Hydrothermal Treatment of Palm Oil Mill Effluent (POME) under Oxidative and Non-oxidative Conditions

To cite this article: Zhan Sheng Lee *et al* 2020 *IOP Conf. Ser.: Mater. Sci. Eng.* **965** 012002

Hydrothermal Treatment of Palm Oil Mill Effluent (POME) under Oxidative and Non-oxidative Conditions

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Abstract. The performances of oxidative (OHT) and non-oxidative (NOHT) subcritical hydrothermal treatments of palm oil mill effluent (POME) were investigated. The experiments were performed in a pressurised 500 mL-autoclave at different temperature (493 K – 533 K) and reaction time (2 h – 8 h). At 533 K and 8 h, the OHT reaction showed the highest removals of 5-day biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD), recording 87.30% and 71.23% respectively, with the pH of liquid product attained 6.5 from an initial value of 3.5. The reduction of COD and BOD_5 in NOHT was lower than that in OHT, which were 61.43% and 68.02%, respectively. The mechanism of OHT reaction was via the free radical's pathway. In contrast, the organic compounds originally present in POME degraded into water-soluble products, accompanied by deoxygenation that consisted of decarboxylation and dehydration during the NOHT.

1. Introduction

The thriving palm oil industry in Malaysia has led to a massive production of viscous organic waste known as palm oil mill effluent (POME). The production of each tonne of fresh fruit bunches generates an approximately 0.66 tonne of POME in the palm oil milling process [1]. POME contains numerous suspended constituents, including the organelles, a number of nitrogenous compounds ranging from amino acids to proteins, various carbohydrates such as simple sugars and hemicellulose, a group of insignificant organic and mineral constituents, as well as free organic acids [2]. POME is acidic with an average pH of 4, attributed to organic acids. The typical 5-day biochemical oxygen demand (BOD_5) and chemical oxygen demand (COD) values of POME are 30,000 mg/L and 54,000 mg/L, respectively, which are higher than the other agricultural effluents [3].

Majority of the oil palm millers in Malaysia practise open ponding system for POME treatment. However, this treatment method needs long hydraulic retention time (up to 60 days) and large land bank for pond creation. Furthermore, the unpleasant odour as well as the complication in collecting biogas and sustaining the liquor distribution are the other drawbacks [4]. Over the years, different POME treatment systems have been evaluated, such as ultrafiltration membrane separation [5], steam reforming [6, 7], and advanced oxidation processes [8-10]. Nevertheless, these studies remained at laboratory-scale and were not investigated for their scalability for industrial application. This could be due to the technical impracticability and infeasible cost.

Subcritical hydrothermal treatment involves initiation of reaction at pressurised condition, without exceeding the critical pressure and temperature. This treatment method has been widely applied on wet biomass as it circumvents the drying pre-treatment. Some of the other benefits are the ease of process implementation, hazard-free reaction as well as the reasonable capital and operational costs due to mild operating conditions [11, 12]. Generally, hydrothermal reaction can be performed under either oxidative or inert (non-oxidative) atmosphere, where the former involves the addition of oxidant in the form of compressed air. Urrea et al. compared the reaction atmosphere on biopolymers in hydrothermal treatment of sludge [13]. They reported that OHT showed better results in terms of solubilisation, settleability and mineralisation in sludge treatment. Yousefifar et al. reported the study of OHT and NOHT on cellulose at different temperatures [14]. These authors concluded that non-oxidative process showed a significant role in solid degradation and solubilisation at temperature higher than 240ºC. To our best knowledge, no studies of OHT and NOHT of POME have been done. POME contains a small portion of suspended solids that made up of lignocellulosic materials. Thus, POME could be treated following the method of lignocellulosic wastewater.

2. Materials and methods

2.1. POME sampling, storage and characteristics

30-L of raw effluent from the end-of-pipe of a local milling facility was acquired. The temperature and pH value of the liquor were measured instantly, recorded readings of 360 K and 3.5, respectively. The average concentration of COD and BOD_5 of the fresh POME were 52,200 ± 800 mg/L and 18,020 ± 640 mg/L. The POME was preserved in a tight-sealed opaque container and stored in a chiller at 277 K. The POME was homogenised prior to hydrothermal reaction.

