



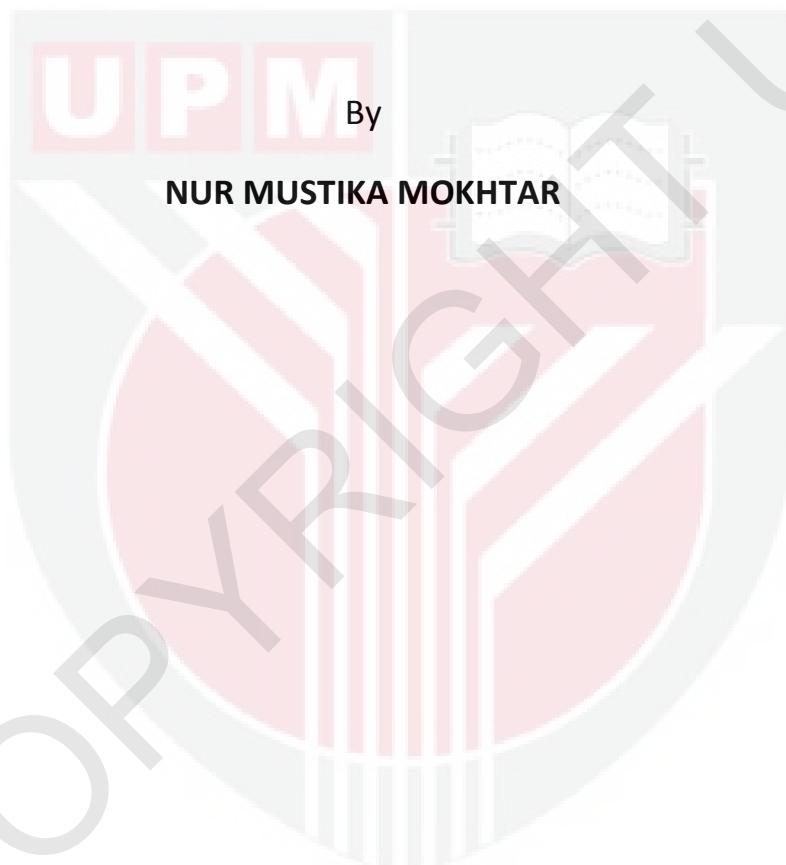
UNIVERSITI PUTRA MALAYSIA

***MICROWAVE PYROLYSIS OF OILY SLUDGE FOR POTENTIAL
SYNTHESIS GAS (SYNGAS) PRODUCTION***

NUR MUSTIKA MOKHTAR

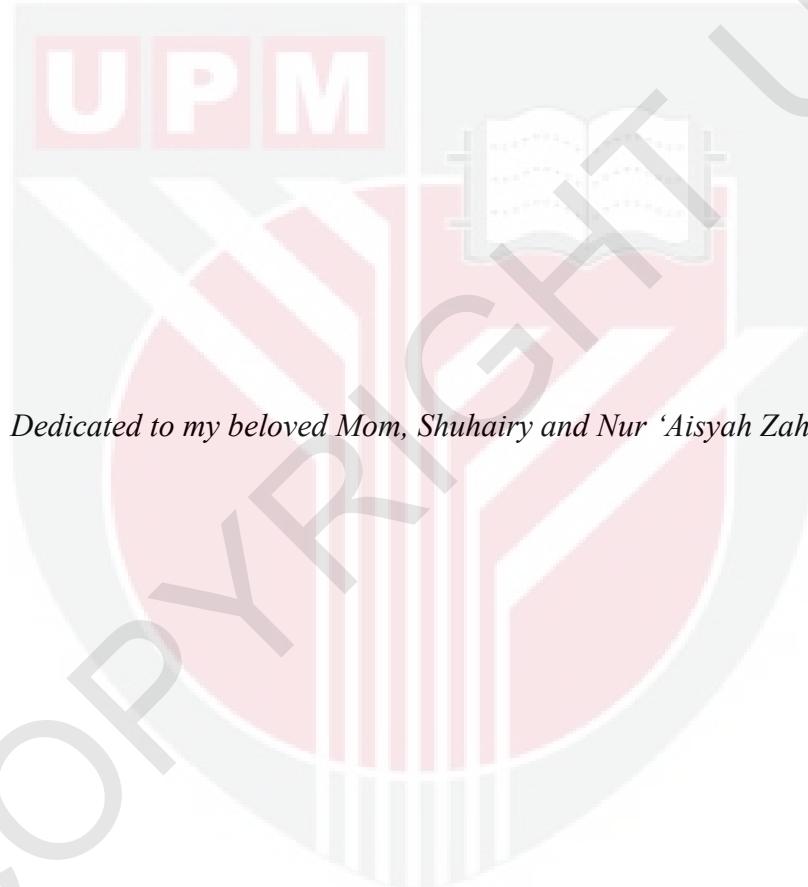
FK 2011 132

**MICROWAVE PYROLYSIS OF OILY SLUDGE FOR POTENTIAL
SYNTHESIS GAS (SYNGAS) PRODUCTION**



Universiti Putra Malaysia in fulfillment of
the requirement for the degree of Master of Science

October 2011



Dedicated to my beloved Mom, Shuhairy and Nur 'Aisyah Zahraa

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfillment of the requirement for the degree of Master of Science.

