Continuous Subcritical Water Hydrolysis for Pre-treatment of Palm Oil Mill Effluent (POME)

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Abstract. The pre-treatment of palm oil mill effluent (POME) was carried out using subcritical water (Sub-CW). Sub-CW has the potential as a clean and green method to extract, hydrolyze, gasifier, and carbonize biomass to produce valuable materials. The experiment was conducted continuously for 1 hour at 190, 220, and 260˚C between 40 and 140 bars. The hydrolysate obtained was separated into liquid and solid phases. The continuous mode stability was investigated at 3 and 7 mL/min, corresponding to the reactor residence time (RT) of 7 and 3 min, respectively. The flowrate gave a steady trend line with less variation at lower temperatures and slight fluctuation for higher temperatures. The highest solid yield was 0.085 wt.% obtained at 260˚C and RT=3 min. The highest sugar yield was 4.44 wt.% at 230˚C and RT=3 min. The lowest COD value was 5,504 mg/L achieved at 230˚C and RT=3 min. The COD was reduced by 78.9 % of the raw POME. High sugar yield paired with reduced COD reached at 230˚C in only 3 min, which is significantly low compared to the ponding system. In conclusion, integrating Sub-CW in a continuous mode as a pre-treatment method offers a promising alternative and sustainable solution for POME treatment.

1. Introduction
The palm oil industry is proliferating as the global demands for its product overcome its production. The large quantity of palm oil waste produced during palm oil extraction and purification processes has created a significant problem with the disposal. Waste management principles should be applied to these agro-industrial wastes to recover energy before disposal, whereby waste should be minimized and recycled.

The most environmentally harmful by-product of the milling processes is the palm oil mill effluent (POME). The oil extraction method from fresh fruit bunches requires enormous water, especially fruit sterilization and oil clarification. This method results in the estimated POME discharge of 3.5 m³ for each ton of raw palm oil produced. POME is well known as an expensive and challenging waste to manage by mill operators due to the large quantity of POME produced at a time [1]. POME sludge produces unpleasant odors and is a source of polluting and harmful environmental waste. Before discharging into the environment, POME must be treated. In response, the government and industry worked together to solve this problem and sought cost-effective, environmentally friendly treatment technologies.
Due to the characteristic of POME, the anaerobic process is an appropriate treatment method. Thus, Ponding systems, open tank digesters, aerated lagoons, and closed anaerobic digesters are currently the most used POME treatment systems. Due to the stabilization of organic matter by bacterial action in methane fermentation requires a long time, this causes the current issue focused on the pre-treatment of methane fermentation. The hydrolysis and acidification processes in the fermentation process to produce sugars and organic acids by bacteria are sluggish. These steps require one to three months before making methane gas [2]. Thus, a pre-treatment method must be developed to produce sugars and organic acids in a brief time.

Furthermore, another problem relates to the need to recover oil as an edible oil in POME. For the extraction process, a method using subcritical water (sub-CW) that is efficient and environmentally friendly was developed. Sub-CW is water at a temperature above its boiling point and pressure above its saturated vapor pressure. Figure 1 shows the dielectric constant and ionic product characteristics of sub-CW as a function of temperature. These characteristics enable water to behave as an organic solvent at a low dielectric constant. Simultaneously, a right hydrolysis agent for decomposing organic material due to its high ionic products [3].

**Figure 1.** Dielectric constant and ionic products of water at sub-critical and supercritical state [4].

The objectives of this research project are 1) to develop a continuous subcritical water hydrolysis process, 2) to extract edible oil from POME by applying sub-critical water treatment in continuous mode, and 3) to produce water-soluble materials (sugars, etc.) from the solid in POME by sub-critical water hydrolysis reaction.

2. Methodology
2.1. Fresh POME collection and analysis
The fresh POME sample in this research was obtained from a local palm oil mill. It was taken directly from the effluent discharge pipe after the crude palm oil extraction process from fresh fruit bunches. This fresh POME was kept in the freezer. The sample was thawed and filtered before, where only the liquid phase was being used in the experiments.

Prior to subcritical water treatment, pH, oil content, TOC, COD, total solids, suspended solids, and the fresh POME sample's moisture content were measured. The pH of the POME sample was measured by a pH meter. Next, the quantity of oil in the fresh POME was extracted by hexane, and the oil was measured. In the centrifuge tube containing POME, an appropriate amount of hexane has been added. TOC was measured using the TOC analyzer. The total solid was measured by evaporating all the water from a POME sample and weighing the remaining solids. A certain amount of POME was filtered using
the membrane filter for the determination of suspended solids. After filtration, the membrane filter was dried, and the weight difference before and after filtration determined the suspended solids left on the membrane filter. Next, a certain amount of POME was dried in the oven at 60°C in three beakers to achieve higher precision average values. The sample weight was measured daily until a constant value has been obtained. The moisture content of the samples can then be calculated on a wet basis.