2.2. Subcritical hydrothermal POME treatment

A pressure vessel (Model: Buchiglasuster Type 3E) of 1.0-L working capacity was used. 500 mL of the wastewater was stirred consistently at 500 rpm using an electromagnetic-driven propeller to maintain its homogeneity. The reactor temperature was varied between 493 K and 533 K with reaction time fixed at 2 h. Meanwhile, the influence of reaction time on POME was examined by varying the reaction time from 2 h to 8 h under a constant temperature of 533 K (highest temperature employed in the current study). All the operating parameters were identical for both NOHT and OHT, except the gas medium used to pressurise the reactor. For NOHT, 99.9995% purity nitrogen gas supplied by Alpha Gas Solution Malaysia was introduced into the vessel for purging and pressurising purpose prior to each experiment. The nitrogen gas was replaced by general industrial compressed air from Alpha Gas Solution Malaysia for OHT study. An initial pressure of 50 bar was fixed in the reactor, followed by gradual autogenous pressure build-up in concurrent with reaction temperature. The liquid product was sampled intermittently from the reactor for further analysis. All the experiment sets were triplicated for reproducibility assessment.

2.3. Liquid product analysis

The major components in fresh POME was identified using a gas chromatography coupled with mass spectroscopy (GC-MS). 50 mL of POME was freeze-dried into solid powder using Labconco freeze dryer. The freeze-drying process was carried out at 193 K under a 0.14 mbar vacuum. The POME powder was transferred to an Agilent 7890A GC-MS via a single packed-bed column, namely Agilent J&W DB 5-ms (30 m × 0.25 mm ID, 0.25 µm df, Fused Silica). The MS detector and injector port of GC-MS were operated at 523 K while the operating temperature of GC oven was 573 K. The GC column temperature was raised from 323 K to 473 K at 8 K/min, and then to 573 K at 10 K/min. The compounds were identified using NIST mass spectral library. The liquid samples from various runs were subjected to pH, COD and BOD_5 analyses. A visual observation was done to compare the colour of all discharged products. A pH indicator strip from Merck was used to measure the pH value of POME and liquid products. For the COD analysis, two mL of the diluted fresh POME and liquid samples was carefully pipetted into the oxidation vials. A vial with distilled water was prepared as a baseline. A Hach DRB200 reactor was employed to digest the COD vials at 423 K for 2 h. The calculation of COD removal is shown in equation (1).

$$\text{COD removal (\%)} = (\text{COD}_f - \text{COD}_i)/\text{COD}_i \times 100 \tag{1}$$

where COD_i represents COD value of POME, ppm
COD_f represents COD value of liquid discharge, ppm

The BOD_5 method was employed to measure the oxygen consumption by the microorganisms in the samples. One mL for each of the calcium chloride, magnesium sulphate, ferric chloride and phosphate buffer solutions were stirred thoroughly. The mixture was subsequently diluted to 1-L of dilution water. The dilution factors of the discharged products and raw POME were 100 and 1500 respectively. The diluted samples were shifted to a 300-mL incubation bottle. 1 N NaOH was added gradually to ensure that the pH was in the region of 6.5 to 7.5. The initial value of dissolved oxygen (DO) was recorded before depositing the incubation bottles in a BOD incubator. The incubation was done at 293 K for five consecutive days. The BOD_5 readings were obtained using equation (2). Equation (3) shows the calculation for BOD_5 removal percentage.

$$\text{BOD}_5 = (\text{DO}_i - \text{DO}_f) / V \tag{2}$$

where DO_i represents the initial DO value in ppm
DO_f represents the DO value after five days in ppm
V represents the decimal volumetric fraction of sample used

$$\text{BOD}_5 \text{ removal (\%)} = (\text{BOD}_{5(f)} - \text{BOD}_{5(i)})/\text{BOD}_{5(i)} \times 100 \tag{3}$$

where $\text{BOD}_{5(i)}$ represents the BOD value of POME, ppm
$\text{BOD}_{5(f)}$ represents the BOD value of liquid discharge, ppm

3. Results & discussion

3.1. Fresh POME Characterisation

The fresh POME from the end-of-pipe of milling process was blackish brown and has unpleasant odour. Table 1 summarises the properties of raw POME in this study and in the past studies. The POME characteristics in this study were similar to literatures [6, 15, 16].

Table 1. The characteristics of fresh POME of the present study and literature works.

