

**UNIVERSITI TEKNOLOGI MARA**

**PALM OIL MILL EFFLUENT  
(POME) TREATMENT AND  
CONVERSION USING NON-  
CATALYTIC HYDROTHERMAL  
METHOD**

**MOHD ZAHID BIN MARZUKI**

Thesis submitted in fulfillment  
of the requirements for the degree of  
**Doctor of Philosophy**  
**(Chemical Engineering)**

**College of Engineering**

**July 2022**

## ABSTRACT

Palm oil mill effluent (POME) is considered as a major environmental pollution source due to its harmful characteristics and large volume of over 60 million tonnes generated annually. It is characterized by high oils and fats, chemical oxygen demand (COD) and biochemical oxygen demand (BOD) concentrations and therefore subjected to strict discharge parameter standard promulgated under Environmental Quality Act (EQA) 1974. The biochemical oxygen demand (BOD) and chemical oxygen demand (COD) of POME are typically in excess of 30,000 ppm and 50,000 ppm respectively. As such, POME is toxic to environment that requires proper management prior to final discharge to inland water bodies. Current POME management, in most palm oil mills adopted conventional ponding treatment system. However, such practice requires large land area and long hydraulic retention time (>40 days) to achieve COD and BOD removal efficiencies of more than 90%. Complementary anaerobic digestion treatment methods have been proposed to reduce the hydraulic retention time and enhance process performance of the existing POME management scheme, but they are yet to be implemented in large scale. Hydrothermal technology has been widely applied either for complete degradation or conversion of wet biomass to generate hydrochar, bio-oils and gaseous products by utilizing the unique properties of water around its critical temperature and pressure ( $T_c$  . 374.4 °C,  $P_c$  219.5 atm). Hence, the aim of this research is to investigate the potential of hydrothermal as complementary treatment method for the POME management. In Part 1, the influence of the hydrothermal process parameters on the POME degradation was assessed at subcritical conditions (200°C, 250 °C, 300 °C and 350 °C) using a slow heating batch reactor, locally fabricated according to ASME BPV (2007) design code. Reaction time was varied between 10 and 60 minutes. In addition, hydrothermal degradation intensification effects were examined by addition of an oxidant (hydrogen peroxide, H<sub>2</sub>O<sub>2</sub>). It was found that in absence of an oxidant, reaction temperature played a significant role over reaction time towards the COD and colour reduction and pH level of the POME derived aqueous phase. Near critical temperature of 350 °C was needed to remove 90% of COD at 60 min reaction time. The final colour (165 ADMI) and pH value (5.2) after hydrothermal treatment was found to be in compliance with the national POME discharge standard (Environmental Quality Industrial Effluent Regulations 2009; BOD less than 100 mg/L, colour less than 200 ADMI and pH between 5 to 9). It was also observed that the addition of H<sub>2</sub>O<sub>2</sub> oxidant led to reductions in COD (92% removal), colour (99% removal) and pH (6.2) at relatively low temperature of 150 °C and short reaction time of 10 min. The results indicated the potential of hydrothermal oxidation as a potential route for POME treatment. Part 2 of this thesis looked at valorization potential of the POME to bio-oils in a fast heating micro-bomb reactor at subcritical and supercritical water conditions. Bio-oils rich in phenolics and organic acids traceable to lignocellulosic and organic constituents of raw POME were produced at supercritical conditions of 400 °C and 30 min. The extent of conversion suggested that a suite of complex free-radical supported degradation and cracking mechanisms were involved. Likewise, addition of glycerol as co-reactant showed synergistic effect which contributed to higher yields of bio-oils. The yields increased by about three to four-fold from the original 13-14% obtained without glycerol. The phenolics, aromatics and organic acids produced are potential precursors to many industrially important biochemicals. This study showed that hydrothermal is a versatile and tuneable technology to achieve specific target of POME management.

## ACKNOWLEDGEMENT

Alhamdulillah, firstly, I wish to thank God for giving me the opportunity to embark on my PhD and for completing this long and challenging journey successfully. I would like to wish special thanks to my mom, Zakiah Tajudin, my wife, Norain Mohamed, my daughter, Ain Husna Mohd Zahid and my son, Ahmad Fadi Mohd Zahid for their help and understanding towards this challenging journey.

