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RESEARCH REPORT UMP GRANT

Laporan Prestasi Skim Geran UMP

FINAL

Final	√	Progress		*Progress Period :* ________________	*√ Please tick*

PROJECT DETAILS *(Keterangan Projek)*

A	**Grant No**	RDU170325
	Faculty/CoE	CARIFF
	Project Title	AN APPLICATION OF HYDROTHERMAL PROCESS TO TREAT PALM OIL MILL EFFLUENT (POME)
	Project Leader	Assoc. Professor Dr. Cheng Chin Kui
	Project Member	1. MD. MAKSUDUR RAHMAN KHAN 2. RUWAIDA BINTI ABDUL RASID 3. CHIN SIM YEE 4. ASMIDA BINTI IDERIS 5. HERMA DINA BINTI SETIABUDI

PROJECT ACHIEVEMENT *(Pencapaian Projek)*

B

ACHIEVEMENT PERCENTAGE				
Project progress according to milestones achieved up to this period	**0 - 25%**	**26 - 50%**	**51 - 75%**	**76 - 100%**
Percentage (please state %)				√

EXPENDITURE *(Perbelanjaan)*

C

Budget Approved *Peruntukan diluluskan*	**Amount Spent** *Jumlah Perbelanjaan*	**Balance** *Baki*	**% of Amount Spent** *Peratusan Belanja*
RM 39,000	**RM 38,000.45**	**RM 999.55**	**% 97.5**

RESEARCH OUTPUT *(Output Penyelidikan)*

D

NO OF PUBLICATION

KPI FOR NO OF PUBLICATION

	ISI	Scopus	Index Proceedings	Others
KPI	3	1	1	-
Achievement	3	1	1	-

The contribution of funder (UMP, MOHE, MOSTI, Industry etc.) as the fund provider must be acknowledged at all times in all forms of publications. Please state the grant number (RDU/UIC) and grant name.

Number of articles/ manuscripts/books *(Please attach the First Page of Publication)*	**ISI**	**Scopus**
	1. Please see attachment 2.	1. Please see attachment 2.

Conference Proceeding *(Please attach the First Page of Publication)*	**International**	**National**
	1. SEGT 2018 (Universiti Malaya) 2.	1. 2.

HUMAN CAPITAL DEVELOPMENT

KPI FOR HUMAN CAPITAL DEVELOPMENT

	PhD Student	Master Student
KPI	-	**1**
Achievement	-	**1**

Human Capital Development	**Number**				**Others** (please specify)
	On-going		**Graduated**		
Citizen	Malaysian	Non Malaysian	Malaysian	Non Malaysian	
PhD Student	1				
Masters Student					
Undergraduate Student			1		
Total	1		1		

Name of Student:	ARICS CHIENG KIE SIONG
ID Matric No:	KA15073
Faculty:	FKKSA
Thesis title:	Hydrothermal processing of POME wastewater
Graduation Year:	2019
Name of Student:	Lee Zhan Sheng
ID Matric No:	MKC18007
Faculty:	FKKSA
Thesis title:	Reaction Mechanism and Kinetics of Hydrochar, Bio-Oil and Syngas Formation from Hydrothermal Treatment of Palm Oil Mill Effluent (POME) using Sol-Gel Synthesized Ni-Ce/Al$_2$O$_3$ and Co-Ce/Al$_2$O$_3$ Catalysts
Graduation Year:	
*** enter for more space*	

INTELECTUAL PROPERTIES

KPI FOR INTELECTUAL PROPERTIES

Patent, Copyright, Trademark,Industrial Design: ____________

Patent, Copyright, Trademark, Industrial Design ect	

OTHERS

KPI FOR OTHERS

Prototype, Technology,Collaborations etc: ____________

Prototype, Technology, Collaborations etc	

ASSET *(Aset)*

E

Bil	**Peralatan** *(Equipment)*	**Model**	**No Daftar Aset** *(Asset Tagging No)*	**Amount** (RM)	**Lokasi** *(Location)*

PRODUCT DESCRIPTION FOR UMP R&D DIRECTORY (SHORT & BRIEF) *Only for Final Report*

F	Not applicable

PRODUCT PICTURE FOR UMP R&D DIRECTORY *Only for Final Report*

G	Not applicable

SUMMARY OF RESEARCH FINDINGS *(Ringkasan Penemuan Projek Penyelidikan)*

H

This study evaluates the effects of subcritical hydrothermal treatment on palm oil mill effluent (POME) and its concomitant formations of solid hydrochar, liquid product and gaseous product. The reactions were carried out at temperatures ranged 493 K to 533 K for 2 h. The highest reduction of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were 58.8% and 62.5%, respectively, at 533 K. In addition, the removal of total suspended solids (TSS) achieved up to 99%, with the pH of POME reaching 6 from the initial pH 4. The gas chromatography coupled with mass spectroscopy (GC-MS) analysis showed that the fresh POME contained n-Hexadecanoic acid as the dominant component, which gradually reduced in the liquid product with reaction temperature, similar to carboxyl compounds whilst opposite of phenolic components. The gaseous products comprised CO_2, CO, H_2, and $C_3 - C_6$ hydrocarbons. Traces of CH_4 appeared at 533 K. CO_2 was the dominant species; its highest value was 3.99 vol% per 500 mL working volume of POME at 533 K. The solid hydrochar did not show any morphological changes over the reaction temperature. The O/C atomic ratio of the hydrochar ranged 0.16 to 0.38, while the H/C atomic ratio was in the range from 0.93 to 1.51. When treatment temperature was increased, the higher heating value (HHV) of the hydrochar improved from 24.624 to 27.513 MJ kg^{-1}. The characteristics of hydrochar make it a fuel source with immense potential. POME decomposed into water-soluble liquid compounds, followed by deoxygenation (dehydration and decarboxylation) to produce hydrochar with lower oxygen content and higher aromatic compounds

PROBLEMS / CONSTRAINTS IF ANY *(Masalah/ Kekangan sekiranya ada)*

I	Progressing well

Date : 01 November 2019
Tarikh

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Project Leader's Signature:
Tandatangan Ketua Projek

COMMENTS, IF ANY/ ENDORSEMENT BY FACULTY *(Komen, sekiranya ada / Pengesahan oleh Fakulti)*

J **Recommend / Not Recommend / KIV / Need Ammendment**

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Name:
Nama:

PROF. MADYA DR. SUMAIYA BT ZAINAL ABIDIN
Timbalan Dekan (Penyelidikan & Pengajian Siswazah)
Fakulti Teknologi Kejuruteraan Kimia dan Proses
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Signature:
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Tarikh: 4/11/19

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K	**Recommend / Not Recommend / KIV / Need Ammendment** …… …… …… **Name:** **Signature:** *Nama:* *Tandatangan:* **Date:** *Tarikh:*

Paper 1 (ISI)

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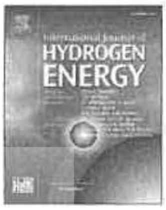

Experimental evaluation and empirical modelling of palm oil mill effluent steam reforming

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ARTICLE INFO

Article history:
Received 11 February 2018
Received in revised form
20 June 2018
Accepted 27 June 2018
Available online 17 July 2018

Keywords:
Palm oil mill effluent
Steam reforming
Syngas
Quadratic models

ABSTRACT

The current work describes a novel application of steam reforming process to treat palm oil mill effluent (POME), whilst co-generating H_2-rich syngas from the treatment itself. The effects of reaction temperature, partial pressure of POME and gas-hourly-space-velocity (GHSV) were determined. High crystallinity 20 wt%Ni/80 wt%Al_2O_3 catalyst with smooth surface was prepared via impregnation method. Baseline runs revealed that the prepared catalyst was highly effective in destructing organic compounds, with a two-fold enhancement observed in the presence of 20 wt% Ni/80 wt%Al_2O_3 catalyst, despite its low specific surface area (2.09 $m^2\ g^{-1}$). In addition, both the temperature and partial pressure of POME abet the COD reduction. Consequently, the highest COD reduction of 99.7% was achieved, with a final COD level of 73 ± 5 ppm from 27,500 ppm, at GHSV of 40,000 mL/h.g_{cat} and partial pressure of POME equivalent to 95 kPa at 1173 K. In terms of gaseous products, H_2 was found to be the major component, with selectivity ranged 51.0% –70.9%, followed by CO_2 (17.7%–34.1%), CO (7.7%–18.4%) and some CH_4 (0.6%–3.3%). Furthermore, quadratic models with high R^2-values were developed.

Introduction

In 2016, 17.32 million tonnes of crude palm oil was produced in Malaysia from 5.74 million hectares of oil palm plantation, generating nearly RM65 billion of export revenue for Malaysia [1]. Unfortunately, it comes at a cost of environmental pollution in the forms of palm oil mill effluent (POME). It is a common knowledge that an extrusion of each tonne of palm oil would generate 7-fold amount of POME [2,3]. Alarmingly, POME is polluting water resources, due to its high COD and BOD levels.

The primary POME treating method employed in Malaysia is a low operating-cost open ponding system. This system consists of a series of anaerobic and aerobic ponds. To date, there are more than 85% of the palm oil millers that rely on this conventional method [4], despite that these ponds would

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https://doi.org/10.1016/j.ijhydene.2018.06.164
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107.07 and CH_4 formation as $0.0636T - 0.177P - 8.8 \times 10^{-5}G - 3 \times 10^{-5}T^2 + 0.00132\,P^2 + 1.05 \times 10^{-9}G^2 - 25.471$.

Acknowledgement

All the authors would like to acknowledge the FRGS research funding (RDU170116) provided by the Ministry of Higher Education Malaysia for this project. Kim Hoong Ng would like to thank Universiti Malaysia Pahang for the provision of a post-doctoral fellowship. CKC is also grateful to Universiti Malaysia Pahang for the UMP Internal Grant (RDU170325) and also UMP Flagship Strategic Leap 3 Grant (RDU172202).

Appendix A. Supplementary data

Supplementary data related to this article can be found at https://doi.org/10.1016/j.ijhydene.2018.06.161.

REFERENCES

[1] MPOB. Overview of Malaysia palm oil industry, vol. 2017; 2016. p. 1–6. http://bepi.mpob.gov.my/images/overview/Overview_of_Industry_2016.pdf. [Accessed 29 December 2017].

[2] Rupani PF, Singh RP, Ibrahim MH, Esa N. Review of current palm oil mill effluent (POME) treatment Methods: vermicomposting as a sustainable practice. World Appl Sci J 2010;10:1190–201.

[3] Subramaniam MN, Goh PS, Lau WJ, Ng BC, Ismail AF. Separation and Purification Technology AT-POME colour removal through photocatalytic submerged filtration using antifouling PVDF-TNT nanocomposite membrane. Separ Purif Technol 2018;191:266–75. https://doi.org/10.1016/j.seppur.2017.09.042.

[4] Yaw Y, Weng K, Norli I. Strategies for improving biogas production of palm oil mill effl uent (POME) anaerobic digestion: a critical review. Renew Sustain Energy Rev 2018;82:2993–3006. https://doi.org/10.1016/j.rser.2017.10.036.

[5] Ng KH, Cheng CK. A novel photomineralization of POME over UV-responsive TiO_2 photocatalyst: kinetics of POME degradation and gaseous product formations. RSC Adv 2015;65:53100–10.

[6] Ng KH, Khan MR, Ng YH, Hossain SS, Cheng CK. Restoration of liquid effluent from oil palm agroindustry in Malaysia using UV/TiO_2 and UV/ZnO photocatalytic systems: a comparative study. J Environ Manag 2017;196:674–80. https://doi.org/10.1016/j.jenvman.2017.03.078.

[7] Tan YH, Goh PS, Ismail AF, Ng BC, Lai GS. Decolourization of aerobically treated palm oil mill effluent (AT-POME) using polyvinylidene fluoride (PVDF) ultrafiltration membrane incorporated with coupled zinc-iron oxide nanoparticles. Chem Eng J 2017;308:359–69. https://doi.org/10.1016/j.cej.2016.09.092.

[8] Said M, Ahmad A, Mohammad AW, Nor MTM, Abdullah SRS. Blocking mechanism of PES membrane during ultrafiltration of POME. J Ind Eng Chem 2015;21:182–8. https://doi.org/10.1016/j.jiec.2014.02.023.

[9] Adeleke AO, Aziz A, Latiff A, Daud Z. Optimization of operating parameters of novel composite adsorbent for organic pollutants removal from POME using response surface methodology. Chemosphere 2017;174:232–42. https://doi.org/10.1016/j.chemosphere.2017.01.110.

[10] Azmi NS, Yunos KFM. Wastewater treatment of palm oil mill effluent (POME) by ultrafiltration membrane separation technique coupled with adsorption treatment as pre-treatment. Agric Agric Sci Procedia 2014;2:257–64. https://doi.org/10.1016/j.aaspro.2014.11.037.

[11] Rushdy R, Reza M, Mckay G. Combined magnetic field and adsorption process for treatment of biologically treated palm oil mill effluent (POME). Chem Eng J 2014;243:31–42. https://doi.org/10.1016/j.cej.2013.12.084.

[12] Parthasarathy S, Mei C, Gomes RL, Manickam S. A novel hybrid approach of activated carbon and ultrasound cavitation for the intensi fi cation of palm oil mill effluent (POME) polishing, vol. 112; 2016. p. 1218–26. https://doi.org/10.1016/j.jclepro.2015.05.125.

[13] Saidu M, Yuzir A, Salim MR, Salmiati Azman S, Abdullah N. Influence of palm oil mill effluent as inoculum on anaerobic digestion of cattle manure for biogas production. Bioresour Technol 2013;141:174–6. https://doi.org/10.1016/j.biortech.2013.03.111.

[14] Saidu M, Yuzir A, Razman M, Azman S. Biological pre-treated oil palm mesocarp fibre with cattle manure for biogas production by anaerobic digestion during acclimatization phase. Int Biodeterior Biodegrad 2014;95:189–94. https://doi.org/10.1016/j.ibiod.2014.06.014.

[15] Khemkhao M, Techkarnjanaruk S, Phalakornkule C. Biomass and Bioenergy Effect of chitosan on reactor performance and population of specific methanogens in a modified CSTR treating raw POME. Biomass Bioenergy 2016;86:11–20. https://doi.org/10.1016/j.biombioe.2016.01.002.

[16] Suksong W, Promnuan K, Seengenyoung J, O-Thong S. Anaerobic Co-Digestion of palm oil mill waste residues with sewage sludge for biogas production. Energy Proc 2017;138:789–94. https://doi.org/10.1016/j.egypro.2017.10.068.

[17] Abdurahman NH, Rosli YM, Azhari NH. Development of a membrane anaerobic system (MAS) for palm oil mill effluent (POME) treatment. Desalination 2011;266:208–12. https://doi.org/10.1016/j.desal.2010.08.028.

[18] MPOB. National key economic areas (NKEA)- National biogas implementation (EPP5). 2014. http://www.mpob.gov.my/images/stories/pdf/2014/2014_nkea.pdf. [Accessed 1 January 2018].

[19] Wang Y, Shi Y, Hoong K, Yeong T, Kui C. Photocatalytic restoration of liquid effluent from oil palm agroindustry in Malaysia using tungsten oxides catalyst. J Clean Prod 2017;162:205–19. https://doi.org/10.1016/j.jclepro.2017.06.023.

