tube. This was repeated until the hexane coming out from the reactor becomes colorless. The test tube was then centrifuged. The hexane-soluble phase is then transferred into a bottle sample. An adequate amount of hexane is added again into the test tube and gently shook without touching the solid before...
centrifuged and transferred into the oil bottle sample. This was repeated until the hexane phase in the test tube was colorless. The bottle sample was then left opened in the fume hoods to allow hexane to vaporize completely.

**Solid residue**

The remaining solid and water content from sub-critical water extraction was centrifuged and the supernatant was removed. An appropriate amount of distilled water was added to the test tube and mixed thoroughly using a tube mixer, centrifuged and the supernatant was removed. This was repeated until the supernatant removed from the test tube becomes colorless. After that, test tube with the remaining solid and the reactor were dried in the dryer at 60°C. Then, a suitable amount of acetone was added into the reactor and it was shaken vigorously. The content was then transferred into the test tube. This was repeated until the acetone coming out from the reactor was colorless. Next, an adequate amount of acetone was added into the test tube and mixed well before centrifuged. After centrifuged, the acetone was removed from the test tube. This was repeated until the acetone coming out from the test tube becomes colorless. The solid in the test tube was then dried at 60°C and weighed periodically until the weight is constant.

**RESULTS AND DISCUSSION**

**Specifications of palm kernel cake**

Figure 4 shows the graph of moisture analysis of the waste palm kernel cake sample. Actual dry weight of the sample charged during the reaction was calculated by using the average moisture content. Moisture was totally removed after one day of continuous drying. The drying temperature shall not affect the mass of the dried waste palm kernel cake but at temperature of 80°C, the graph shows that it underwent moderate drying rate and thus the drying curve was observed. The moisture content of waste palm kernel cake obtained was 6.75%. It was almost the same as the information provided on the certificate of analysis that was randomly provided by the supplier of the sample and also near to the moisture content that was reported by R. Razuan which is 6.3% and 7.92% respectively [24].

Figure 5 shows the photos of sample products after undergone sub-critical water treatment for 5 minutes of residence time at temperatures ranging from 180°C to 280°C. Based on the picture, there are two layer phases which are water or supernatant phase and solid phase. In normal room temperature, palm kernel cake can be seen does not really able to dissolve in water. However, supernatant was obtained after the sub-critical water treatment. At reaction temperature of 180°C to 280°C, the color of the supernatant changed from
slightly brown and cloudy to dark brown and translucent. This is probably because as the temperature went higher, more sample degraded into smaller form instead of decomposed into other water soluble materials.

**Yield of oil**

Figure 6 demonstrates the effect of sub-critical water reaction temperature for 5 minutes of residence time on oil yield. Oil yield increased from 180°C to 240°C with the maximum oil yield of 52.9 mg-oil/g-dry waste palm kernel cake. Then, it decreased to 15.4 mg-oil/g-dry waste palm kernel cake at 280°C. The increasing trend of oil yield from temperature of 180°C to 240°C is due to solubility of non-polar phase increasing with temperature. High temperature will changed the properties of water causing the attractive forces of water become closer to those non-polar compounds and hence provide the maximum oil extraction at temperature reaction of 240°C. However, the decreasing trend at temperature of 280°C can be explained by rapid extracted compound degradation at a very high temperature which then reduces the recoveries substantially [25]. Thus, at a higher temperature, the oil yield shall continue to decrease as well.

Maximum extracted oil via supercritical carbon dioxide method was 92.62 mg-oil/g-dry waste palm kernel cake at 41.36 MPa and 70°C [7]. Although this result was higher than the maximum yield of oil obtained via sub-critical water, the pressure requires for supercritical carbon dioxide method was significantly higher. It may be corrosive and may require high cost of equipments and higher energy consumption when compared to sub-critical water method [26].

**Soxhlet extraction**

Soxhlet extracted most of the oil when compared to the sub-critical water method. The oil yielded by Soxhlet method was 9.7% of the dry waste palm kernel cake whereas A. R. Alimon and T. S. Tang stated that the oil content in waste palm kernel cake could be 4% to 10% [9], [10]. However, due to high concern regarding food safety and environmental issues over the years, it is vital that newly studied oil-processing technologies minimize or completely avoid the usage of hexane. Even though hexane was not completely avoided in this study because of the necessity of high purity oil analysis, separation of the water and oil phase for a large scale application of subcritical water would probably sufficient to be separated via centrifugation [8].

In Figure 7, oil yield obtained via Soxhlet method was used as a reference to determine the efficiency of waste palm kernel cake oil extraction via sub-critical water. At 240°C, sub-critical water extraction accomplished to extract 54.4% of the oil yielded by Soxhlet method. This is approximately half of the Soxhlet method, but sub-critical water method can still be considered as a competent method as it requires a significant shorter time when compared to the Soxhlet method.

**Dielectric constant of water**

Figure 8 shows the relationship between dielectric constant of water and oil yielded by sub-critical water at temperatures of 180°C to 240°C for 5 minutes of residence time. The correlation coefficient obtained from this relationship was 0.97. This shows that below 240°C, the oil yield obtained via sub-critical water was almost inversely proportional to the dielectric constant of water.
Thus, organic non-polar compounds became more soluble in water and hence provided maximum oil extraction as temperature elevated to 240°C. However, this relationship is not valid at temperature higher than 240°C probably due to waste palm kernel cake has physically changed and consequently reduced the extraction recovery [25].

Solid residue

Effect of sub-critical water reaction temperature for 5 minutes of residence time on solid residue is shown in Fig. 9. At 180°C, yield of solid residue was 0.75 g-solid residue/g-dry waste palm kernel cake whereas at 280°C, lowest yield of solid residue was obtained which is 0.10 g-solid residue/g-dry waste palm kernel cake. The relationship shows that the solid residue decreased as the reaction temperature increased because of the degradation of hemicelluloses, celluloses and lignins which degraded more as temperature increases [19]. Thus, at a higher temperature above 280°C, the degradation will be more rapid and might further reduce the solid residue. Therefore, waste palm kernel cake can be reduced up to 90% using sub-critical water treatment at 280°C.

CONCLUSION

Sub-critical water extraction has been successfully applied on the waste palm kernel cake to recover the oil residue where the highest yield of oil was 52.9 mg-oil/g-dry waste palm kernel cake at reaction temperature of 240°C. When using the amount of waste palm kernel cake produced in Malaysia in 2015, sub-critical water extraction might save 132,250 tonnes of palm kernel oil annually. Another interesting finding was sub-critical water extraction also able to reduce up to 90% of the solid residue at reaction temperature of 280°C. This shows that sub-critical water extraction able to recover oil from waste palm kernel cake and at the same time reduce environmental issues related to palm waste.

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REFERENCES