Properties	**Typical range [6, 15]**	**Present study [16]**
Temperature (K)	353-363	360
COD (ppm)	44,300-70,900	52,200
BOD_5 (ppm)	11,000-27,000	18,020
pH	3.6-4.3	3.5

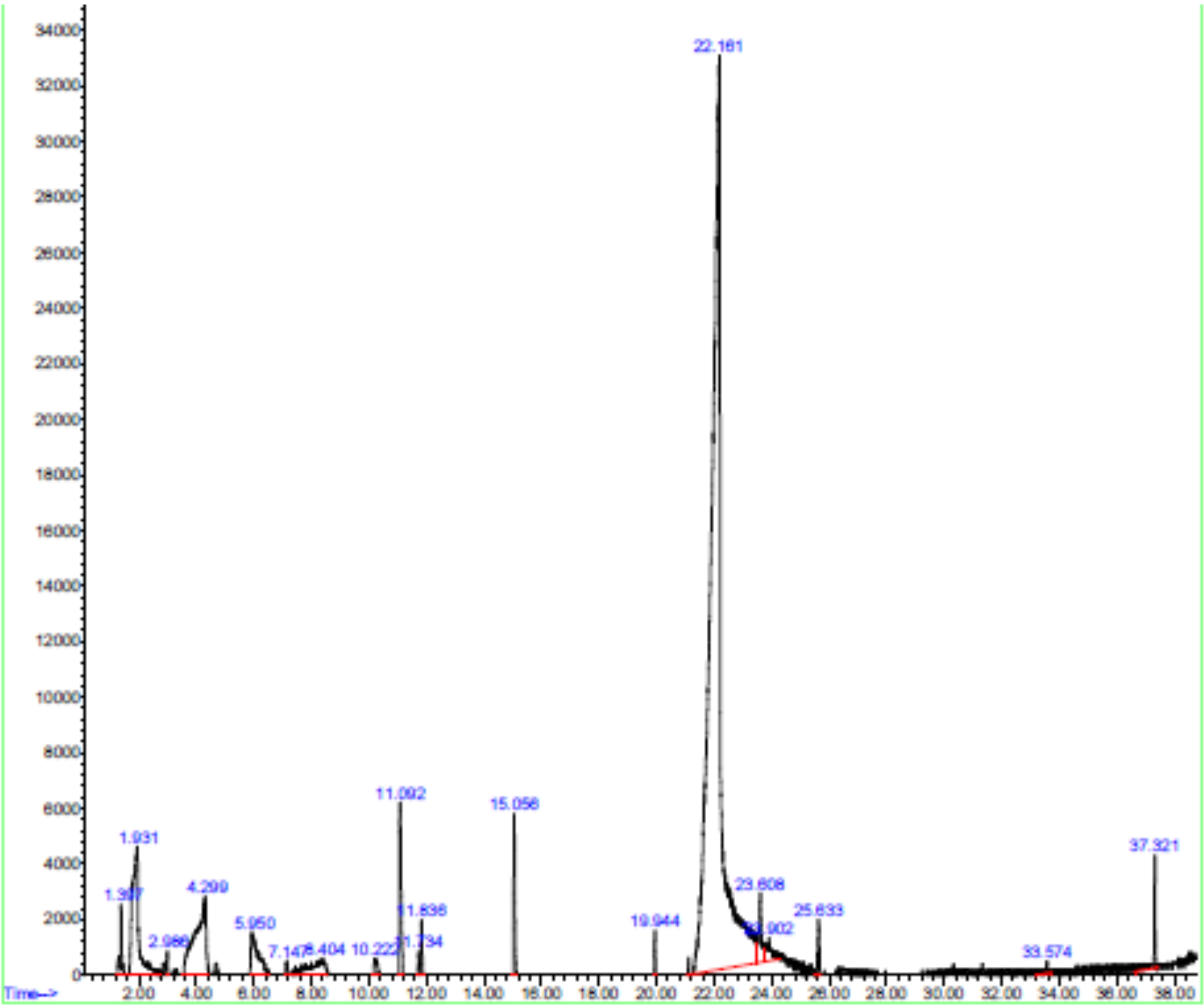

Figure 1. GC-MS spectra of the freeze-dried POME.