[20] Ng KH, Lee CH, Khan MR, Cheng CK. Photocatalytic degradation of recalcitrant POME waste by using silver doped titania: photokinetics and scavenging studies. Chem Eng J 2016;286:282–90. https://doi.org/10.1016/j.cej.2015.10.072.

[21] Ng KH, Cheng YW, Khan MR, Cheng CK. Optimization of photocatalytic degradation of palm oil mill effluent in UV/ZnO system based on response surface methodology. J Environ Manag 2016;184:487–93. https://doi.org/10.1016/j.jenvman.2016.10.034.

[22] Ng KH, Cheng CK. Photo-polishing of POME into CH4-lean biogas over the UV-responsive ZnO photocatalyst. Chem Eng J 2016;300:127–38. https://doi.org/10.1016/j.cej.2016.04.105.

[23] Cheng CK, Deraman MR, Ng KH, Khan MR. Preparation of titania doped argentum photocatalyst and its photoactivity towards palm oil mill effluent degradation. J Clean Prod 2014;112:1128–35. https://doi.org/10.1016/j.jclepro.2015.06.104.

[24] Trisakti B, Manalu V, Taslim I, Turmuzi M. Acidogenesis of palm oil mill effluent to produce biogas: effect of hydraulic

Paper 2 (ISI)

ARTICLE IN PRESS

INTERNATIONAL JOURNAL OF HYDROGEN ENERGY XXX (2018) 1–14

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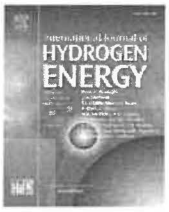
journal homepage: www.elsevier.com/locate/he



A study into syngas production from catalytic steam reforming of palm oil mill effluent (POME): A new treatment approach

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ARTICLE INFO

Article history:
Received 2 April 2018
Received in revised form
26 April 2018
Accepted 29 April 2018
Available online xxx

Keywords:
Palm oil mill effluent
Steam reforming
Syngas
Waste treatment

ABSTRACT

This paper reports on the novel application of catalytic steam reforming process to convert palm oil mill effluent (POME) into syngas over a 20wt%Ni/80wt%Al_2O_3 catalyst. The catalyst possessed high degree of crystallinity and was impurity-free, judging from the obtained XRD pattern. Furthermore, the BET specific surface area of catalyst was low (2.09 $m^2\ g^{-1}$), consistent with smooth surface captured by the FESEM images. CO_2-desorption and NH_3-desorption profiles showed a presence of both acid and basic sites on the surface of catalyst. In the absence of catalyst, about 7.0% reduction of chemical oxygen demand (COD) was achieved at 6.0 mL h^{-1} flow rate of POME, reforming temperature of 873 K and 20 mL min^{-1} of N_2-flow. Significantly, the COD reduction shot up to 93.7% in the presence of catalyst and liquid-hourly-space-velocity (LHSV) of POME of 90 mL $h^{-1}\ g_{cat}^{-1}$ at 873 K. The corresponding biochemical oxygen demand (BOD) reduction recorded was 93.8%. However, normalized carbon loss indicates that a high LHSV would favour carbon deposition. In addition to high LHSV, the carbon deposition was also influenced by reaction temperature. High reaction temperature has reduced carbon deposition, as well as organics removal. COD reduction was 99.41% and BOD reduction was 99.52% at 1173 K when LHSV was 60 mL $h^{-1}\ g_{cat}^{-1}$. In the gas phase, four species were consistently detected, viz. H_2, CO_2, CO and CH_4, with H_2 as the major component. The H_2 selectivity increased with both LHSV and reaction temperature.

Introduction

With the increasing population growth, food consumption, particularly palm oil, is also on the upward trajectory. Over the past decades, the production of palm oil is dominated by Indonesia and Malaysia, with a combined production of 85% [1]. In Malaysia, palm oil industry is the most important agro-based industry, with a total production of 37.2 million tons of crude palm oil for the past two years [2]. Consequently, more arable land has been converted into oil palm plantation,

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https://doi.org/10.1016/j.ijhydene.2018.04.232

Please cite this article in press as: Ng KH, 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), https://doi.org/10.1016/j.ijhydene.2018.04.232

Table 5 – Summary of findings related to different techniques to treat POME.

Technology	Pre-treatment	Significant findings	Reference
Open ponding system (biological processes)	None	Long retention time up to months and not compatible with the discharge threshold. Final COD and BOD value: 360 ppm and 139.2 ppm.	[14,17]
Advanced oxidation process	Dilution or filtration often required	Discharge threshold could be achieved in short time. Highest COD reduction achieved: 80% with TiO_2 photocatalyst after 22 h under UV irradiation.	[5,13,17]
Membrane processes	Dilution often required	High TSS and organic removal. Almost 100% TSS removal and the organic removal achieved ranged from 80% to almost 100%.	[42–45]
Adsorption process	Depends	Not efficient. Usually coupled with other technique for better quality of effluent. 68.05%, 93.71% and 100% of colour, TSS and COD reduction were achieved by activated carbon with assistance of magnetic field adsorption, complemented with biological treatment.	[48,49]
Coagulation process	Commonly used as pre-treatment	TSS and COD reduction up to 81.58% and 48.22% at with alum and C. *Obtusifolia* seed gum coagulant. Complementary treatment is required to further degrade POME.	[50–52]

with 60 mL h^{-1} g_{cat}^{-1} of POME and 20 mL min^{-1} of N_2 carrier gas at 1173 K, which fulfils existing requirement.

Another two technologies, adsorption and coagulation process, are also commonly employed in POME treatment. Based on past researches [46,47], adsorption process could be a potential method for POME treatment too. However, both adsorption and coagulation process are mainly applied as pre-treatment in POME waste treatment.

The palm oil mills are over-relying on the open ponding system due to its simplicity and low treatment costs. However, a more effective POME treating method is required to meet a tighter regulation. Catalytic steam reforming process appears to be a good candidate for POME treatment. Hence, the application of catalytic steam reforming in POME treatment should be further investigated to maximize its potential.

Conclusions

Post-filtration POME waste with high organic content (27000 ppm of COD & 16800 ppm of BOD, according to POME characterization) is a good candidate for syngas generation through steam reforming over 20wt%Ni/80wt%Al_2O_3 catalyst. Based on the results, the BOD and COD reduction of POME can be enhanced by increasing the LHSV. The highest BOD and COD reduction achieved were 93.7% and 93.8% with H_2 selectivity of 51.44% achieved under the flow of 90 mL h^{-1} g_{cat}^{-1} of POME and 20 mL min^{-1} of N_2 carrier gas at 873 K. However, the H_2 production of this experiment reduces with time due to the severe carbon deposition. Normalized carbon loss analysis accurately predicted the extent of carbon deposition at high LHSV experiment (90 mL h^{-1} g_{cat}^{-1}), which eventually confirmed by the post-reaction analysis of spent catalyst. Coke formation can be minimized by increasing the reaction temperature, judging from the normalized carbon loss. In addition, the BOD reduction, COD reduction and H_2 selectivity can also be enhanced with elevated reaction temperature. At reaction temperature of 1173 K, 99.41% of COD reduction and 99.50% of BOD reduction were achieved at LHSV of 90 mL h^{-1} g_{cat}^{-1} of LHSV and 20 mL min^{-1} of N_2 carrier gas, generating product gas with 66.38% of H_2 gas. In addition, POME waste was also successfully decolourized in all set of experiment with decolourization efficiency of more than 99.5%. As a conclusion, steam reforming of POME over 20wt%Ni/80wt%Al_2O_3 catalyst could be a new alternative for POME waste treatment.

Acknowledgement

Authors acknowledge the Fundamental Research Grant Scheme (RDU170116) provided by Ministry of Higher Education Malaysia and short term grant (RDU170325) provided by Universiti Malaysia Pahang for current study. In addition, authors also like to acknowlegde the financial support from Flagship Leap 3 Grant (RDU172202) provided by Universiti Malaysia Pahang.

REFERENCES

[1] Ahmed Y, Yaakob Z, Akhtar P, Sopian K. Production of biogas and performance evaluation of existing treatment processes in palm oil mill effluent (POME). Renew Sustain Energy Rev 2015;42:1260–78. https://doi.org/10.1016/j.rser.2014.10.073.

[2] MPOB. Monthly Production of Oil Palm Products Summary (Tonnes); n.d. http://bepi.mpob.gov.my/index.php/en/statistics/production/168-production-2016/747-production-of-oil-palm-products-2016.html. [Accessed 6 June 2017].

[3] Ferdous Alam ASA, Er AC, Begum H. Malaysian oil palm industry: prospect and problem. J Food Agric Environ 2015;13:143–8.

[4] Wu TY, Mohammad AW, Jahim JM, Anuar N. A holistic approach to managing palm oil mill effluent (POME): biotechnological advances in the sustainable reuse of POME. Biotechnol Adv 2009;27:40–52. https://doi.org/10.1016/j.biotechadv.2008.08.005.

[5] Ng KH, Cheng YW, Khan MR, Cheng CK. Optimization of photocatalytic degradation of palm oil mill effluent in UV/ZnO system based on response surface methodology. J Environ Manag 2016;184:487–93. https://doi.org/10.1016/j.jenvman.2016.10.034.

[6] Bello MM, Nourouzi MM, Abdullah LC, Choong TSY, Koay YS, Keshani S. POME is treated for removal of color from biologically treated POME in fixed bed column: applying

Please cite this article in press as: Ng KH, 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), https://doi.org/10.1016/j.ijhydene.2018.04.232

Paper 3 (ISI)

Environmental Technology & Innovation 15 (2019) 100377

Contents lists available at ScienceDirect

Environmental Technology & Innovation

journal homepage: www.elsevier.com/locate/eti

Treatment technologies of palm oil mill effluent (POME) and olive mill wastewater (OMW): A brief review

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HIGHLIGHTS

- The sources and characteristics of POME and OMW are reviewed.
- The treatment methods for both POME and OMW are compared.
- Biological treatment is common in POME but not in OMW.
- Thermochemical method especially hydrothermal treatment has great potential.
- The future prospects of are proposed.

ARTICLE INFO

Article history:
Received 10 February 2019
Received in revised form 14 April 2019
Accepted 15 April 2019
Available online 19 April 2019

Keywords:
Agricultural effluent
Olive mill wastewater
Palm oil mill effluent
Wastewater treatment

ABSTRACT

Attributable to the enormous population growth, tonnes of effluents are unavoidably generated throughout the agricultural activities. The inadequate effluents disposal induces perpetual contamination to the sea and river water sources, which has subsequently raised the public environmental concern. For that reason, the handling protocol of agricultural effluents was flagged up as an interest area for research. Despite the environmental hazards, agricultural effluents have the potential to be transformed from wastes into wealth via biological, physicochemical, thermochemical or a combination of processes thereof. The identical characteristics of palm oil mill effluent (POME) and olive mill wastewater (OMW) render the possibility of treating these wastes using the similar treatment method. Generally, biological treatment requires a longer process time compared to physicochemical and thermochemical technologies despite its easy and low-cost operation. Comparatively, physicochemical and thermochemical methods extend their potentiality in converting the agricultural effluents into higher value products more efficiently. This paper reviews the source and characteristics of both POME and OMW. Subsequently, a comparison of the current and alternative treatments for both effluents was done before the future perspectives of both effluents' treatment are paved based on the well-being of the human, environment, and economic.

Contents

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https://doi.org/10.1016/j.eti.2019.100377

Table 6
Comparison of treatment methods for OMW and POME.

Method	Description	Superiority	Drawbacks
Biological	Use of microbes in POME to degrade the organics.	Tackle on the biodegradable compounds. Low cost in overall.	Time-consuming. Large area is needed.
Physicochemical	Use of physical separation	Simple and less time-consuming compared to biological method.	Ineffective treatment output. Costly.
Thermochemical	Use of heat and chemical	Able to valorise organic-rich wastewater.	Energy-intensive. Costly.

2016; Molinos-Senante et al., 2015). Besides, the expensive materials and long term stable operation are the concerns in commercialising the treatment research from lab-scale to the industrial level (Krishnan et al., 2019). In the future perspective, both the wastewater treatment systems should consume the least time and be able to meet the discharge standard at the end-of-pipe of the treatment process. Beyond that, the conversion of these wastes into value-added products, such as syngas, activated carbon solid and organic compounds like residual oil is highly appreciated. The cost of materials and operation stability should be taken into consideration in designing the alternative POME and OMW treatment systems. The utilisation of safer, more convenient and profitable system could be the favoured treatment option in the future.

6. Conclusion

The inexperience of agricultural operators and absence of sophisticated treatment technology are the major causes of the improper disposal of the agricultural effluents. The environmental concern and stringent waste discharge guidelines have pressured both the edible oil industries to design a more effective wastewater treatment system. On the other hand, the insufficient effort from the legislative bodies in providing incentives to optimise the agricultural practice, and vague regulations enforcement have discouraged the proper treatment of effluents. Energy recovery from the wastewater treatment is the latest ultimate target from the viewpoint of the sustainability agenda. Both agricultural effluents exhibit similar composition and characteristics. Owing to the abundant organic constituents both POME and OMW, more effort should be paid in recovering them from POME using economically profitable and environmental-benign tactics. Majority of the biological treatment methods such as anaerobic digestion, co-composting and vermicomposting are claimed to be ineffective in harnessing energy. Despite that, biological treatment especially anaerobic digestion method is still the common treatment for POME due to the simplicity and effectiveness in biodegradation. Meanwhile, more studies on thermochemical and physicochemical methods were done in OMW treatment, owing to the high recalcitrant polyphenols content. Thermochemical treatment especially hydrothermal gasification under supercritical state was widely discussed in handling OMW but not POME. However, the limitation of energy-intensive reaction owing to its process condition should be overcome. This novel approach is recommended to be carefully studied for its potentiality in converting POME into value-added products.

Acknowledgements

This work is funded by Universiti Malaysia Pahang via UMP Internal Grant (RDU170325) and UMP Flagship Strategic Leap 3 Grant (RDU172202).

References

Abdullah, N., Sulaiman, F., 2013. The oil palm wastes in malaysia. In: Matovic, M.D. (Ed.), Biomass Now – Sustainable Growth and Use. InTech, Rijeka, Ch. 03.

Abu-Lafi, S., et al., 2017. Enrichment of phenolic compounds from olive mill wastewater and in vitro evaluation of their antimicrobial activities. Evid.-Based Complement. Altern. Med. 2017, 9.

Alavi, N., et al., 2017. Investigating the efficiency of co-composting and vermicomposting of vinasse with the mixture of cow manure wastes, bagasse, and natural zeolite. Waste Manage. 69, 117–126.

Alfano, G., et al., 2009. Present and future perspectives of olive residues composting in the mediterranean basin (CompMed). In: Dynamic Soil, Dynamic Plant. Global Science Books, Isleworth, UK, pp. 39–56.

Alhaji, M.H., et al., 2018. Photo-oxidation of pre-treated palm oil mill effluent using cylindrical column immobilized photoreactor. In: Process Safety and Environmental Protection.

Aly, A.A., Hasan, Y.N.Y., Al-Farraj, A.S., 2014. Olive mill wastewater treatment using a simple zeolite-based low-cost method. J. Environ. Manag. 145, 341–348.