My gratitude and thanks go to my supervisor, Assoc. Prof. Ir. Dr. Ahmad Rafizan Mohamad Daud and my co-supervisor, Assoc. Prof. Ir. Dr. Syed Shatir Asghrar Syed Hassan for patiently guiding me through all these years.

My appreciation also goes to the Ministry of Higher Education for my PhD fund, lecturers and technician from Faculty of chemical engineering and applied science, University Technology of Mara, Shah Alam who provided the facilities and assistance during sampling. Special thanks to my colleagues and friends for helping me with this project.

Finally, this thesis is dedicated to the loving memory of my very dear late father for the vision and determination to educate me. This piece of victory is dedicated to both of my parent.

# TABLE OF CONTENTS

	<b>Page</b>
<b>CONFIRMATION BY PANEL OF EXAMINERS</b>	<b>ii</b>
<b>AUTHOR'S DECLARATION</b>	<b>iii</b>
<b>ABSTRACT</b>	<b>iv</b>
<b>ACKNOWLEDGEMENT</b>	<b>v</b>
<b>TABLE OF CONTENTS</b>	<b>vi</b>
<b>LIST OF TABLES</b>	<b>x</b>
<b>LIST OF FIGURES</b>	<b>xiii</b>
<b>LIST OF PLATES</b>	<b>xviii</b>
<b>LIST OF SYMBOLS</b>	<b>xviii</b>
<b>LIST OF ABBREVIATIONS</b>	<b>xix</b>
<b>CHAPTER ONE: INTRODUCTION</b>	<b>1</b>
1.1 Research Background	1
1.2 Problem Statement	4
1.3 Research Objectives	6
1.4 Scope and Limitation	7
1.5 Significance of Research	8
1.6 Organization of the Thesis	9
<b>CHAPTER TWO: LITERATURE REVIEW</b>	<b>11</b>
2.1 Oil Palm Industry and POME generation	11
2.2 Palm Oil Mill Effluent (POME)	13
2.2.1 Generation of POME	13
2.2.2 Characteristics of POME	15
2.2.3 POME Discharge Regulations	18
2.2.4 POME Treatment Technologies	19
2.2.4.1 Advanced POME treatment methods	21
2.3 Hydrothermal as an Alternative Treatment Method for POME	23

2.3.1	Development of Hydrothermal Technology	23
2.3.2	Water Properties	23
2.3.3	Hydrothermal Technology Classifications	27
2.3.3.1	Hydrothermal Carbonization (HTC) of Oil Palm Biomass	27
2.3.3.2	Hydrothermal Liquefaction (HTL) of Oil Palm Biomass	28
2.3.3.3	Hydrothermal Gasification (HTG) of Oil Palm Biomass	33
2.3.3.4	Summary of Hydrothermal Treatment of Oil Palm Biomass and Model Compounds	36
2.3.4	Hydrothermal Reaction System	37
2.4	Hydrothermal Treatment of POME	39
2.5	Hydrothermal Oxidation as Method for Enhanced Biomass Degradation	40
2.6	Hydrothermal Treatment with Glycerol Additives as Method for Enhanced Conversion of POME into Biochemicals	43
2.7	Summary	48
<b>CHAPTER THREE: RESEARCH METHODOLOGY</b>		<b>50</b>
3.1	POME Samples Collection and Preparation	50
3.2	Chemicals and Materials	52
3.3	Overall Experimental Work Flow and Activities	52
3.4	Hydrothermal of Reactor Design	55
3.4.1	Slow Heating Hydrothermal Reactor Design	55
3.4.2	Fast Heating Micro-bomb Hydrothermal Reactor Design	57
3.5	Procedures and Experimental Design	58
3.5.1	Hydrothermal Degradation of POME	58
3.5.2	Hydrothermal Conversion of POME to Bio-oils	60
3.6	Analytical Techniques	61
3.6.1	Higher Heating Value (HHV) using Bomb Calorimeter	62
3.6.2	Chemical Element (C, H, N And S) Determination using Elemental Analyzer	62
3.6.3	pH Determination using pH meter	63
3.6.4	Biological Oxygen Demand (BOD <sub>5</sub> ) Determination	63
3.6.5	Chemical Oxygen Demand (COD) Determination using COD Reactor and Spectrophotometer	63
3.6.6	Colour Determination using Spectrophotometer	64