The GC-MS spectra of raw POME after being freeze-dried is as in figure 1. Eleven compounds were positively-identified from the NIST mass spectral library and summarised in Table 2. Significant amount of N-hexadecanoic acid (palmitic acid) was found in the fresh POME. This compound is a natural component of palm oil. The other minor organic compounds were in a good agreement with the literatures [17, 18].

Table 2. Identification of organic compounds in POME using GC-MS analysis.

Retention time	Organics	Molecular formula	Molecular weight	x_i (%)
4.297	Allyl ethyl ether	$C_9H_{10}O$	134.18	7.26
5.949	1-Buten-3-yne, 2-methyl-	C_5H_6	66.10	2.65
11.091	4-Hydroxy-2-methylacetophenone	$C_9H_{10}O_2$	150.17	2.42
11.735	1-Ethyl-2,2,6-trimethylcyclohexane	$C_{11}H_{22}$	154.292	0.17
11.835	Ethyl (Z)-non-3-enyl carbonate	$C_{12}H_{22}O_3$	214.30	0.44
15.056	Benzene, 1,4-dimethoxy-2-methyl-	$C_9H_{12}O_2$	152.1904	1.62
19.942	1-Propanol, 2-methyl-	$C_4H_{10}O$	74.122	0.28

22.162	n-Hexadecanoic acid	$C_{16}H_{32}O_2$	256.40	81.84
23.607	5-Octadecene, (E)-	$C_{18}H_{36}$	252.49	1.54
33.572	Propylene oxide	C_3H_6O	58.079	0.42
37.319	1,4-Hexadiene, 3,3,5-trimethyl-	C_9H_{16}	124.223	1.35

3.2. Visual Appearance

Figure 2 visualises the comparison among the raw POME and liquid products. The colour of liquid discharge of NOHT was darker than OHT. The presence of solid hydrochar (also found deposited on the reactor wall) may describe the dark colour of NOHT liquid product. The liquid discharge of NOHT exhibited a burnt charcoal smell while the OHT product was odourless. Therefore, the discolouration occurred in OHT could be due to the oxidation of tannins in POME.

Figure 2. (from left) Fresh POME, liquid product of NOHT at 533 K & 8 h and liquid product of OHT at 533 K & 8 h.

3.3. Effect of Hydrothermal Treatment Conditions

The pH, COD and BOD_5 values for all the liquid products from both OHT and NOHT are tabulated in Table 3. The pH value of treatment effluent was higher than the fresh POME and showed a consistent increase with the elevation of reaction temperature and time. The However, the pH value indicated that the liquid discharge still exhibited a mild acidic nature. It could be caused by the remaining refractory organic acids in the discharged products [19]. The increase of pH supports the idea that the organic acids in POME showed further reactions as reaction temperature and time increased under hydrothermal treatment [20].

In NOHT, both BOD_5 and COD reduction increased gradually with the hydrothermal temperature. This was reported before by [21]. At 493 K, the final COD reading was 36400 ± 550 ppm while the final BOD_5 was 9178 ± 150 ppm. At 533 K, the COD reading was the lowest, at 21500 ± 300 ppm while the BOD_5 showed a mean value of 6763 ± 75 ppm. Based on the removal percentage shown in Table 3, prolonging the reaction time from 2 h to 8 h only marginally increased both the COD and BOD_5 reduction. The increments were only 8.88% and 4.46%. The highest COD and BOD_5 removal were achieved through NOHT at 533 K for 8 h at 61.43% and 68.02% respectively. The detailed reaction pathways were described in our previous work [14]. In NOHT, the reaction mechanism can be summarised as in a course of reactions, comprising of hydrolysis, decarboxylation and dehydration, that occur con-currently. Hydrolysis occurs in the beginning of the reaction to initiate the decomposition of POME into water-soluble intermediates [22]. The reaction is followed by decarboxylation and dehydration of the hydrolysed components that take place simultaneously.

For the OHT process, the COD and BOD_5 removal percentage were higher than NOHT under similar operating condition. The highest COD reduction was 71.23%, which was achieved at 533 K after an 8-

hour OHT duration. The superior COD and BOD_5 reduction were ascribed to the enhanced oxidation of organic compounds in the presence of air. The increase of temperature resulted a higher oxidation effectiveness, which is consistent with the literature finding [14]. The reactions that occurred during OHT is more complicated as it involves an additional series of oxidation reactions that are expected to take place in the organic content of POME. The chemical step involves the reaction between the supplied oxygen molecules or the oxidation intermediates and the organic compounds in POME. The organic compounds could be oxidised by a free-radical intermediate generated during the oxidation of another compound [23]. The formation of free radicals should be further investigated and supported with evidence, such as by using electron spin resonance or free radical inhabitation technique [24].