MICROWAVE PYROLYSIS OF OILY SLUDGE FOR POTENTIAL SYNTHESIS GAS (SYNGAS) PRODUCTION

By

NUR MUSTIKA MOKHTAR

October 2011

Chair: Rozita Omar, PhD

Faculty: Faculty of Engineering

Abundant amount of oily sludge generated from petroleum refinery wastewater treatment plant is becoming a serious problem in our country due to the high production of petroleum usable products. The toxicity of the sludge is the major obstacle to treat this waste using conventional method such as landfarming and incineration due to the adverse environmental impacts and human health. The success of thermal treatment on others biomass to produce gas, char and bio-oil inspired this study to assess the possibility of oily sludge to be pyrolyzed in a modified microwave oven targeting at high synthesis gas (syngas) production. The oily sludge was taken from a local petroleum refinery plant and placed directly into a fixed-bed quartz reactor fixed in a modified microwave. Microwave absorbers were added to raise the temperature during for pyrolysis reaction. The effect of four parameters on products yield were investigated including microwave absorbers addition and composition, sweep gas flow rate and initial moisture content.

In summary, microwave energy can successfully pyrolyze untreated oily sludge with addition of 10% of CAC as absorber using nitrogen gas at flow rate of 200 mL/min to produce medium-amount gas and high volume reduction of 93% for lower cost disposal. Besides, this method was proven to save time as only 30 minutes was need for both drying and pyrolysis with no pre-treatment is needed prior to the pyrolysis treatment. The produced gas concentration of H₂ (15%) and CO (13.3%) giving lower heating value (LHV) at 5.57 MJ/m³ in this study. The calorific value of the char is 7.03 MJ/kg which is higher than that of the sewage sludge char, but still low to be used as biofuel. The relatively large pore volume in the mesoporous range is expected to have low adsorption capacity. Monoaromatic compounds dominate the bio-oils for those without absorber and added with 10% of CAC although low polycyclic aromatic hydrocarbon (PAH) was noticed in the pyrolytic bio-oils.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Master Sains.

**PIROLISIS GELOMBANG MIKRO ENAPCEMAR BERMINYAK UNTUK
POTENSI PENGHASILAN GAS SINTESIS (SINGAS)**

Oleh

NUR MUSTIKA MOKHTAR

Oktober 2011

Pengerusi: Rozita Omar, PhD

Fakulti: Fakulti Kejuruteraan

Jumlah enapcemar berminyak yang teramat banyak dihasilkan dari loji rawatan sisa air penapisan petroleum menjadi suatu masalah yang serius di negara kita disebabkan oleh tingginya pengeluaran produk petroleum yang boleh digunakan. Ketoksikan enapcemar ini menjadi penghalang utama untuk merawat bahan buangan ini menggunakan kaedah konvensional seperti tanah pertanian dan insinerasi berikutan kepada kesan buruk terhadap alam sekitar dan kesihatan manusia. Kejayaan rawatan secara terma ke atas biojisim yang lain untuk menghasilkan gas, arang dan minyak-bio telah mengilhamkan kajian ini untuk menilai kemungkinan untuk enapcemar berminyak ini dipirolysis menggunakan ketuhar gelombang mikro yang diubahsuai untuk menghasilkan sintesis gas (singas). Enapcemar berminyak yang telah diambil dari loji penapisan petroleum tempatan ditempatkan secara langsung ke dalam reactor lapisan tetap yang diperbuat daripada kuarza yang terletak di dalam ketuhar gelombang mikro yang diubah suai. Bahan penyerap gelombang mikro telah ditambahkan untuk meningkatkan suhu tindak

balas pirolisis. Kesan empat parameter terhadap produk-produk yang terhasil telah dikaji termasuklah penambahan bahan penyerap dan komposisi bahan penyerap. kadar aliran gas penggerak dan kandungan awal lembapan.