Amor, C., et al., 2015. Combined treatment of olive mill wastewater by Fenton's reagent and anaerobic biological process. J. Environ. Sci. Health Part A 50 (2), 161–168.

Anastasiou, C.C., et al., 2011. Approaches to olive mill wastewater treatment and disposal in Cyprus. Environ. Res. J. 5 (2), 49–58.

Angenent, L.T., et al., 2004. Production of bioenergy and biochemicals from industrial and agricultural wastewater. Trends. Biotechnol. 22 (9), 477–485.

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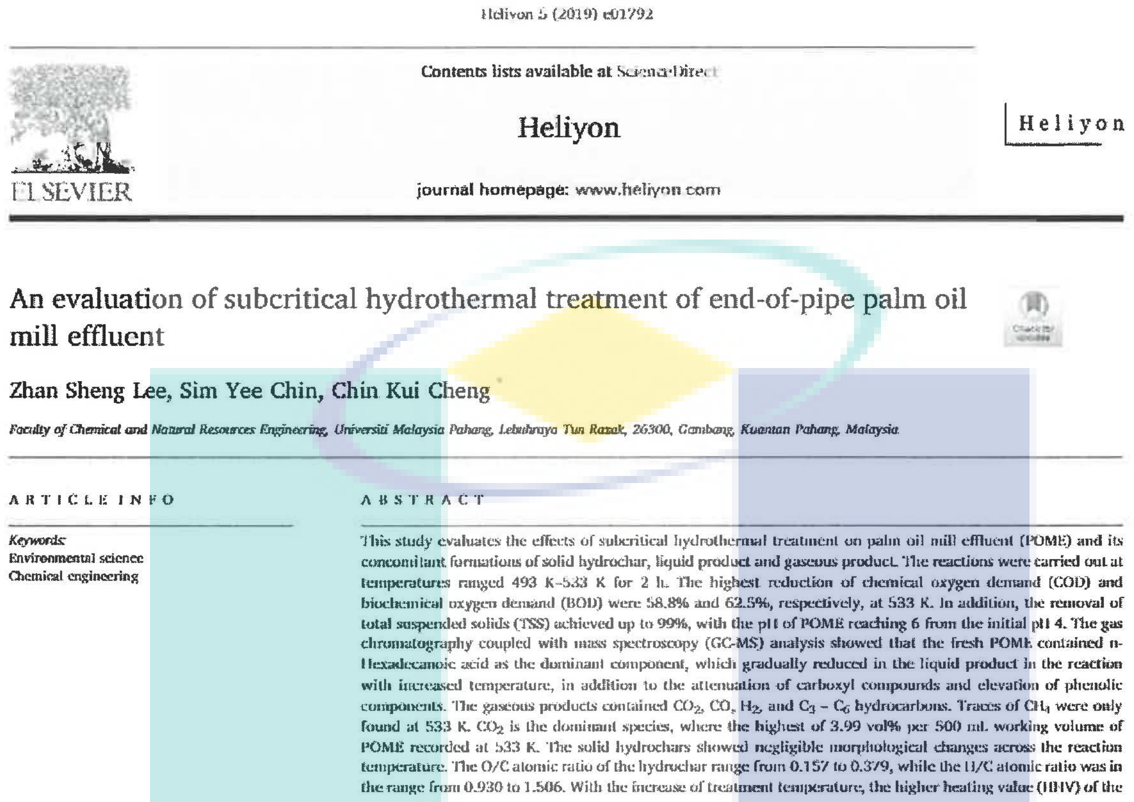

Heliyon 5 (2019) e01792

Contents lists available at ScienceDirect

Heliyon

journal homepage: www.heliyon.com

An evaluation of subcritical hydrothermal treatment of end-of-pipe palm oil mill effluent

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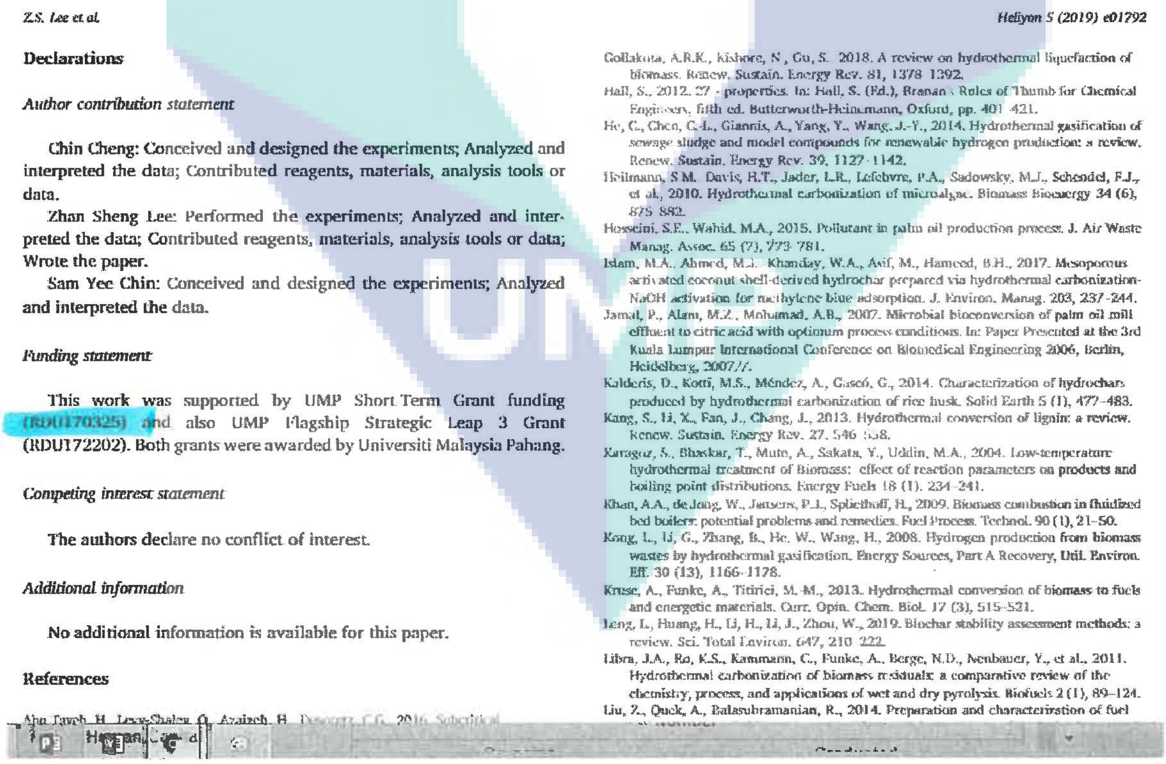
ARTICLE INFO

Keywords:
Environmental science
Chemical engineering

ABSTRACT

This study evaluates the effects of subcritical hydrothermal treatment on palm oil mill effluent (POME) and its concomitant formations of solid hydrochar, liquid product and gaseous product. The reactions were carried out at temperatures ranged 493 K–533 K for 2 h. The highest reduction of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were 58.8% and 62.5%, respectively, at 533 K. In addition, the removal of total suspended solids (TSS) achieved up to 99%, with the pH of POME reaching 6 from the initial pH 4. The gas chromatography coupled with mass spectroscopy (GC-MS) analysis showed that the fresh POME contained n-Hexadecanoic acid as the dominant component, which gradually reduced in the liquid product in the reaction with increased temperature, in addition to the attenuation of carboxyl compounds and elevation of phenolic components. The gaseous products contained CO_2, CO, H_2, and $C_3 - C_6$ hydrocarbons. Traces of CH_4 were only found at 533 K. CO_2 is the dominant species, where the highest of 3.99 vol% per 500 mL working volume of POME recorded at 533 K. The solid hydrochars showed negligible morphological changes across the reaction temperature. The O/C atomic ratio of the hydrochar range from 0.157 to 0.379, while the H/C atomic ratio was in the range from 0.930 to 1.506. With the increase of treatment temperature, the higher heating value (HHV) of the



Declarations

Author contribution statement

Chin Cheng: Conceived and designed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data.

Zhan Sheng Lee: Performed the experiments; Analyzed and interpreted the data; Contributed reagents, materials, analysis tools or data; Wrote the paper.

Sam Yee Chin: Conceived and designed the experiments; Analyzed and interpreted the data.

Funding statement

This work was supported by UMP Short Term Grant funding (RDU170325) and also UMP Flagship Strategic Leap 3 Grant (RDU172202). Both grants were awarded by Universiti Malaysia Pahang.

Competing interest statement

The authors declare no conflict of interest.

Additional information

No additional information is available for this paper.

References

Abu Tayeh, H., Levy-Shalev, O., Azaizeh, H., Dosoretz, C.G., 2016. Subcritical

Gollakota, A.R.K., Kishore, N., Gu, S., 2018. A review on hydrothermal liquefaction of biomass. Renew. Sustain. Energy Rev. 81, 1378–1392.

Hall, S., 2012. 27 - properties. In: Hall, S. (Ed.), Branan's Rules of Thumb for Chemical Engineers, fifth ed. Butterworth-Heinemann, Oxford, pp. 401–421.

He, C., Chen, C.-L., Giannis, A., Yang, Y., Wang, J.-Y., 2014. Hydrothermal gasification of sewage sludge and model compounds for renewable hydrogen production: a review. Renew. Sustain. Energy Rev. 39, 1127–1142.

Heilmann, S.M., Davis, H.T., Jader, L.R., Lefebvre, P.A., Sadowsky, M.J., Schendel, F.J., et al., 2010. Hydrothermal carbonization of microalgae. Biomass Bioenergy 34 (6), 875–882.

Hosseini, S.E., Wahid, M.A., 2015. Pollutant in palm oil production process. J. Air Waste Manag. Assoc. 65 (7), 773–781.

Islam, M.A., Ahmed, M.J., Khanday, W.A., Asif, M., Hameed, B.H., 2017. Mesoporous activated coconut shell-derived hydrochar prepared via hydrothermal carbonization-NaOH activation for methylene blue adsorption. J. Environ. Manag. 203, 237–244.

Jamal, P., Alam, M.Z., Mohamad, A.B., 2007. Microbial bioconversion of palm oil mill effluent to citric acid with optimum process conditions. In: Paper Presented at the 3rd Kuala Lumpur International Conference on Biomedical Engineering 2006, Berlin, Heidelberg, 2007//.

Kalderis, D., Kotti, M.S., Méndez, A., Gascó, G., 2014. Characterization of hydrochars produced by hydrothermal carbonization of rice husk. Solid Earth 5 (1), 477–483.

Kang, S., Li, X., Fan, J., Chang, J., 2013. Hydrothermal conversion of lignin: a review. Renew. Sustain. Energy Rev. 27, 546–558.

Karagoz, S., Bhaskar, T., Muto, A., Sakata, Y., Uddin, M.A., 2004. Low-temperature hydrothermal treatment of Biomass: effect of reaction parameters on products and boiling point distributions. Energy Fuels 18 (1), 234–241.

Khan, A.A., de Jong, W., Jansens, P.J., Spliethoff, H., 2009. Biomass combustion in fluidized bed boilers: potential problems and remedies. Fuel Process. Technol. 90 (1), 21–50.

Kong, L., Li, G., Zhang, B., He, W., Wang, H., 2008. Hydrogen production from biomass wastes by hydrothermal gasification. Energy Sources, Part A Recovery, Util. Environ. Eff. 30 (13), 1166–1178.

Kruse, A., Funke, A., Titirici, M.-M., 2013. Hydrothermal conversion of biomass to fuels and energetic materials. Curr. Opin. Chem. Biol. 17 (3), 515–521.

Leng, L., Huang, H., Li, H., Li, J., Zhou, W., 2019. Biochar stability assessment methods: a review. Sci. Total Environ. 647, 210–222.

Libra, J.A., Ro, K.S., Kammann, C., Funke, A., Berge, N.D., Neubauer, Y., et al., 2011. Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, process, and applications of wet and dry pyrolysis. Biofuels 2 (1), 89–124.

Liu, Z., Quek, A., Balasubramanian, R., 2014. Preparation and characterization of fuel