2.2. Continuous sub-CW reactor

The process was designed from the feed, the reaction, and the outlet product section. The feed tank, pump, reactor, heater, condenser, and valve were installed. The designed process of safety was taken into account. Figure 2 shows the schematic diagram, where the unit was assembled to extract and hydrolyzed lignocellulosic. The reactor is made of tubular geometry 316-stainless steel with an internal volume of 79 mL, a maximum working temperature of 400°C, and a maximum working pressure of 40 MPa. The reactor was heated in a molten salt bath. The POME supply flowrate and pressure were controlled using the HPLC pump. The reaction temperature was adjusted using a heating bath. After the reactor, the flow was cooled down immediately to terminate the reaction. The reaction pressure was manipulated using the backpressure valve opening at the end of the process. The experiments in sub-CW were performed at a pressure range from 8 bar to 50 bar. This pressure has been selected to ensure continuous operation of the liquid phase. Previous work showed that reaction pressure is a minor variable, provided the pressure remains above the vaporization point. Experiments on hydrolysis were conducted at 190–260°C for 3, 7, and 10 min. Approximately 25 ml of the product was harvested in the reactor for each parameter. All experiments were applied in duplicate. At the end of the investigation, three-phase containing oil phase, aqueous phase, and residual solid was produced. During the treatment, the samples were conducted for 10 min each run. 25 ml of each product with different parameters were collected into a centrifuge tube. All product collected was centrifuge for the further separation process.

![Figure 2. Equipment for Continuous Subcritical Water Treatment](image)

2.3. Analytical methods

2.3.1. Analysis of Edible Oil. The gravimetric analysis assessed the oil extracted from hexane. The following equation defines the oil yield.

\[
\text{Oil yield} = \frac{(\text{Wt. of oil (g)})}{(\text{Wt of oil extracted from raw POME (g-oil-raw)})}
\]

2.3.2. Water-soluble materials in aqueous phase. The phenol-sulphuric acid method has been used to measure total sugar. It is a sugar colorimetric test based on the color reaction of sugar dehydration.
products to phenol. The absorbance was measured at 490 nm using an ultraviolet-visible absorption spectrometer (Shimadzu, UV-160A). The standard substance was a hexose of glucose.

\[
Yield\ of\ total\ sugar = \frac{Wt \ of \ total\ sugar \ in \ aqueous\ phase (g)}{Dry\ wt \ of \ charged\ POME \ (g - dry\ POME)} \tag{2}
\]

2.3.3. Analysis of Residual Solid. A gravimetric analysis evaluated the residual solid. The following equation determines the residual solid’s yield.

\[
Yield\ of\ residual\ solid = \frac{Weight\ of\ residual\ solid \ (kg)}{Dry\ weight\ of\ charged\ POME \ (kg - dry\ POME)} \tag{3}
\]

3. Results and Discussion
3.1. Raw POME properties
Table 1 shows the characteristics of POME obtained from the mill. The average moisture content of the POME was 92.7%. It was slightly lower by 3% than reported data by MPOB, ranging from 95-96% [9]. The average moisture content calculated were based on the same weight basis.

| Properties* | General range (MPOB, 2014) | This study |
|-------------|-----------------------------|------------|
| pH          | 4.7                         | 4.75       |
| COD         | 80,000                      | 26,144     |
| TOC         | -                           | 3,159      |
| MC          | 95.96%                      | 92.7%      |
| BOD         | 25,000                      | -          |

* Units are in mg/L except for pH and MC

3.2. Development of Continuous Process Continuous process
A continuous process is a streamlined process involving the ongoing production of end products; thus, it is essential to have a stable flowrate throughout the work. Figure 3 illustrates the flowrate trendline after subjecting POME continuously into the reactor over 60 min. The flowrate was obtained by measuring the amount of volume collected at every 10-minute interval. The feed flow rate of 3 mL/min and 7 mL/min set on the HPLC pump correspond to a residence time of 7 and 3 min, respectively. At shorter residence time, flowrate is mostly stable for a lower temperature of 190˚C. In contrast, a more fluctuated trend is observed at higher temperature settings. However, the pressure for each flow fluctuated between 8 and 14 MPa. Maintaining pressure at the higher temperature required more consistent control of the backpressure needle valve to keep the sample in liquid condition. This deviation could be due to H⁺ and OH⁻ ions faster collision in decomposing the lignocellulose. In general, the flowrate calculated showed a relatively steady and stable trendline for performing Sub-CW in the continuous mode.
Figure 3. Flowrates of POME in the continuous sub-CW process at various conditions.

3.3. POME after sub-CW treatment

| Temperature: 190°C | Temperature: 210°C |
|--------------------|--------------------|
| 10 Bar             | 20 Bar             |
| 20 Bar             | 30 Bar             |
| 20 Bar             | 30 Bar             |
| 30 Bar             | 40 Bar             |

| Temperature: 230°C | Temperature: 250°C |
|--------------------|--------------------|
| 30 Bar             | 40 Bar             |
| 40 Bar             | 50 Bar             |
| 40 Bar             | 50 Bar             |
| 50 Bar             | 60 Bar             |

Figure 4. POME images after reaction at various pressure and temperature.