Kesimpulannya, tenaga gelombang mikro dengan jayanya dapat mempirolisis enapcemar berminyak yang tidak dirawat dengan penambahan 10% Karbon Kelapa Teraktif (KKT) sebagai penyerap menggunakan nitrogen pada kadar aliran 200 mL/min untuk menghasilkan jumlah gas yang sederhana dan pengurangan isipadu yang tinggi sebanyak 93% untuk kos pelupusan yang lebih rendah. Di samping itu, kaedah ini telah terbukti menjimatkan masa apabila hanya 30 minit diperlukan untuk kedua-dua pengeringan dan pirolisis dengan tanpa pra-rawatan diperlukan sebelum rawatan pirolisis. Kepekatan gas H₂ (15%) dan CO (13.3%) yang terhasil memberikan nilai kalori (LHV) sebanyak 5.57 MJ/m³ dalam kajian ini. Nilai kalori arang ialah 7.03 MJ/kg adalah lebih tinggi berbanding arang enapcemar kumbahan tetapi masih rendah untuk digunakan sebagai bahan-bio bakar. Isipadu liang yang relatif besar dalam julat liang-meso dijangka menjadikannya mempunyai kebolehan penyerapan yang rendah. Sebatian monoaromatik mendominasi minyak-bio bagi bahan yang tidak ditambah penyerap dan yang ditambah 10% KKT walaupun hidrokarbon aromatik polisiklik (HAP) telah didapati di dalam minyak-bio pirolisis.



ACKNOWLEDGEMENTS

“In the name of Allah, the most Benevolent and Merciful”

Alhamdulillah to Lord of the Worlds for giving me the high patience, the beneficial knowledge, the good healthy and the strength in writing until this thesis has been completed. To my beloved husband, little princess, parents and family, I grateful for all your understanding and encouragement. I would like to convey my sincerest gratitude for the advice and guidance of Dr. Rozita Omar, Dr. Mohamad Amran Mohd Salleh and Prof. Dr. Azni Idris. I acknowledge the assistance and technical support provided by lecturers, technicians, research officers and science officers at Department of Chemical Engineering, Department of Physics and Chemistry, and Department of Biological and Agricultural Engineering. In my daily work I have been blessed with a friendly and cheerful group of fellow students and housemates (especially during my pregnancy period). Thanks a lot for their help and concern to Baiti, Aini, Taibah, Wani, Jehan, Fadhilah, Fizah, Azian, Nadiah, Nadhirah, Mustafa, Amir, Taha, Faiz, Meg, Nadh, Syafiqah, Maziah, Hasliza, Yusof, Mohamed, Mahmood, Pak Azhari, Yong and others that I failed to remember. My gratitude also dedicated to the Universiti Putra Malaysia for the financial support given under the Research University Grant Scheme to successfully carry out this study. Lastly, to those I forgot to mention, thank you very much.

I certify that a Thesis Examination Committee has met on (4 December 2011) to conduct the final examination of Nur Mustika Mokhtar on her thesis entitled "**Microwave Pyrolysis of Oily Sludge for Potential Synthesis Gas (Syngas) Production**" in accordance with the Universities and University Colleges Act 1971 and the Constitution of the Universiti Putra Malaysia [P.U.(A) 106] 15 March 1998. The Committee recommends that the student awarded the Master of Science.

Members of the Examination Committee were as follows:

Mohd Halim Shah Ismail, PhD

Faculty of Engineering
Universiti Putra Malaysia
(Chairmain)

Wan Azlina Wan Abdul Karim Ghani, PhD

Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

Azmi Zakaria, PhD

Professor
Faculty of Science
Universiti Putra Malaysia
(Internal Examiner)

Abdul Rahman Mohamed, PhD

Professor
Faculty of Engineering
Universiti Sains Malaysia
(External Examiner)

SEOW HENG FONG, PhD

Professor and Deputy Dean
School of Graduate Studies
Universiti Putra Malaysia

Date:

This thesis was submitted to the Senate of Universiti Putra Malaysia and has been accepted as fulfillment of the requirement for the degree of Master of Science. The members of the Supervisory Committee were as follows:

Rozita Omar, PhD

Senior Lecturer

Faculty of Engineering

Universiti Putra Malaysia

(Chairman)

Mohamad Amran Mohd Salleh, PhD

Senior Lecturer

Faculty of Engineering

Universiti Putra Malaysia

(Member)

Azni Idris, PhD

Professor

Faculty of Engineering

Universiti Putra Malaysia

(Member)

BUJANG BIN KIM HUAT, PhD

Professor and Dean

School of Graduates Studies

Universiti Putra Malaysia

Date:

DECLARATION

I declare that the thesis is my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously, and is not currently, submitted for any other degree at Universiti Putra Malaysia or at any other institution.