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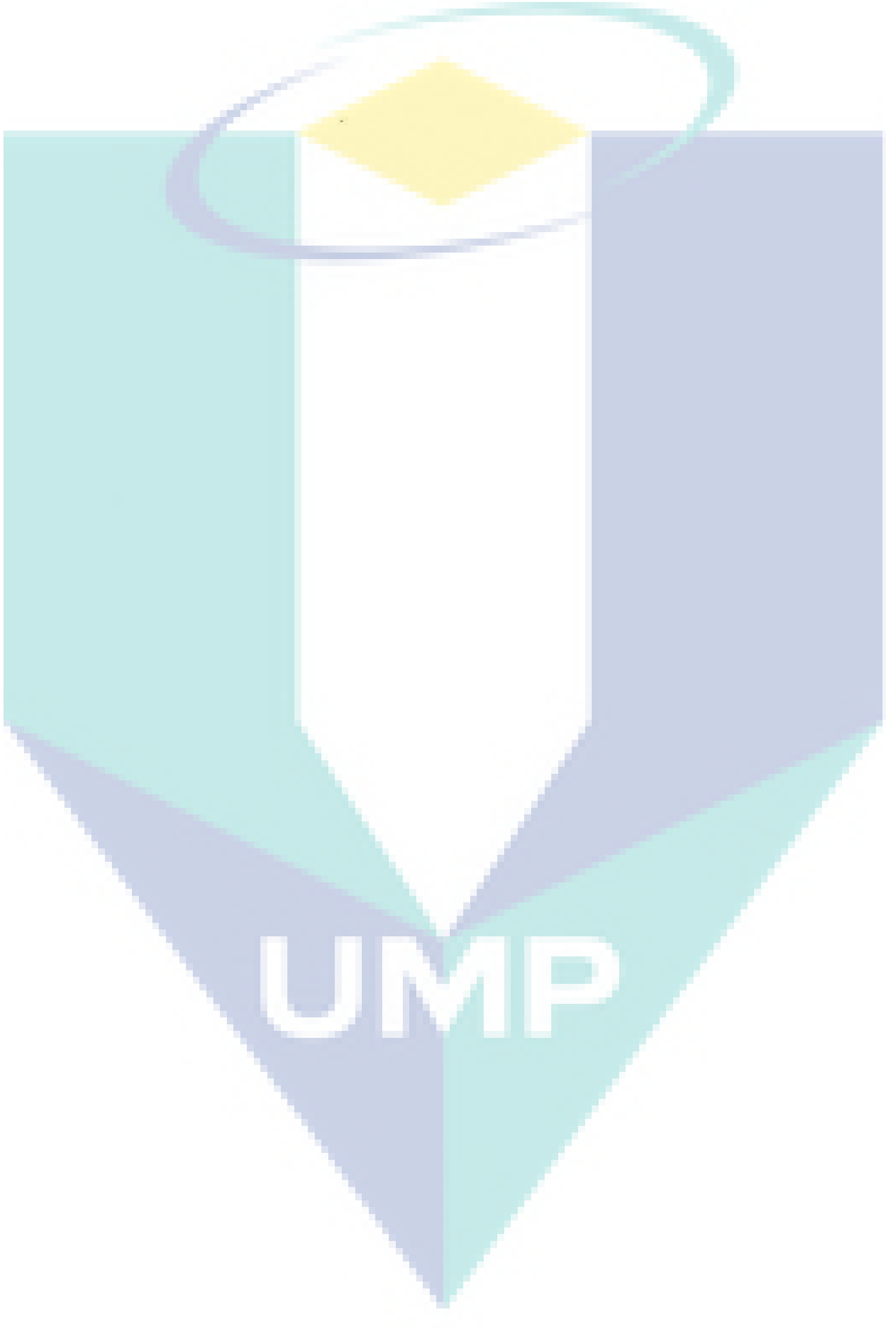
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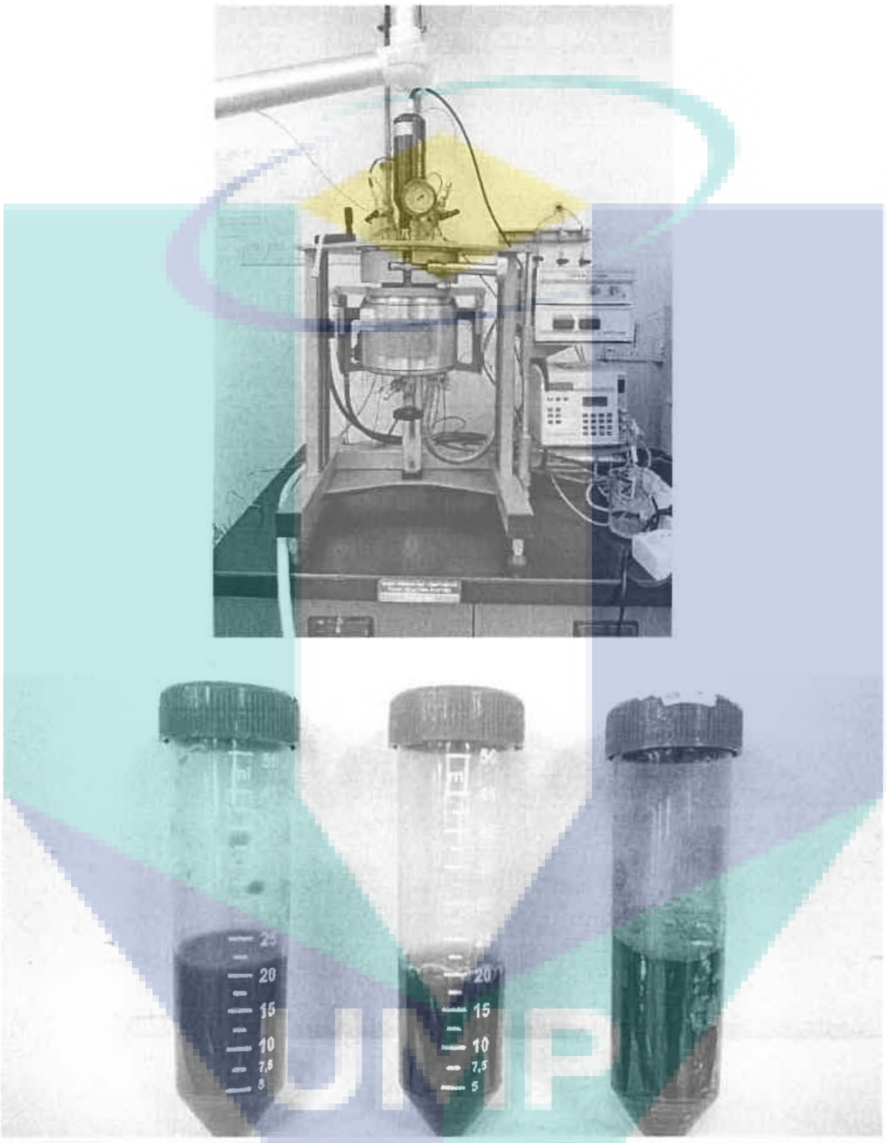

AN APPLICATION OF HYDROTHERMAL PROCESS TO TREAT PALM OIL MILL EFFLUENT

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ABSTRACT

This study evaluates the effects of subcritical hydrothermal treatment on palm oil mill effluent (POME) and its concomitant formations of solid hydrochar, liquid product and gaseous product. The reactions were carried out at temperatures ranged 493 K–533 K for 2 h. The highest reduction of chemical oxygen demand (COD) and biochemical oxygen demand (BOD) were 58.8% and 62.5%, respectively, at 533 K. In addition, the removal of total suspended solids (TSS) achieved up to 99%, with the pH of POME reaching 6 from the initial pH 4. The gas chromatography coupled with mass spectroscopy (GC-MS) analysis showed that the fresh POME contained n-Hexadecanoic acid as the dominant component, which gradually reduced in the liquid product in the reaction with increased temperature, in addition to the attenuation of carboxyl compounds and elevation of phenolic components. The gaseous products contained CO_2, CO, H_2, and $C_3 – C_6$ hydrocarbons. Traces of CH_4 were only found at 533 K. CO2 is the dominant species, where the highest of 3.99 vol% per 500 mL working volume of POME recorded at 533 K. The solid hydrochars showed negligible morphological changes across the reaction temperature. The O/C atomic ratio of the hydrochar range from 0.157 to 0.379, while the H/C atomic ratio was in the range from 0.930 to 1.506. With the increase of treatment temperature, the higher heating value (HHV) of the hydrochar improved from 24.624 to 27.513 MJ kg^{-1}. The characteristics of hydrochar make it a fuel source with immense potential. POME decomposed into water-soluble compounds, followed by deoxygenation (dehydration and decarboxylation) in producing hydrochar with lower oxygen content and higher aromatic compounds in the liquid product. Little gaseous hydrocarbons were produced due to subcritical hydrothermal gasification at low temperature.

1. INTRODUCTION

Hydrotreating POME, which is a recalcitrant organic-rich wastewater, represents another frontier of knowledge that remains unexplored. This work was undertaken to investigate the effects of subcritical hydro-treatment, a condition achieved below the $P_{critical}$ and $T_{critical}$ of water, on the solid and gas production from POME. Parameters of POME, after treatment, were analysed and reported herein.

2. RESEARCH METHODOLOGY

2.1. Feedstock collection and storage

30-L of fresh POME was collected from a local palm oil mill based in Gambang, Kuantan. The collection point was at the end-of-pipe and was not pre-treated to preserve the originality. The temperature of the effluent was measured directly using a thermometer. It was characterised on the same day to obtain the initial properties. The POME was then tightly-sealed in a black container and kept in the fridge at temperature of 277 K. Prior to the hydrothermal subcritical treatment, the POME in the container was gently shaken to ensure its homogeneity.

2.2. Subcritical hydrothermal treatment of POME

The reactor was operated in a batch mode from 493 K to 533 K for 2 h. The liquor was stirred at a single speed of 500 rpm. A working volume of 500 mL was used in all subcritical, highly-pressurised hydrothermal reaction. Inert N_2 gas was channelled into the reactor for purging, prior to each experiment. Initial pressure in the reactor was set at

50 bar, followed by an autogenous pressure built up throughout the reaction to maintain the POME at liquid phase. In the heating phase, 30 min–40 min were required to achieve the set point temperature. The temperature remained constant for 2 h during the holding phase, where the high pressure hydrothermal process occurred. To ensure the reproducibility of the reaction, all the experiments were run in triplicates. Sampling of gas product was done after the 2 h reaction. For the liquid product, it was discharged into a 500-mL beaker from a drain valve located at the bottom of the reactor. The liquid sample was subsequently stored in sampling bottles for further analysis. The wet hydrochar was collected using a spatula by removing it from the inner wall of reactor and magnetic stirrer. The wet hydrochar was then oven-dried at 378 K for 3 h to remove the physically-bound moisture, prior to further analyses.

2.3. Liquid product analysis

Liquid samples from different runs were selectively chosen for analyses of their wastewater qualities, such as pH, chemical oxygen demand (COD), biological oxygen demand (BOD) and total suspended solids (TSS). The pH value of POME was determined using pH indicator strips, sourced from Merck. For COD analysis, a total 2 mL of diluted POME sample was pipetted into the oxidation vial. Meanwhile, a vial with distilled water was used as the datum. The vials were then placed in the vial socket of DRB200 reactor followed by heating to 423 K and maintained at the stipulated temperature for 2 h. The reading of each vial was repeated for three times. In addition, BOD for 5 days (BOD5) was measured to determine the oxygen uptake by the microorganisms in the samples. A total of 1 mL for each of the phosphate buffer, magnesium sulphate ($MgSO_4$), calcium chloride ($CaCl_2$), ferric chloride ($FeCl_3$) solutions were mixed and diluted to a 1000 mL dilution water. The fresh POME and liquid products were diluted at dilution factors of 1500 and 100, respectively, using the dilution water. The prepared samples were transferred to 300 mL incubation bottle, with drop-wise addition of 1 N NaOH to maintain the pH in the range of 6.5–7.5. The incubation bottles were stored in a BOD incubator at 293 K for 5 days after measuring the initial DO.

TSS of POME was checked using vacuum filtration through a 47-mm nylon membrane with a pore size of 0.45 µm. 100 mL of diluted POME sample was filtered through the membrane, which was washed and dried to a constant weight. After the filtration process, the membrane was dried repeatedly at 323 K until a constant weight obtained. The TSS in mg/L was calculated based on the weight difference of the membrane.

The fresh POME and liquid stream were subjected to freeze-drying process to obtain the residues for gas chromatography coupled with mass spectroscopy (GC-MS) analysis. The freeze-drying process was done by subjecting 50 mL of each sample into Labconco freeze dryer at 193 K and 0.14 mbar. The freeze-dried sample was then fed to Agilent 7890A GC-MS with thermal desorption system to identify the organic components in the POME sample. The freeze-dried sample powder was loaded on a micro-vial before inserting to the GC injector, where the available compounds were eluted by 1 mL/min of He gas through a capillary column, viz. Agilent J&W DB 5-ms (30 m × 0.25 mm ID, 0.25 µm df, Fused Silica). A ramping rate of 8 K/min was employed to raise the initial temperature of GC column from 323 K to 473 K, followed by ramping rate of 10 K/min to 573 K. The GC oven was operated at 573 K while the injector port and MS detector were operated at 523 K. NIST mass spectral library was available for identification of compounds.

2.4. Gaseous product analysis

Gas sampling bags were used to collect the gaseous product before it was injected to a gas chromatography (GC) instrument to determine the composition of gas. The GC-Agilent 6890 N series was equipped with TCD and two packed columns; Supelco Molecular Sieve 13× (10 ft × 1/8 in OD × 2 mm ID, 60/80 mesh, stainless steel) and Agilent Hayesep DB (30 ft × 1/8 in OD × 2 mm ID, 100/120 mesh, stainless steel) for detecting CO_2, CH_4, H_2 and CO. Helium was used as a carrier gas with effective column temperature of 393 K and flowrate of 20 mL/min. A full separation of the gas components required a retention time of around 15 min.

2.5. Solid product analysis

The percentages of fixed carbon (FC), volatile matter (VM) and ash are commonly measured via thermogravimetric analysis (TGA) for quality characterisation of fuel materials and their thermal properties (Stirling et al., 2018; Zhao et al., 2016). The hydrochars were dried in oven at 378 K for 24 h to remove the moisture content prior to dry-basis TGA work. In this work, the thermogravimetric profile of 6.5 mg hydrochar on an aluminium pan was conducted using Hitachi STA7000. The temperature was ramped from 303 K to 623 K under 50 mL/min of N_2 flow, followed by 50 mL/min air flow up to 1273 K, at a heating rate of 5 K/min. At the end of the analysis, the sample was held at 1273 K for 15 min to determine the ash content.

The high heating value (HHV) of the hydrochar was estimated using Channiwala and Parikh formula (Channiwala and Parikh, 2002) which is typically employed for its acceptable accuracy, where 1.45% and 0.00% for average absolute error and bias error, respectively. All the spectrum of the hydrochar consisting of gas, liquid and solid phase would be included entirely in the formula as well (Zhang et al., 2015).

The elemental analysis on dry basis of hydrochar for C, H, S and N contents was performed using Perkin Elmer Series II CHNS/O Analyser 2400 and the elemental O content was determined by difference.

The surface morphology of hydrochar samples was analysed using SEM-EDX (Brand: FEI Quanta 450). The integrated EDX detector was utilised to study the elemental distribution on the samples surface. FEI software was used in interpreting and quantifying data. For the sample preparation, the hydrochar was oven-dried at 378 K for 24 h to evaporate the moisture content. 50 mg of dried samples were cut with a razor blade in the desired shape before it was evenly dispersed onto a carbon conductive pad on top of an aluminium stub. The prepared samples were then coated with Pt to minimise the charging effect. The stubs were placed on the sample rack in the specimen chamber of the microscope. Images of the hydrochar were generated by using an electron beam of 10 kV with a spot size of 4. High vacuum mode was prioritised in the SEM imaging with sputter coating done on the samples surface to get the best images.

3. LITERATURE REVIEW

POME is not a single-source wastewater but consists of a combination of wastewater from three main sources, viz. clarification (60%), sterilisation (34%) and hydrocyclone (6%) (Ahmad and Ghufran, 2018). POME contains various suspended constituents, namely cell walls, short fibres, organelles, a series of carbohydrates ranging from hemicellulose to simple sugars, various nitrogenous compounds from proteins to amino acids, free organic acids, and an assembly of minor organic and mineral components (Ahmad and Ghufran, 2018; Wu et al., 2010).

Environmental Quality Act 1974 regulates the effluent disposal from the palm oil industry. Malaysia's Department of Environmental (DoE) has enforced a comprehensive wastewater discharge policy; the BOD value of POME must be reduced to 100 ppm threshold. Since 2006, 20 ppm BOD discharge limit has been enforced in East Malaysia (MPOA, 2014). However, there is no regulatory control for both COD and total solids (TS) from DoE after 1984, for POME discharge.

In spite of strict regulations, it can be difficult to meet the discharge criteria, which can be attributed to obsolete waste treatment system (Ng and Cheng, 2016). More than 85% of the oil palm millers employ open ponding system for POME treatment as this method is relatively cheap and incurs low operating cost (Poh and Chong, 2009). Nevertheless, this treatment system suffers from long hydraulic retention time (HRT), typically around 45–60 days, vast land area for pond creation, terrible odour and difficulty in sustaining liquor distribution and biogas collection (Zinatizadeh et al., 2006).

Over the years, numerous alternate POME treatment methods to overcome the drawbacks of current system have been evaluated. Methods such as coagulation-flocculation (Zahrim et al., 2017; Teh et al., 2016), microbial fuel cell (Cheng et al., 2010), up-flow anaerobic sludge blanket – hollow centred packed bed (UASB-HCPB) (Chan et al., 2015; Poh and Chong, 2014), membrane filtration (Ali et al., 2015), advanced oxidation processes (AOP) (Alhaji et al., 2018; Ng et al., 2016; Ng and Cheng, 2015) and ultrasonic-assisted membrane anaerobic system (USMA) (Jamal et al., 2007) were reported. Nevertheless, these systems have limited scale up potential, mainly due to both capital and operating cost. In addition, most of the studies were only conducted at laboratory-scale, far from industrial practicality.