Despite the high COD and BOD_5 reduction, the final BOD_5 of the hydrothermally treated POME still did not comply the discharge regulatory (below 100 ppm). The increase in hydrothermal temperature did not improve dramatically the treatment performance. This may be owed to the refractory phenolic compounds present in POME. It was reported that POME has high lignin-to-cellulose ratio [25]. A catalytic reaction study is necessary in the future work to determine a suitable catalyst in achieving higher organic pollutants degradation. The heterogeneous catalytic reaction is potential to offer a higher versatility and greater efficiency in the treatment of pollutants with a promising economic benefit [26] Nonetheless, the degradability of the organic substances in POME by hydrothermal reaction is still remarkable compared to the existing open ponding treatment method [27].

Table 3. The analyses of pH, COD and BOD_5 of the end-of-pipe POME and all the liquid discharges.

Process	Reaction temperature (K)	Reaction Time (h)	pH[a]	BOD_5[a] removal (%)	COD[a] removal (%)
NOHT	493	2	5.5	49.07	30.27
NOHT	503	2	5.5	57.09	46.74
NOHT	513	2	5.8	59.92	48.85
NOHT	523	2	6.0	61.16	50.38
NOHT	533	2	6.3	62.47	58.81
NOHT	533	4	6.3	63.50	59.23
NOHT	533	6	6.5	66.21	61.00
NOHT	533	8	6.5	68.02	61.43
OHT	493	2	6.0	69.90	58.21
OHT	503	2	6.3	73.16	60.98
OHT	513	2	6.5	77.39	63.45
OHT	523	2	6.5	79.31	65.39
OHT	533	2	6.5	80.25	66.93
OHT	533	4	6.5	83.31	69.21
OHT	533	6	6.5	85.12	70.71
OHT	533	8	6.5	87.30	71.23

[a] Mean values from the triplicate measurement

4. Conclusion

Subcritical hydrothermal process is deemed a new pathway for a more effective POME treatment. The treatment performance was evaluated in the aspects of COD and BOD_5 removal, where OHT showed promising results compared to the NOHT. The best operating condition was determined at the temperature of 533 K and process time of 8 h under oxidative environment, with the highest COD (71.23%) and BOD_5 (87.30%) removal, respectively. In addition, the pH was 6.5 due to the elimination of carboxylic compounds. The liquid product from the treatment was comparable with the effluent via open ponding method. Post treatment of the hydrothermally treated liquid product is suggested to meet the local discharge standard. For NOHT, deoxygenation that comprises of both dehydration and decarboxylation is most likely the dominant post-hydrolysis process. In contrast, free radical pathway could be the major degradation process of the organics in OHT.

Acknowledgments

The authors appreciate Universiti Malaysia Pahang for supporting this project through UMP Flagship Strategic Leap 3 Grant (RDU172202) and UMP Short-Term Grant (RDU170325).