Figure 4 shows the product after the treatment at various temperatures and pressure. All the samples consist of 3 layers. The top, middle and bottom layers are the oil phase, aqueous phase, and the solid phase, respectively. By treatment with sub-CW treatment for 10 min, the solids sink rapidly. The separating of oil, aqueous phase, and solids occurred quickly. Thus, sub-CW treatment is an efficient method of separating POME since it took 10 minutes to complete.

3.4. Solid yield

Figure 5 is the overall solid yield trendline for reaction temperature at 190, 220, and 260°C for both shorter and longer residence time. No significant yield was observed at 190°C for longer residence time. The highest yield was obtained at 260°C for longer residence time. However, the highest steady yield is at 3 min, 260°C with 0.085 wt.%. Solid yield showed a more fluctuated trendline pattern as compared to sugar. This study observed the strong influence of changes in flowrate. In work performed by Lachos et al., char formation of sugarcane straw was obtained at >200°C [10]. While generating a newly added value product seemed to offer a new advantage, holocellulose hydrolysis competes with sugar degradation, especially char formation. Hence, a balanced approach in acquiring desired products would affect the reactor's design and configuration to perform Sub-CW hydrolysis pre-treatment.
3.5. **Total sugars**

Under sub-critical water conditions, the cellulosic parts in POME could be converted to a wide range of water-soluble sugars by hydrolysis. Figure 6 shows the overall sugar yield trendline for reaction temperatures performed at 190, 220, and 260 °C. Sugar yield is lowest at the highest temperature for shorter residence time. The reason for the low yields of monomeric sugar by sub-CW could be explained in two ways: Firstly, total sugars are a convenient way to quantify hydrolysis but do not provide information on the source of sugar, whether it is from cellulose or hemicellulose. Meanwhile, undetectable sugars such as dimeric or oligomeric forms of sugars may exist in the aqueous fraction. Secondly, monomeric sugars may be further degraded to low molecular weight compounds by pyrolytic reaction [11]. Overall, sugar yield showed a stable trendline for all reaction temperature except at 230°C. A longer duration of reaction time needs to be performed to gain valuable insights as to why a consistent increase in yield was observed. Data obtained from this study is insufficient to draw a conclusion for the maximum yield was obtained.

![Figure 6](image)

**Figure 6.** Yield of sugar after POME was subjected to sub-CW at various temperatures and times.

3.6. **COD**

Figure 7 illustrates the overall COD trendline obtained after experimenting with temperature 190, 220, and 260°C at short and longer residence time. Time 0 min represents the COD of fresh raw POME.
sample with a value of 26,144 mg/L. Maturation pond represents the reduced COD value achieved from the conventional ponding system implemented in the palm oil mill. The final pond was able to reduce COD until 5,504 mg/L with a retention time of 10.46 days. Amazingly, continuous treatment of POME by sub-CW for 60 min resulted in a significant reduction of COD. After 60 min of continuous operation, the lowest COD value of 5,504 mg/L was achieved at 230°C for 3 min residence time. High sugar yield was also obtained at the same operating parameters. It was reported with a higher COD removal efficiency of 70-97% gives a higher methane emission rate between 0.15 and 0.42 L/g COD removed [12]. On the other hand, the highest COD reduction obtained is 11,008 mg/L at a half reduction from the raw POME. This reduction proves a promising outlook for integrating sub-CW as a pre-treatment method towards achieving a more sustainable approach for the oil palm industry.

![Figure 7](image_url)

**Figure 7.** COD after POME was subjected to sub-CW continuously at various temperatures and times.

### 4. Conclusion

POME was treated by sub-CW in a continuous mode for the 1-hour duration. The continuous mode stability was investigated by measuring the output parameters (flowrate, pH, COD, solid yield, and sugar yield). Although some fluctuation in pressure, the flowrate gave a steady trendline with less variation at lower temperatures and slight fluctuation for higher temperatures. The highest steady, solid yield was obtained at 260°C for residence time 3 min with 0.085 wt.%. Highest sugar yield observed at 230°C, for residence time 3 min yielding a maximum of 4.44 wt.%. After 60 min continuous treatment with sub-CW, the lowest COD value of 5,504 mg/L was achieved at 230°C for a shorter residence time of 3 min with a 78.9% reduction. High sugar yield, paired with high reduced COD reached at 230°C for residence time 3 min, gave a valuable insight into the high-speed methane fermentation of organic waste using the sub-CW hydrolysis reaction. In conclusion, integrating sub-CW in a continuous mode as a pre-treatment method offers a promising alternative sustainable solution for the oil palm industry.

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