Recently, the conversion of wet biomass into useful hydrochar, bio-oil and gaseous products using pressurised hydrothermal process has gained a lot of interest due to its perceived "green pathway". Hydrochar is a carbon-rich solid residue product generated from the hydrothermal treatment. Extensive studies have been done on hydrochar production from different biomass, such as wood chips, empty fruit bunches, microalgae, pine and fruit wastes (Zhang et al., 2018; Simsir et al., 2017; Wu et al., 2017; Parshetti et al., 2013; Heilmann et al., 2010). Hydrochar as an intermediate product that can be further processed into some value-added substance, such as a low-cost adsorbent (Islam et al., 2017; Takaya et al., 2016), solid fuels (Liu et al., 2014; Liu et al., 2013), supercapacitors (Gao et al., 2015; Ding et al., 2013) and for carbon sequestration as well as soil amendment (Windeatt et al., 2014; Tsai et al., 2012; Sevilla and Fuertes, 2009).

From our search in the literature, hydrothermal treatment of POME in subcritical condition remains unexplored. Subcritical water is a state in the temperature range of 373–647 K and the pressure in the system must be at or above saturated pressure to ensure the water remains as liquid (Kruse et al., 2013; Cheng et al., 2009). Subcritical hydrothermal treatment possesses several benefits as it is easy to implement, and has low capital and operational costs (Abu Tayeh et al., 2016), due to low temperature requirement (Osada et al., 2004).

In comparison to the open ponding system, hydrothermal process could treat POME in a substantially reduced reaction time without requiring large area of land, while producing value-added products as the treatment output. Besides, hydrothermal process is more energy-saving compared to conventional bioenergy production, because the organic-rich wastewater such as POME can be converted to useful products without prior-drying. To the best of our knowledge, no systematic study has been done on investigating the products from POME hydrothermal treatment. Thus, pressurised subcritical hydrothermal treatment of POME was carried out in the current work to evaluate the process. The effects of reaction temperature on the wastewater quality treatment and its concomitant product distribution was investigated.

4. FINDINGS

Liquid Product Characterisation

Characterisation of POME post-treatment showed an overall reduction in COD, BOD_5 and TSS, as well as an increase in pH value. The pH values for all samples are acidic as shown in Figure 1. It may be attributed to the remaining organic acids in the products that was originated from the decomposition of monosaccharides content in fresh POME (Berge *et al.*, 2011). The pH values were higher in all the liquid products and showed a consistent increase from 493 K to 533 K, as shown in Figure 1. As indicated by the GC-MS analysis results in Table 1, the carboxylic compounds in the fresh POME probably has transformed into a carbon-densified hydrochar and gases such as CO_2 and CO with the increase of reaction temperature. The step-up of phenolic compounds was derived from the slow degradation of lignin in POME at the increase of reaction temperature.

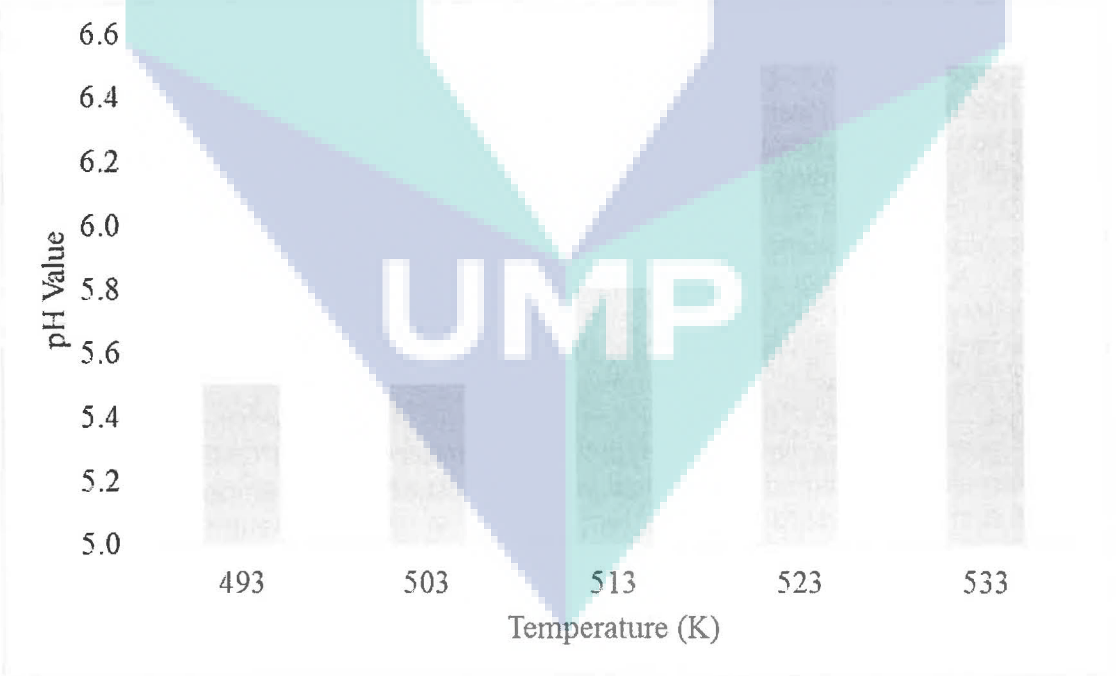


Figure 1: pH value of the liquid output.

Table 1: Qualitative analysis of major organic compounds via GC-MS.

Organic Components	**Area (%)**					
	Fresh POME	493 K	503 K	513 K	523 K	533 K
Methylamine, N,N-dimethyl-	0.64	0.71	1.18	0.56	0.53	-
1,3-Propanediamine, N,N-dimethyl-	-	1.34	-	-	-	-
Hydrazine, ethyl-	-	6.62	-	-	-	-
Butanoic acid, 3-methyl-	-	-	-	0.74	-	-
Hydrazine, 1,1-dimethyl-	6.54	0.93	0.62	-	-	-
Hydrazine, 1,2-dimethyl-	-	-	0.74	-	-	-
Pentanoic acid	-	0.97	-	1.13	1.98	-
Butanoic acid, 3-methyl-	-	2.13	-	-	-	-
L-Serine, ethyl ester	-	-	3.97	-	-	-
1,2-Ethanediol, diformate	-	-	-	-	2.35	-
Allyl ethyl ether	6.44	-	-	-	-	-
Silacyclopentane	-	0.64	-	-	-	-
Hexanoic acid	-	-	-	-	-	5.43
Butanal, 2-methyl-	-	0.71	-	-	-	-
Pyrrolidine, 1-methyl-	-	-	-	-	0.58	0.84
Pyrrolidin-2-one, 5-[2-butyrylethyl]-	-	-	-	-	3.51	-
2-Hexanone, 4-methyl-	-	0.6	-		-	-
Piperidine, 1-methyl-	-	-	-	-	-	1.01
Thiophene	-	-	-	-	0.63	-
Azetidine, 2,2,3,3-tetramethyl-	-	-	-	-	0.9	-
Aziridine, 2,2,3,3-tetramethyl-	-	-	-	-	-	3.85
1-Buten-3-yne, 2-methyl-	2.35					
N-Ethyl-2-methylallylamine	-	-	-	-	-	0.82
2,2,4,7-Tetramethyl-3,6,9-trioxa-2-silatridecane	-	-	1.34	-	-	-
2-Mercaptothiazole	-	0.75	-	-	-	-
N-t-Butyl-N'-2-[2-thiophosphatoethyl] aminoethylurea	-	-	-	-	-	5.84
2-Octanone	-	-	2.29	-	-	-
5,6-Diamino-1,3-dimethyluracil	-	-	-	0.82	0.6	-
Phenol	-	3.26	-	5.07	3.94	9.01
1,6-Dideoxy-l-mannitol	-	-	-	-	1.97	0.98
1,6-Anhydro-2,4-dideoxy-.beta.-D-ribo-hexopyranose	-	-	-	-	-	1.01
Ethanone, 1-(1H-pyrrol-2-	-	-	-	-	6.98	3.43

Organic Components	Area (%)					
	Fresh POME	493 K	503 K	513 K	523 K	533 K
yl)-						
m-Guaiacol		-	-	-	0.78	-
Methanamine, N-methoxy-	1.81	-	-	-	-	-
1,1-Dimethylbutyl(prop-2-enyl)sulfide	-	-	-	-	1.17	-
1-Pentanol, 2,2-dimethyl-	-	-	-	-	-	1.47
O-Methoxy-.alpha.-methylbenzyl alcohol	-	-	-	-	-	1.15
(Z)-4-Methyl-5-(2-oxopropylidene)- 5H-furan-2-one	-	0.52	-	-	-	-
4-Isopropylthiophenol	-	-	-	0.81	-	-
Phenol, 2-(dimethylamino)-	-	-	-	-	-	0.82
Silane, diethoxymethyl-	-	0.92	-	-	-	-
4-Hydroxy-2-methylacetophenone	2.15	-	-	-	-	-
Benzene, 1-isocyano-3-methoxy-	-	2.12	-	-	-	-
Oxime-, methoxy-phenyl-	-	3.29	-	-	-	-
2,3-Dimethylbenzaldoxime	-	21.52	-	-	-	-
4-Ethylbenzoic acid, 2-butyl ester	-	21.36	-	-	-	-
Phenol, 2,6-dimethoxy-	-	-	21.26	23.39	23.93	16.13
1,4-Pentadiene, 2,3,4-trimethyl-	-	1.03	-	-	-	-
6-Acetamido-1,4-benzodioxane	-	3.43	-	-	-	-
Ethanol, 2,2-diethoxy-	-	-	10.21	-	-	-
2,4-Hexadienoyl chloride	-	1.6	-	-	-	-
Cyclohexene, 1-chloro-6-methyl-	-	-	6.43	-	-	-
1H-Indole, 2-methyl-	-	-	-	-	15.95	-
2-Isopropylimidazole	-	-	-	-	13.34	-
1-(1-Propynyl)cyclohexanol	-	-	-	35.89	17.17	40.42
2',4'-Dihydroxyacetophenone oxime	-	-	0.84	-	-	-
5-tert-Butylpyrogallol	-	-	-	-	1.05	-
1-Methyl-1,6-diazaplenalene	-	-	-	-	-	4.09
Phenol, 2-	1.44	-	-	-	-	-

Organic Components	**Area (%)**					
	Fresh POME	493 K	503 K	513 K	523 K	533 K
(dimethylamino)-						
Hexadecane	-	6.13	-	-	-	-
Phenol, 4-amino-	-	-	-	-	-	1.96
Hexadecanoic acid, methyl ester	-	4.28	23.18	14.38	-	-
Hexadecanoic acid, ethyl ester	-	1.23	-	-	-	-
Heptadecanoic acid, ethyl ester	-	-	-	0.93	-	-
E-11-Tetradecenoic acid	-	-	-	0.55	-	-
n-Hexadecanoic acid	72.58	-	5.14	-	-	-
5-Octadecene, (E)-	1.37					
10-Octadecenoic acid, methyl ester	-	2.23	-	-	-	-
Octadecanoic acid	-	-	-	0.77	-	-
1H-Tetrazol-5-amine	0.92					
cis-13-Octadecenoic acid, methyl ester	-	-	11.36	8.53	-	-
Tetradecanoic acid, 12-methyl-, methyl ester	-	-	0.84	-	-	-
Oleic Acid	-	0.6	-	-	-	-
n-Propyl 9-octadecenoate	-	-	-	1.03	-	-
10-Octadecenoic acid, methyl ester	-	-	1.65	-	-	-
N-[Dimethylaminomethyl]aziridine	-	-	0.56	-	-	-
9-Octadecenamide, (Z)-	-	-	0.63	1.03	-	-
Bis(2-ethylhexyl) phthalate	-	0.79	-	-	-	-
Oxazole	1.2	-	-	-	-	-

Figure 2 shows that both COD and BOD_5 reduction gradually increased with the increase of hydrothermal temperature. The COD and BOD_5 readings at 493 K were 36400 ppm and 9178 ppm, respectively, while the COD reading recorded 21500 ppm and 7477 ppm for the BOD_5 reading at 533 K. The liquid product achieved a COD reduction of 30.3% and 58.8% at 493 K and 533 K respectively. Meanwhile, highest BOD_5 reduction also recorded at 533 K, which has a value of 67.6%, compared to the lowest of 35.6% at 493 K. Compared to the open ponding system, these results are remarkable, assuming a 2 h hydrothermal treatment in the commercial-scale batch reactor is with proper design that could minimise the limitation of mixing, mass and heat transfer to maintain the lab-scale performance (Coker, 2001).

Figure 2 also displays a TSS reduction of more than 90% in all experiment sets. TSS reduction showed a gradual increase from 493 K to 533 K, equivalent to reductions of

90.12% and 99.42%, respectively. The improving reduction percentage could be due to the increased amount of hydrochar which was readily separable from the liquid product.

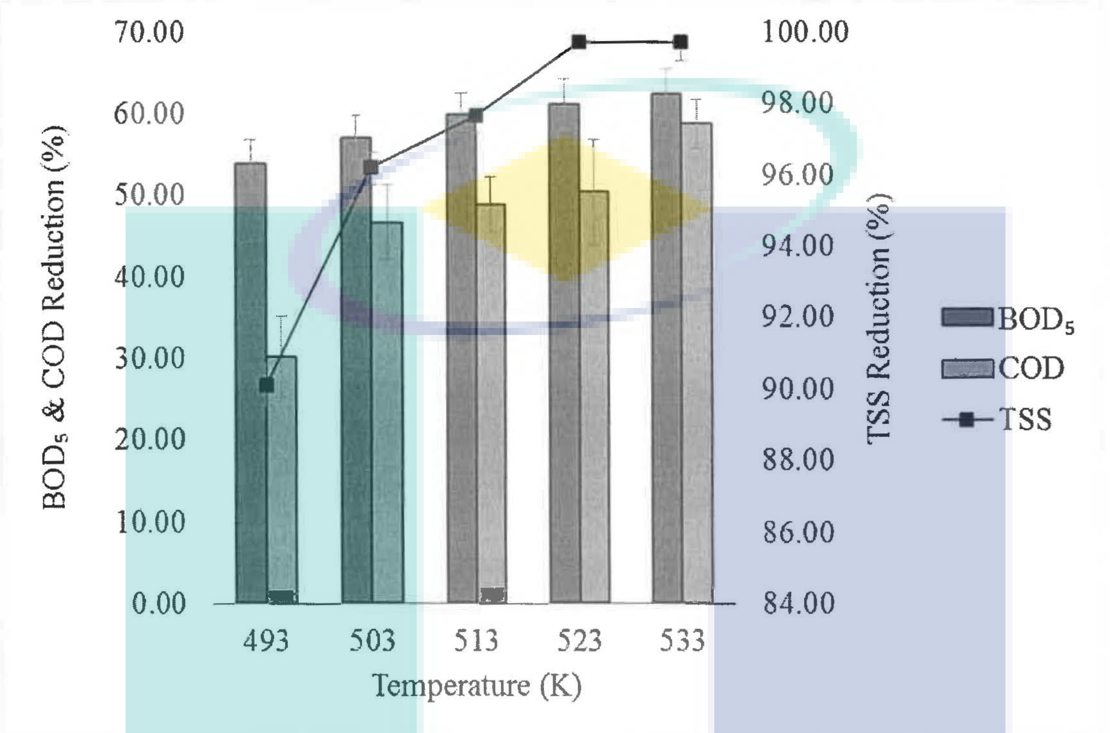


Figure 2: BOD_5, COD and TSS reduction from 493 K to 533 K.