References

[1] Stichnothe, H. and F. Schuchardt, Life cycle assessment of two palm oil production systems. Biomass and Bioenergy, 2011. 35(9): p. 3976-3984.
[2] Wu, T.Y., et al., Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. Journal of Environmental Management, 2010. 91(7): p. 1467-1490.
[3] Tabassum, S., Y. Zhang, and Z. Zhang, An integrated method for palm oil mill effluent (POME) treatment for achieving zero liquid discharge – A pilot study. Journal of Cleaner Production, 2015. 95: p. 148-155.
[4] Lee, Z.S., et al., Treatment technologies of palm oil mill effluent (POME) and olive mill wastewater (OMW): A brief review. Environmental Technology & Innovation, 2019: p. 100377.
[5] Ali, A.N.A., et al., Tackling colour issue of anaerobically-treated palm oil mill effluent using membrane technology. Journal of Water Process Engineering, 2015. 8: p. 221-226.
[6] Cheng, Y.W., et al., Syngas from catalytic steam reforming of palm oil mill effluent: An optimization study. International Journal of Hydrogen Energy, 2019. 44(18): p. 9220-9236.
[7] Cheng, Y.W., et al., Harnessing renewable hydrogen-rich syngas from valorization of palm oil mill effluent (POME) using steam reforming technique. Renewable Energy, 2019. 138: p. 1114-1126.
[8] Ng, K.H., et al., Photocatalytic degradation of recalcitrant POME waste by using silver doped titania: Photokinetics and scavenging studies. Chemical Engineering Journal, 2016. 286: p. 282-290.
[9] Ng, K.H. and C.K. Cheng, A novel photomineralization of POME over UV-responsive TiO2 photocatalyst: kinetics of POME degradation and gaseous product formations. RSC Advances, 2015. 5(65): p. 53100-53110.
[10] Saeed, M.O., et al., Treatment of POME using Fenton oxidation process: removal efficiency, optimization, and acidity condition. Desalination and Water Treatment, 2016. 57(50): p. 23750-23759.
[11] Abu Tayeh, H., et al., Subcritical hydrothermal pretreatment of olive mill solid waste for biofuel production. Bioresource Technology, 2016. 199: p. 164-172.
[12] Osada, M., et al., Low-Temperature Catalytic Gasification of Lignin and Cellulose with a Ruthenium Catalyst in Supercritical Water. Energy & Fuels, 2004. 18(2): p. 327-333.
[13] Urrea, J. L., García, M., Collado, S., Oulego, P., & Díaz, M. (2018). Sludge hydrothermal treatments. Oxidising atmosphere effects on biopolymers and physical properties. Journal of Environmental Management, 206, 284-290.
[14] Yousefifar, A., et al., Hydrothermal processing of cellulose: A comparison between oxidative and non-oxidative processes. Bioresource Technology, 2017. 226: p. 229-237.
[15] Ng, K.H., et al., A study into syngas production from catalytic steam reforming of palm oil mill effluent (POME): A new treatment approach. International Journal of Hydrogen Energy, 2018.
[16] Lee, Z.S., S.Y. Chin, and C.K. Cheng, An evaluation of subcritical hydrothermal treatment of end-of-pipe palm oil mill effluent. Heliyon, 2019. 5(6): p. e01792.
[17] Cheng, J., et al., Palm oil mill effluent treatment using a two-stage microbial fuel cells system integrated with immobilized biological aerated filters. Bioresource Technology, 2010. 101(8): p. 2729-2734.

[18] Cheng, Y.W., et al., Hydrogen-rich syngas production via steam reforming of palm oil mill effluent (POME) – A thermodynamics analysis. International Journal of Hydrogen Energy, 2018.
[19] Berge, N.D., et al., Hydrothermal Carbonization of Municipal Waste Streams. Environmental Science & Technology, 2011. 45(13): p. 5696-5703.
[20] Arauzo, P., Olszewski, M., & Kruse, A. (2018). Hydrothermal Carbonization Brewer's Spent Grains with the Focus on Improving the Degradation of the Feedstock. Energies, 11, 3226.
[21] Karagöz, S., et al., Low-Temperature Hydrothermal Treatment of Biomass: Effect of Reaction Parameters on Products and Boiling Point Distributions. Energy & Fuels, 2004. 18(1): p. 234-241.
[22] Williams, P.T. and J. Onwudili, Subcritical and Supercritical Water Gasification of Cellulose, Starch, Glucose, and Biomass Waste. Energy & Fuels, 2006. 20(3): p. 1259-1265.
[23] Bhargava, S.K., et al., Wet Oxidation and Catalytic Wet Oxidation. Industrial & Engineering Chemistry Research, 2006. 45(4): p. 1221-1258.
[24] Robert, R., et al., Intermediates in wet oxidation of cellulose: identification of hydroxyl radical and characterization of hydrogen peroxide. Water Research, 2002. 36(19): p. 4821-4829.
[25] Kang, S., et al., Hydrothermal conversion of lignin: A review. Renewable and Sustainable Energy Reviews, 2013. 27: p. 546-558.
[26] Arena, F., et al., Recent advances on wet air oxidation catalysts for treatment of industrial wastewaters. Inorganica Chimica Acta, 2015. 431: p. 101-109.
[27] Othman, M.R., et al., Treatment of effluents from palm oil mill process to achieve river water quality for reuse as recycled water in a zero emission system. Journal of Cleaner Production, 2014. 67: p. 58-61.