NUR MUSTIKA MOKHTAR

Date: 31 October 2011

TABLE OF CONTENTS

	page
DEDICATIONS	ii
ABSTRACT	iii
ABSTRAK	vii
ACKNOWLEDGEMENTS	xi
APPROVAL	xii
DECLARATION	xiv
LIST OF TABLES	xviii
LIST OF FIGURES	xix
LIST OF NOMENCLATURE	xxii
LIST OF ABBREVIATION AND ACRONYMS	xxiii
 CHAPTER	
1 INTRODUCTION	
1.1 Background	1.1
1.2 Problem Statements	1.3
1.3 Research Objectives	1.6
1.4 Thesis Layout	1.6
2 LITERATURE REVIEW	
2.1 Introduction	2.1
2.2 Treatment of Oily Sludge	2.2
2.2.1 Biological Treatment of Oily Sludge	2.2
2.2.2 Physical/Chemical Treatment of Oily Sludge	2.4
2.2.3 Thermal Treatment of Oily Sludge	2.5
2.3 Type of Thermal Treatment	2.6
2.3.1 Combustion in a Fluidized Bed Reactor	2.6
2.3.2 Fast Pyrolysis of Oily Sludge	2.8
2.4 Pyrolysis Process	2.11
2.4.1 Conventional Pyrolysis	2.14
2.4.2 Fast Pyrolysis	2.14
2.5 Microwave Fundamentals	2.15
2.5.1 Microwave/Material Interaction	2.16
2.5.2 Polarization	2.18
2.5.3 Conductive Losses	2.19
2.5.4 Microwave Absorber	2.19
2.6 Microwave Pyrolysis of Biomass	2.20
2.6.1 Microwave Pyrolysis of Sludge	2.21
2.6.2 Microwave Pyrolysis of Wood	2.23
2.6.3 Microwave Pyrolysis of Rock Phosphate	2.26
2.6.4 Microwave Pyrolysis of Coffee Hulls	2.27

2.6.5	Microwave Pyrolysis of Glycerol	2.28
2.6.6	Microwave Pyrolysis of Rice Straw	2.29
2.6.7	Microwave Pyrolysis of Plastic Wastes	2.30
2.7	Effect of Parameter on Product Yields	2.31
2.7.1	Effect of Temperature	2.31
2.7.2	Effect of Microwave Absorber Addition and Concentration	2.32
2.7.3	Effect of Initial Moisture Content	2.34
2.7.4	Sweep Gas Flow Rate	2.34
2.8	Pyrolysis Products	2.35
2.8.1	Syngas	2.36
2.8.2	Bio-char	2.37
2.8.3	Bio-oil	2.38
3	MATERIALS AND METHODS	
3.1	Oily Sludge	3.1
3.2	Microwave Absorbers	3.1
3.3	Characterization of Oily Sludge	3.3
3.3.1	Moisture Content	3.3
3.3.2	Proximate Analysis	3.3
3.3.3	Ultimate Analysis	3.4
3.3.4	Inorganic Element Analysis	3.5
3.3.5	Heating Value	3.5
3.3.6	Apparent Density	3.6
3.3.7	Thermal Conductivity and Specific Heat	3.6
3.4	Dielectric Properties	3.7
3.5	Experimental Set-up	3.8
3.6	Experimental Procedure	3.12
3.7	Product Recovery	3.13
3.8	Product Analysis	3.14
3.8.1	Gas Product Analysis	3.14
3.8.2	Bio-oil Product Analysis	3.16
3.8.3	Char Product Analysis	3.17
4	RESULTS AND DISCUSSIONS	
4.1	Characteristic of Oily Sludge	4.1
4.1.1	Proximate and Ultimate Analysis	4.1
4.1.2	Dielectric Properties	4.7
4.2	Microwave Pyrolysis of Oily Sludge	4.12
4.2.1	Effects of Sweep Gas Flow Rate	4.12
4.2.2	Effects of Absorber Addition	4.14
4.2.3	Effects of Absorber Concentration	4.16
4.2.4	Effects of Initial Moisture Content	4.19
4.4	Characteristics of Bio-char	4.25
4.5	Identification of Chemical Compounds in Bio-oils	4.31
5	CONCLUSION AND RECOMMENDATIONS	
5.1	Conclusions	5.1

5.2 Recommendations for Future Works	5.3
REFERENCES	R.1
APPENDICES	
APPENDIX A.1	A.1
APPENDIX A.2	A.3
BIODATA OF STUDENT	A.4
LIST OF RELATED PUBLICATIONS	A.5