Gaseous product analysis

The gas produced from the subcritical hydrothermal treatment of POME for 2 h in various temperature was also analysed. The gaseous products mainly comprised of CO_2, CO, H_2 and traces of higher number carbon gases ($C_3 - C_6$). Traces of CH_4 were observed at 533 K as it can only be produced at higher temperature through CO methanation. The gas composition at different reaction temperatures is depicted in Figure 3. The dominant gas product was CO_2, where the lowest of 3.10 vol% at 493 K while the highest of 3.99 vol% per working volume of 500 mL POME at 533 K. By ignoring CH_4, the H_2 production was the smallest, which in the range of 0.0005 – 0.03 vol% over 500 mL POME. The insignificant production of H_2 could be possibly due to two main reasons. Firstly, POME contains higher lignin-to-cellulose ratio compared to the other agricultural fibrous residues (Wong *et al.*, 2008). Biomass with higher composition of cellulose and hemicellulose would produce more H_2, while H_2 yield will be inhibited by the existence of lignin in the structure of biomass (Salimi *et al.*, 2016). Another reason for the low volume of H_2 generated was due to the absence of catalyst in this range of temperature. The catalyst is suggested to aid in turning the big molecules into smaller molecules on the catalyst surface, followed with steam gasification of small molecules to produce CO and H_2, followed by CO methanation and CO shift reaction to produce CH_4 and CO_2 (Kong *et al.*, 2008; Sharma, Nakagawa & Miura, 2006).

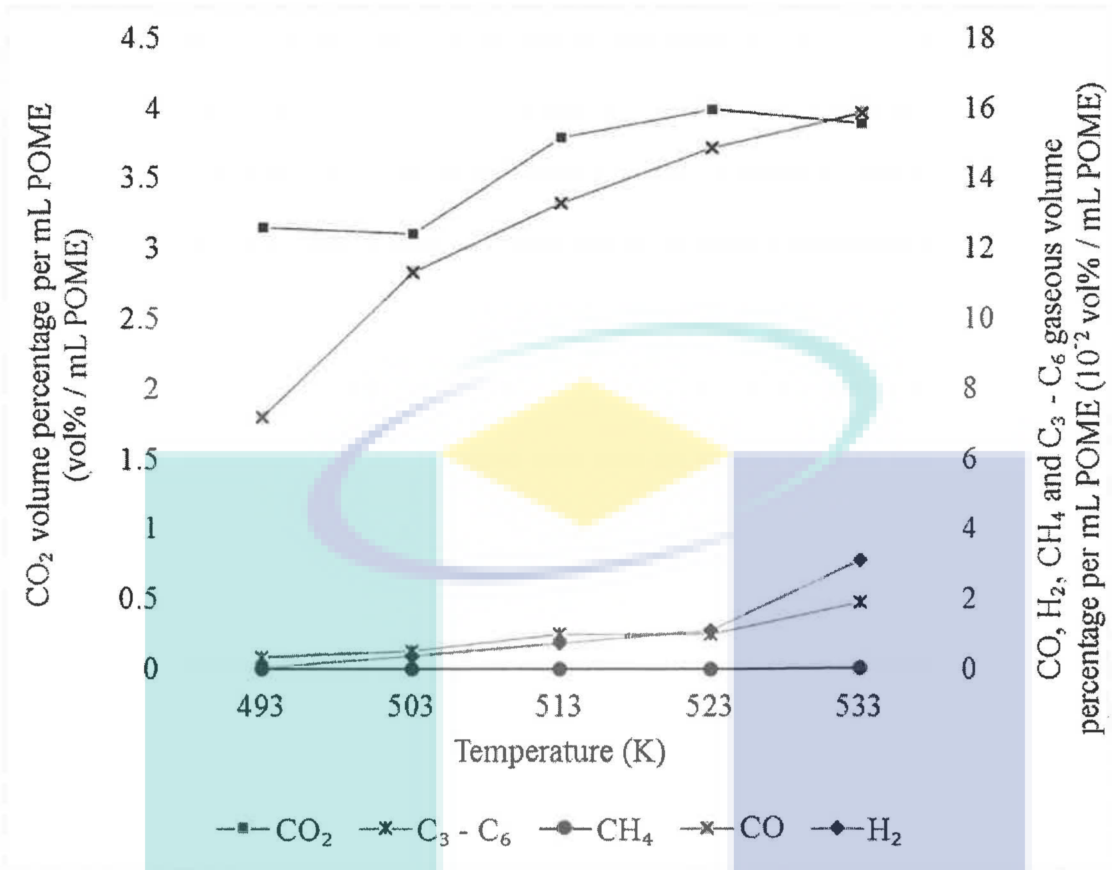


Figure 3: Composition of gaseous products (vol% / mL POME) in the range of 493 K to 533 K.

Solid product Characterisation

Visual Observation

From the visual observation, wet hydrochar obtained from reactions at 513 K to 533 K were stickier than the wet hydrochar obtained at 493 K and 503 K. The collected hydrochar was placed on an aluminium boat and dried at 378 K for 3 h. The dried hydrochar from experiments 513 K to 533 K possessed gummy texture, retaining its sticky and dense consistency, whereas the hydrochar obtained at lower reaction temperature, *viz.* 493 K and 503 K were of powder form.

Proximate & Elemental Analyses

The proximate analysis was estimated from TGA analysis, as shown in Figures 4(a) to 4(d). The VM, FC, ash content and corresponding HHVs of the POME and hydrochar samples are summarised in Table 2. In comparison to POME, the FC content of the hydrochar increased gradually about 56.69% to 63.65%, from 41.47% of the fresh POME), suggesting an increasing conversion of ash-free organic constituents into carbon at higher temperature. Besides, the VM in the hydrochar was significantly lower than that in the fresh POME. Similar findings were reported by Kalderis and co-workers (Kalderis *et al.*, 2014). The decrease of VM content was with the increase in gaseous products when hydrothermal temperature was increased. The ash content showed an increasing uptrend from 7.21% (493 K) to 12.05% (533 K), compared to the fresh POME at 11.54%. The increase of ash content with the elevation of reaction temperature suggests us the decomposition of organic components (Mäkelä & Yoshikawa, 2016).

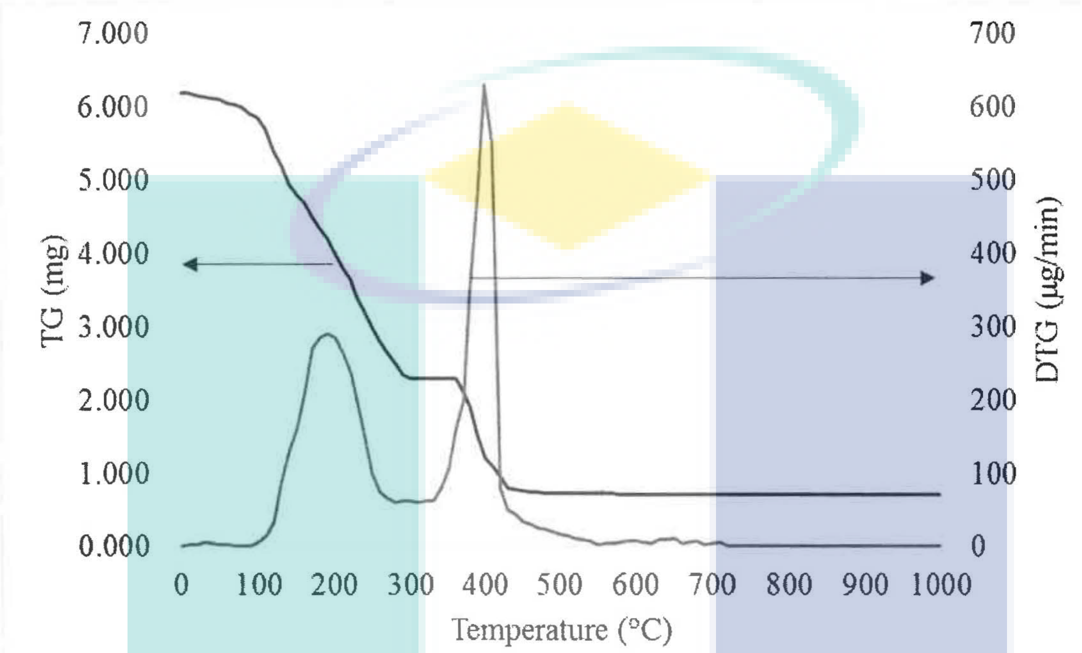


Figure 4(a): TGA for freeze-dried fresh POME.

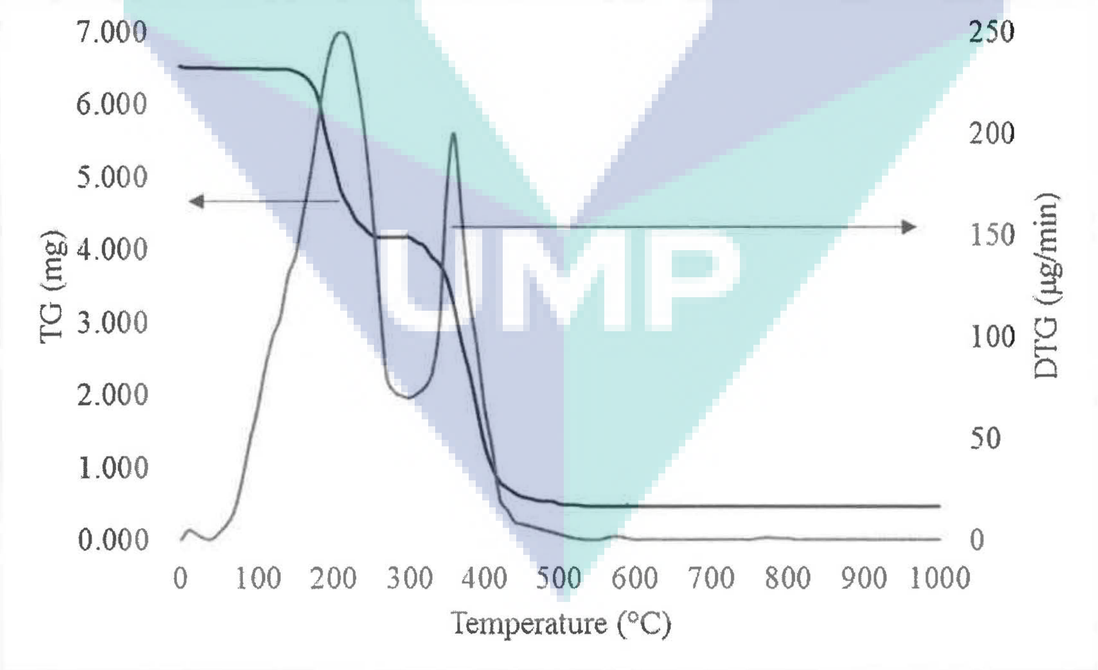


Figure 4(b): TGA for hydrochar at 493 K.

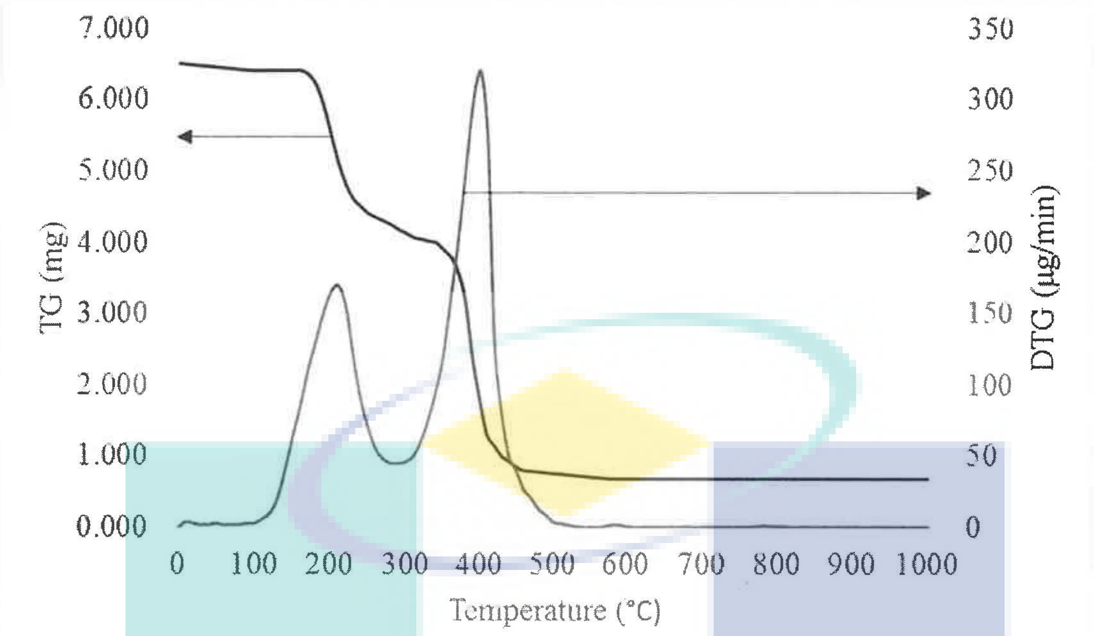


Figure 4(c): TGA for hydrochar at 513 K.

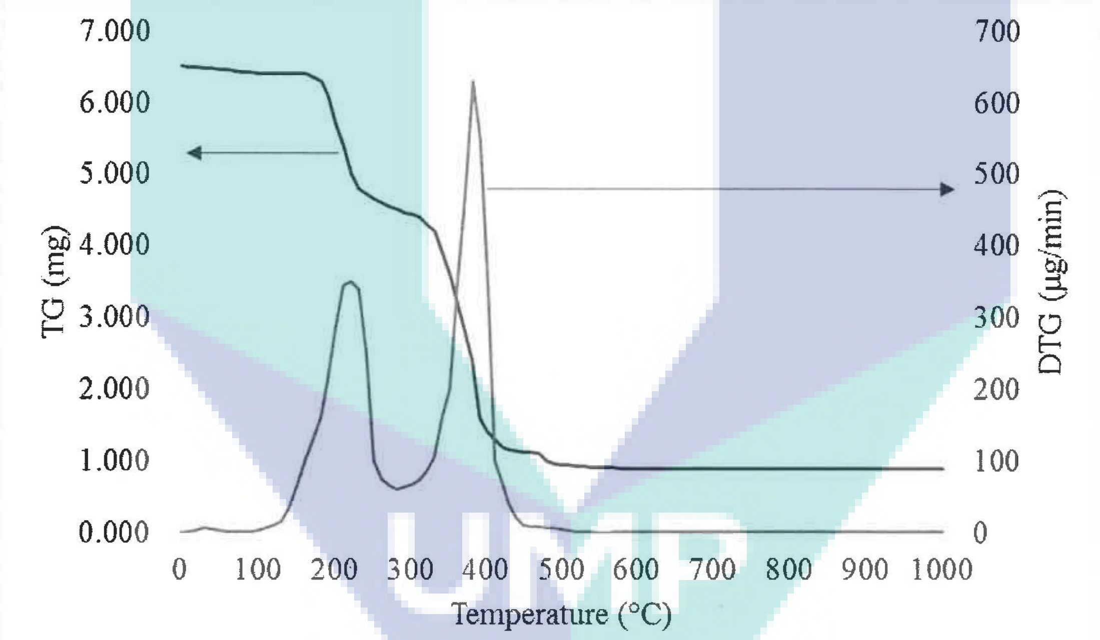


Figure 4(d): TGA for hydrochar at 533 K.

Table 2: Proximate analysis on a dry weight basis of the freeze-dried fresh POME and hydrochar produced at different reaction temperatures.

Sample	VM (%)	FC (%)	Ash Content (%)
Raw POME	46.99	41.47	11.54
493 K	36.10	56.69	7.21
503 K	33.70	57.36	8.94
513 K	30.90	58.60	10.50
523 K	27.40	60.90	11.70
533 K	24.30	63.65	12.05

5. CONCLUSIONS

Hydrothermal treatment under subcritical condition provides a new idea for the treatment and utilisation of POME. Optimum reaction temperature was at 533 K as it resulted the highest COD, BOD_5 and TSS removal, which recorded at 58.81%, 62.47% and 99.71% respectively, with pH of around 6.5 due to the reduction of carboxylic compounds. Organic compounds with phenolic group increased with reaction temperature. The liquid product wastewater quality is comparable with the effluent in anaerobic section of open ponding system. Further treatment of liquid product, such as aerobic treatment, is recommended as the BOD5 still has not achieved the local discharge standard. The dominant gaseous product was CO_2, followed by CO, H_2 and higher number hydrocarbons, i.e. C_3 – C_6. CH_4 was found in traces amount at 533 K. Gaseous production increased with the increase of temperature. The FC increased whereas VM reduced in the hydrochar produced at higher temperature. Both the O/C and H/C atomic ratio of the hydrochar produced at 533 K were at the lowest, recorded 0.157 and 0.930 respectively, giving hydrochar a promising behaviour as a combustion fuel. For hydrothermal reaction under subcritical condition, deoxygenation which consisted of dehydration and decarboxylation is proposed to be the major reaction after hydrolysis took place. As POME is richer in lignin, slow polymerisation of lignin into phenolic compounds was suggested with the increase of reaction temperature. Based on the positive treatment output, hydrothermal treatment has a great potentiality to be focused on to overcome the weakness of current open ponding system. A continuous flow study is recommended in future work in order to satisfy the application of this novel POME treatment at elevated scale. One of the industrial concerns of having hydrothermal process for POME treatment will be the plugging problem in continuous flow system. Two-stage hydrothermal treatment (Sintamarean et al., 2017; He et al., 2014) and continuous stirred tank reactor (CSTR) (Ocfemia et al., 2006) are good attempts to overcome the plugging obstacle. In addition, catalytic study is necessary to enhance the organic compounds degradation and to reduce the operation severity. From there, kinetic and process optimisation studies can be performed to deepen the understanding of this novel wastewater treatment.

ACHIEVEMENT

i) **Name of articles/ manuscripts/ books published**
https://doi.org/10.1016/j.eti.2019.100377

https://doi.org/10.1016/j.heliyon.2019.e01792

ii) **Title of Paper presentations (international/ local)**

SEGT 2018 (International Conference on Sustainable Energy and Green Technology 2018)

iii) **Human Capital Development**
Lee Zhan Sheng, MKC18007 (PhD – ongoing)
Arics Chieng Kie Siong, KA15073 (Degree – Graduated)

iv) **Awards/ Others**
Nil

v) **Others**
Nil

REFERENCES

Abu Tayeh, H., Levy-Shalev, O., Azaizeh, H., & Dosoretz, C. G. (2016). Subcritical hydrothermal pretreatment of olive mill solid waste for biofuel production. *Bioresource Technology, 199*, 164-172. doi:https://doi.org/10.1016/j.biortech.2015.08.138

Ahmad, A., & Ghufran, R. (2018). Review on industrial wastewater energy sources and carbon emission reduction: towards a clean production. *International Journal of Sustainable Engineering*, 1-11. doi:10.1080/19397038.2018.1423647

Alhaji, M. H., Sanaullah, K., Salleh, S. F., Baini, R., Lim, S. F., Rigit, A. R. H., . . . Khan, A. (2018). Photo-oxidation of pre-treated palm oil mill Effluent using cylindrical column immobilized photoreactor. *Process Safety and Environmental Protection*. doi:https://doi.org/10.1016/j.psep.2018.04.012

Ali, A. N. A., Tan, Y. H., Lau, W. J., Lai, G. S., Ong, C. S., Mokhtar, N. M., . . . Lai, S. O. (2015). Tackling colour issue of anaerobically-treated palm oil mill effluent using membrane technology. *Journal of Water Process Engineering, 8*, 221-226. doi:https://doi.org/10.1016/j.jwpe.2015.10.010

Berge, N. D., Ro, K. S., Mao, J., Flora, J. R. V., Chappell, M. A., & Bae, S. (2011). Hydrothermal Carbonization of Municipal Waste Streams. *Environmental Science & Technology, 45*(13), 5696-5703. doi:10.1021/es2004528

Chan, Y. J., Tan, W. J. R., How, B. S., Lee, J. J., & Lau, V. Y. (2015). Fuzzy optimisation approach on the treatment of palm oil mill effluent (POME) via up-flow anaerobic sludge blanket–hollow centered packed bed (UASB–HCPB) reactor. *Journal of Water Process Engineering, 5*, 112-117. doi:https://doi.org/10.1016/j.jwpe.2015.01.005

Channiwala, S. A., & Parikh, P. P. (2002). A unified correlation for estimating HHV of solid, liquid and gaseous fuels. *Fuel, 81*(8), 1051-1063. doi:https://doi.org/10.1016/S0016-2361(01)00131-4

Cheng, J., Zhu, X., Ni, J., & Borthwick, A. (2010). Palm oil mill effluent treatment using a two-stage microbial fuel cells system integrated with immobilized biological aerated filters. *Bioresource Technology, 101*(8), 2729-2734. doi:https://doi.org/10.1016/j.biortech.2009.12.017

Cheng, L., Ye, X. P., He, R., & Liu, S. (2009). Investigation of rapid conversion of switchgrass in subcritical water. *Fuel Processing Technology, 90*(2), 301-311. doi:https://doi.org/10.1016/j.fuproc.2008.09.009

Cheng, Y. W., Lee, Z. S., Chong, C. C., Khan, M. R., Cheng, C. K., Ng, K. H., & Hossain, S. S. (2018). Hydrogen-rich syngas production via steam reforming of palm oil mill effluent (POME) – A thermodynamics analysis. *International Journal of Hydrogen Energy*. doi:https://doi.org/10.1016/j.ijhydene.2018.05.119

Coker, A. (2001). *Modeling of Chemical Kinetics and Reactor Design / A.K. Coker*.

Danso-Boateng, E., Holdich, R., Shama, G., Wheatley, A. D., Sohail, M., & Martin, S. (2013). Kinetics of faecal biomass hydrothermal carbonisation for hydrochar production. *Applied energy, 111*, 351-357.

Ding, L., Zou, B., Li, Y., Liu, H., Wang, Z., Zhao, C., . . . Guo, Y. (2013). The production of hydrochar-based hierarchical porous carbons for use as electrochemical supercapacitor electrode materials. *Colloids and Surfaces A: Physicochemical and Engineering Aspects, 423*, 104-111. doi:https://doi.org/10.1016/j.colsurfa.2013.02.003

DOSM, D. o. S. M. (2017). Selected Agricultural Indicators, Malaysia, 2017.

Eibisch, N., Helfrich, M., Don, A., Mikutta, R., Kruse, A., Ellerbrock, R., & Flessa, H. (2013). *Properties and Degradability of Hydrothermal Carbonization Products* (Vol. 42).

Foong, S. Z. Y., Lam, Y. L., Andiappan, V., Foo, D. C. Y., & Ng, D. K. S. (2018). A Systematic Approach for the Synthesis and Optimization of Palm Oil Milling Processes. *Industrial & Engineering Chemistry Research, 57*(8), 2945-2955. doi:10.1021/acs.iecr.7b04788

Funke, A., & Ziegler, F. (2010). Hydrothermal carbonization of biomass: A summary and discussion of chemical mechanisms for process engineering. *Biofuels, Bioproducts and Biorefining, 4*(2), 160-177. doi:doi:10.1002/bbb.198

Gao, F., Shao, G., Qu, J., Lv, S., Li, Y., & Wu, M. (2015). Tailoring of porous and nitrogen-rich carbons derived from hydrochar for high-performance supercapacitor electrodes. *Electrochimica Acta, 155*, 201-208. doi:https://doi.org/10.1016/j.electacta.2014.12.069

Gollakota, A. R. K., Kishore, N., & Gu, S. (2018). A review on hydrothermal liquefaction of biomass. *Renewable and Sustainable Energy Reviews, 81*, 1378-1392. doi:https://doi.org/10.1016/j.rser.2017.05.178

Hall, S. (2012). 27 - Properties. In S. Hall (Ed.), *Branan's Rules of Thumb for Chemical Engineers (Fifth Edition)* (pp. 401-421). Oxford: Butterworth-Heinemann.

He, C., Chen, C.-L., Giannis, A., Yang, Y., & Wang, J.-Y. (2014). Hydrothermal gasification of sewage sludge and model compounds for renewable hydrogen production: A review. *Renewable and Sustainable Energy Reviews, 39*, 1127-1142. doi:https://doi.org/10.1016/j.rser.2014.07.141

Heilmann, S. M., Davis, H. T., Jader, L. R., Lefebvre, P. A., Sadowsky, M. J., Schendel, F. J., . . . Valentas, K. J. (2010). Hydrothermal carbonization of microalgae. *Biomass and Bioenergy, 34*(6), 875-882. doi:https://doi.org/10.1016/j.biombioe.2010.01.032

Hosseini, S. E., & Wahid, M. A. (2015). Pollutant in palm oil production process. *Journal of the Air & Waste Management Association, 65*(7), 773-781. doi:10.1080/10962247.2013.873092

Islam, M. A., Ahmed, M. J., Khanday, W. A., Asif, M., & Hameed, B. H. (2017). Mesoporous activated coconut shell-derived hydrochar prepared via hydrothermal carbonization-NaOH activation for methylene blue adsorption. *Journal of Environmental Management, 203*, 237-244. doi:https://doi.org/10.1016/j.jenvman.2017.07.029

Jamal, P., Alam, M. Z., & Mohamad, A. B. (2007, 2007//). *Microbial Bioconversion of Palm Oil Mill Effluent to Citric Acid with Optimum Process Conditions.* Paper presented at the 3rd Kuala Lumpur International Conference on Biomedical Engineering 2006, Berlin, Heidelberg.

Kalderis, D., Kotti, M. S., Méndez, A., & Gascó, G. (2014). Characterization of hydrochars produced by hydrothermal carbonization of rice husk. *Solid Earth, 5*(1), 477-483. doi:10.5194/se-5-477-2014

Kang, S., Li, X., Fan, J., & Chang, J. (2013). Hydrothermal conversion of lignin: A review. *Renewable and Sustainable Energy Reviews, 27*, 546-558. doi:https://doi.org/10.1016/j.rser.2013.07.013

Karagöz, S., Bhaskar, T., Muto, A., Sakata, Y., & Uddin, M. A. (2004). Low-Temperature Hydrothermal Treatment of Biomass: Effect of Reaction Parameters on Products and Boiling Point Distributions. *Energy & Fuels, 18*(1), 234-241. doi:10.1021/ef030133g

Khan, A. A., de Jong, W., Jansens, P. J., & Spliethoff, H. (2009). Biomass combustion in fluidized bed boilers: Potential problems and remedies. *Fuel Processing Technology, 90*(1), 21-50. doi:https://doi.org/10.1016/j.fuproc.2008.07.012

Kong, L., Li, G., Zhang, B., He, W., & Wang, H. (2008). Hydrogen Production from Biomass Wastes by Hydrothermal Gasification. *Energy Sources, Part A: Recovery, Utilization, and Environmental Effects, 30*(13), 1166-1178. doi:10.1080/15567030701258246

Kruse, A., Funke, A., & Titirici, M.-M. (2013). Hydrothermal conversion of biomass to fuels and energetic materials. *Current Opinion in Chemical Biology, 17*(3), 515-521. doi:https://doi.org/10.1016/j.cbpa.2013.05.004

Leng, L., Huang, H., Li, H., Li, J., & Zhou, W. (2019). Biochar stability assessment methods: A review. *Science of The Total Environment, 647*, 210-222. doi:https://doi.org/10.1016/j.scitotenv.2018.07.402

Libra, J. A., Ro, K. S., Kammann, C., Funke, A., Berge, N. D., Neubauer, Y., . . . Emmerich, K. H. (2011). Hydrothermal carbonization of biomass residuals: a comparative review of the chemistry, process, and applications of wet and dry pyrolysis. *Biofuels, 2*(1), 89-124.

Liu, Z., Quek, A., & Balasubramanian, R. (2014). Preparation and characterization of fuel pellets from woody biomass, agro-residues and their corresponding hydrochars. *Applied energy, 113*, 1315-1322. doi:https://doi.org/10.1016/j.apenergy.2013.08.087

Liu, Z., Quek, A., Hoekman, S. K., & Balasubramanian, R. (2013). Production of solid biochar fuel from waste biomass by hydrothermal carbonization. *Fuel, 103*, 943-949.

Ma, X., Zhou, B., Budai, A., Jeng, A., Hao, X., Wei, D., . . . Rasse, D. (2016). Study of Biochar Properties by Scanning Electron Microscope – Energy Dispersive X-Ray Spectroscopy (SEM-EDX). *Communications in Soil Science and Plant Analysis, 47*(5), 593-601. doi:10.1080/00103624.2016.1146742

Madaki, Y. S., & Lau, S. (2013). Palm Oil Mill Effluent (Pome) from Malaysia Palm Oil Mills: Waste or Resource. *International Journal of Science, Environment ISSN 2278-3687 (O) and Technology, 2*(6), 1138-1155.

Mäkelä, M., Forsberg, J., Söderberg, C., Larsson, S. H., & Dahl, O. (2018). Process water properties from hydrothermal carbonization of chemical sludge from a pulp and board mill. *Bioresource Technology, 263*, 654-659. doi:https://doi.org/10.1016/j.biortech.2018.05.044

Mäkelä, M., & Yoshikawa, K. (2016). *Ash behavior during hydrothermal treatment for solid fuel applications. Part 2: Effects of treatment conditions on industrial waste biomass* (Vol. 121).

Montoya, C., Cochard, B., Flori, A., Cros, D., Lopes, R., Cuellar, T., . . . Billotte, N. (2014). Genetic Architecture of Palm Oil Fatty Acid Composition in Cultivated Oil Palm (Elaeis guineensis Jacq.) Compared to Its Wild Relative E. oleifera (H.B.K) Cortés. *PLOS ONE, 9*(5), e95412. doi:10.1371/journal.pone.0095412

MPOA. (2014). BOD Level and POME Tertiary Treatment Technologies. *MPOA News*. Retrieved from http://mpoa.org.my/bod-level-and-pome-tertiary-treatment-technologies/

MPOB, M. P. O. B. (2017). Monthly Export of Oil Palm Products - 2017.

Nasrullah, M., Singh, L., Mohamad, Z., Norsita, S., Krishnan, S., Wahida, N., & Zularisam, A. W. (2017). Treatment of palm oil mill effluent by electrocoagulation with presence of hydrogen peroxide as oxidizing agent and polialuminum chloride as coagulant-aid. *Water Resources and Industry, 17*, 7-10. doi:https://doi.org/10.1016/j.wri.2016.11.001

Ng, K., & Cheng, C. (2016). Photo-polishing of POME into CH4-lean biogas over the UV-responsive ZnO photocatalyst. *Chemical Engineering Journal, 300*, 127-138.

Ng, K. H., & Cheng, C. K. (2015). A novel photomineralization of POME over UV-responsive TiO2 photocatalyst: kinetics of POME degradation and gaseous product formations. *RSC Advances, 5*(65), 53100-53110. doi:10.1039/C5RA06922J

Ng, K. H., Cheng, Y. W., Lee, Z. S., & Cheng, C. K. (2018). A study into syngas production from catalytic steam reforming of palm oil mill effluent (POME): A new treatment approach. *International Journal of Hydrogen Energy*. doi:https://doi.org/10.1016/j.ijhydene.2018.04.232

Ng, K. H., Lee, C. H., Khan, M. R., & Cheng, C. K. (2016). Photocatalytic degradation of recalcitrant POME waste by using silver doped titania: Photokinetics and scavenging studies. *Chemical Engineering Journal, 286*, 282-290. doi:10.1016/j.cej.2015.10.072

Ocfemia, S. K., Zhang, Y., & Funk, T. (2006). Hydrothermal Processing of Swine Manure to Oil Using a Continuous Reactor System: Effects of Operating Parameters on Oil Yield and Quality. *Transactions of the ASABE, 49*(6), 1897-1904. doi:https://doi.org/10.13031/2013.22291

Olivier, B., Pierre, F., Bill, C., & Keith, P. S. (2009). The indirect global warming potential and global temperature change potential due to methane oxidation. *Environmental Research Letters, 4*(4), 044007.

Osada, M., Sato, T., Watanabe, M., Adschiri, T., & Arai, K. (2004). Low-Temperature Catalytic Gasification of Lignin and Cellulose with a Ruthenium Catalyst in Supercritical Water. *Energy & Fuels, 18*(2), 327-333. doi:10.1021/ef034026y

Parshetti, G. K., Hoekman, K. S., & Balasubramanian, R. (2013). Chemical, structural and combustion characteristics of carbonaceous products obtained by hydrothermal carbonization of palm empty fruit bunches. *Bioresource Technology, 135*, 683-689. doi:https://doi.org/10.1016/j.biortech.2012.09.042

Poerschmann, J., Weiner, B., Koehler, R., & Kopinke, F.-D. (2017). Hydrothermal Carbonization of Glucose, Fructose, and Xylose—Identification of Organic Products with Medium Molecular Masses. *ACS Sustainable Chemistry & Engineering, 5*(8), 6420-6428. doi:10.1021/acssuschemeng.7b00276

Poh, P. E., & Chong, M. F. (2009). Development of anaerobic digestion methods for palm oil mill effluent (POME) treatment. *Bioresource Technology, 100*(1), 1-9. doi:https://doi.org/10.1016/j.biortech.2008.06.022

Poh, P. E., & Chong, M. F. (2014). Upflow anaerobic sludge blanket-hollow centered packed bed (UASB-HCPB) reactor for thermophilic palm oil mill effluent (POME) treatment. *Biomass and Bioenergy, 67*, 231-242. doi:https://doi.org/10.1016/j.biombioe.2014.05.007

Reza, M. T., Andert, J., Wirth, B., Busch, D., Pielert, J., Lynam, J., & Mumme, J. (2014). *Review Article: Hydrothermal Carbonization of Biomass for Energy and Crop Production* (Vol. 1).

Reza, M. T., Yan, W., Uddin, M. H., Lynam, J. G., Hoekman, S. K., Coronella, C. J., & Vásquez, V. R. (2013). Reaction kinetics of hydrothermal carbonization of loblolly pine. *Bioresource Technology, 139*, 161-169. doi:https://doi.org/10.1016/j.biortech.2013.04.028

Sakaki, T., Shibata, M., Miki, T., Hirosue, H., & Hayashi, N. (1996). Decomposition of Cellulose in Near-Critical Water and Fermentability of the Products. *Energy & Fuels, 10*(3), 684-688. doi:10.1021/ef950160+

Salimi, M., Safari, F., Tavasoli, A., & Shakeri, A. (2016). Hydrothermal gasification of different agricultural wastes in supercritical water media for hydrogen production: a comparative study. *International Journal of Industrial Chemistry, 7*(3), 277-285. doi:10.1007/s40090-016-0091-y

Sevilla, M., & Fuertes, A. B. (2009). The production of carbon materials by hydrothermal carbonization of cellulose. *Carbon, 47*(9), 2281-2289. doi:https://doi.org/10.1016/j.carbon.2009.04.026

Sharma, A., Nakagawa, H., & Miura, K. (2006). A novel nickel/carbon catalyst for CH4 and H2 production from organic compounds dissolved in wastewater by catalytic hydrothermal gasification. *Fuel, 85*(2), 179-184. doi:https://doi.org/10.1016/j.fuel.2005.04.035

Simsir, H., Eltugral, N., & Karagoz, S. (2017). Hydrothermal carbonization for the preparation of hydrochars from glucose, cellulose, chitin, chitosan and wood chips via low-temperature and their characterization. *Bioresource Technology, 246*, 82-87. doi:https://doi.org/10.1016/j.biortech.2017.07.018

Sintamarean, I. M., Grigoras, I. F., Jensen, C. U., Toor, S. S., Pedersen, T. H., & Rosendahl, L. A. (2017). Two-stage alkaline hydrothermal liquefaction of wood to biocrude in a continuous bench-scale system. *Biomass Conversion and Biorefinery, 7*(4), 425-435. doi:10.1007/s13399-017-0247-9

Stichnothe, H., & Schuchardt, F. (2011). Life cycle assessment of two palm oil production systems. *Biomass and Bioenergy, 35*(9), 3976-3984. doi:https://doi.org/10.1016/j.biombioe.2011.06.001

Stirling, R. J., Snape, C. E., & Meredith, W. (2018). The impact of hydrothermal carbonisation on the char reactivity of biomass. *Fuel Processing Technology, 177*, 152-158. doi:https://doi.org/10.1016/j.fuproc.2018.04.023

Tabassum, S., Zhang, Y., & Zhang, Z. (2015). An integrated method for palm oil mill effluent (POME) treatment for achieving zero liquid discharge – A pilot study. *Journal of Cleaner Production, 95*, 148-155. doi:https://doi.org/10.1016/j.jclepro.2015.02.056

Takaya, C. A., Fletcher, L. A., Singh, S., Anyikude, K. U., & Ross, A. B. (2016). Phosphate and ammonium sorption capacity of biochar and hydrochar from different wastes. *Chemosphere, 145*, 518-527. doi:https://doi.org/10.1016/j.chemosphere.2015.11.052

Teh, C. Y., Budiman, P. M., Shak, K. P. Y., & Wu, T. Y. (2016). Recent Advancement of Coagulation–Flocculation and Its Application in Wastewater Treatment. *Industrial & Engineering Chemistry Research, 55*(16), 4363-4389. doi:10.1021/acs.iecr.5b04703

Tsai, W.-T., Liu, S.-C., Chen, H.-R., Chang, Y.-M., & Tsai, Y.-L. (2012). Textural and chemical properties of swine-manure-derived biochar pertinent to its potential use as a soil amendment. *Chemosphere, 89*(2), 198-203. doi:https://doi.org/10.1016/j.chemosphere.2012.05.085

Williams, P. T., & Onwudili, J. (2006). Subcritical and Supercritical Water Gasification of Cellulose, Starch, Glucose, and Biomass Waste. *Energy & Fuels, 20*(3), 1259-1265. doi:10.1021/ef0503055

Windeatt, J. H., Ross, A. B., Williams, P. T., Forster, P. M., Nahil, M. A., & Singh, S. (2014). Characteristics of biochars from crop residues: Potential for carbon sequestration and soil amendment. *Journal of Environmental Management, 146*, 189-197. doi:https://doi.org/10.1016/j.jenvman.2014.08.003

Wong, K. M., Nor'aini, A. R., Suraini, A., Vikineswary, S., & Hassan, M. A. (2008). Enzymatic Hydrolysis of Palm Oil Mill Effluent Solid Using Mixed Cellulases from Locally Isolated Fungi. *Research Journal of Microbiology, 3*, 474-481. doi:10.3923/jm.2008.474.481

Wu, Q., Yu, S., Hao, N., Wells, T., Meng, X., Li, M., . . . Ragauskas, A. J. (2017). Characterization of products from hydrothermal carbonization of pine. *Bioresource Technology, 244*(Pt 1), 78-83. doi:10.1016/j.biortech.2017.07.138

Wu, T. Y., Mohammad, A. W., Jahim, J. M., & Anuar, N. (2010). Pollution control technologies for the treatment of palm oil mill effluent (POME) through end-of-pipe processes. *Journal of Environmental Management, 91*(7), 1467-1490. doi:https://doi.org/10.1016/j.jenvman.2010.02.008

Zahrim, A. Y., Dexter, Z. D., Joseph, C. G., & Hilal, N. (2017). Effective coagulation-flocculation treatment of highly polluted palm oil mill biogas plant wastewater using dual coagulants: Decolourisation, kinetics and phytotoxicity studies. *Journal of Water Process Engineering, 16*, 258-269. doi:https://doi.org/10.1016/j.jwpe.2017.02.005

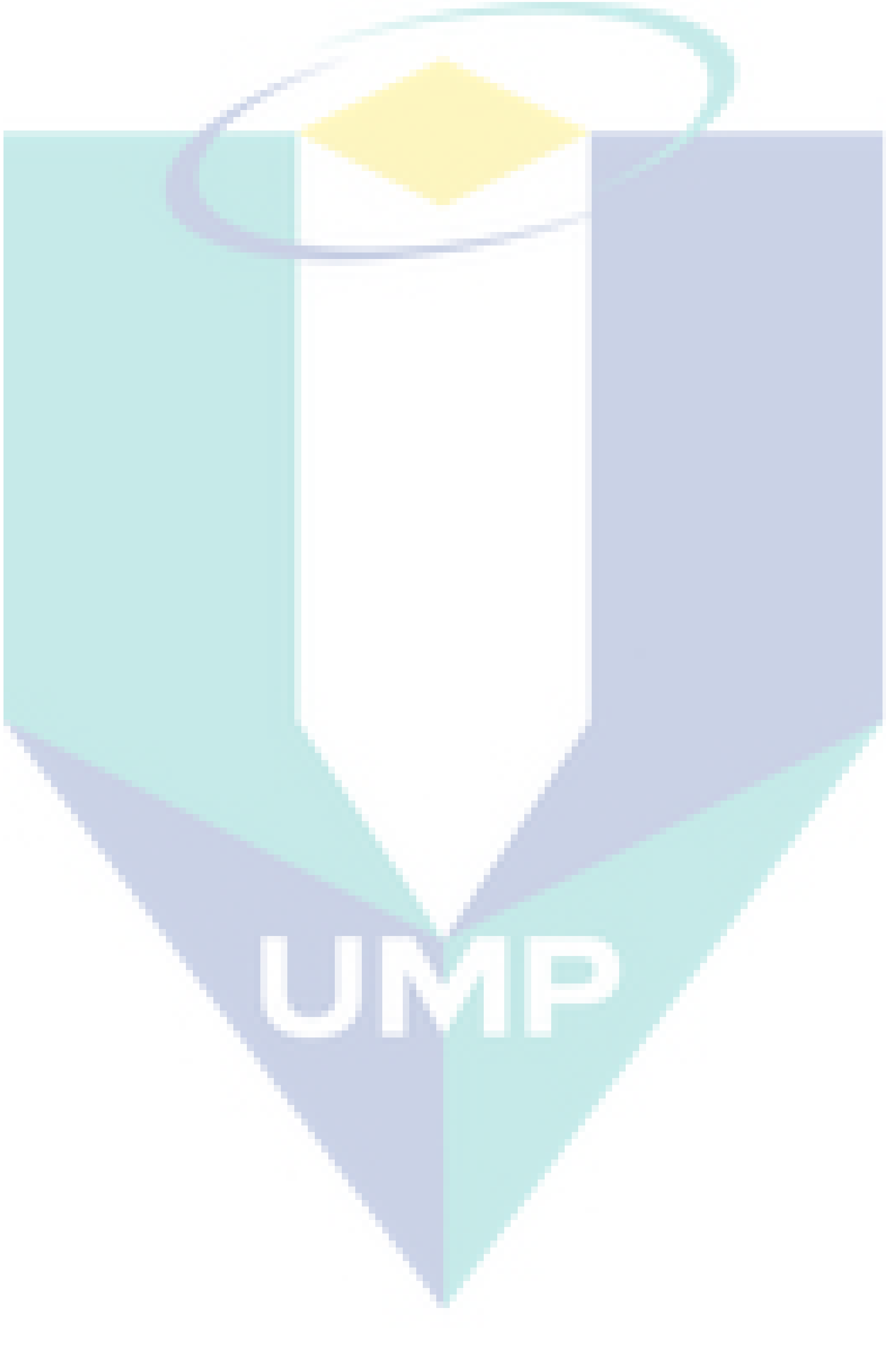
Zhang, B., Heidari, M., Regmi, B., Salaudeen, S., Arku, P., Thimmannagari, M., & Dutta, A. (2018). *Hydrothermal Carbonization of Fruit Wastes: A Promising Technique for Generating Hydrochar* (Vol. 11).

Zhang, L., Wang, Q., Wang, B., Yang, G., Lucia, L. A., & Chen, J. (2015). Hydrothermal Carbonization of Corncob Residues for Hydrochar Production. *Energy & Fuels, 29*(2), 872-876. doi:10.1021/ef502462p

Zhao, M., Li, B., Cai, J.-X., Liu, C., McAdam, K. G., & Zhang, K. (2016). Thermal & chemical analyses of hydrothermally derived carbon materials from corn starch. *Fuel Processing Technology, 153*, 43-49. doi:https://doi.org/10.1016/j.fuproc.2016.08.002

Zhu, X., Liu, Y., Qian, F., Zhou, C., Zhang, S., & Chen, J. (2015). Role of Hydrochar Properties on the Porosity of Hydrochar-based Porous Carbon for Their Sustainable Application. *ACS Sustainable Chemistry & Engineering, 3*(5), 833-840. doi:10.1021/acssuschemeng.5b00153

Zinatizadeh, A. A. L., Mohamed, A. R., Najafpour, G. D., Hasnain Isa, M., & Nasrollahzadeh, H. (2006). Kinetic evaluation of palm oil mill effluent digestion in a high rate up-flow anaerobic sludge fixed film bioreactor. *Process Biochemistry, 41*(5), 1038-1046. doi:https://doi.org/10.1016/j.procbio.2005.11.011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