THE DIRECT AND CATALYTIC PYROLYSIS OF RICE STRAW

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UNIVERSITI MALAYSIA PERLIS
2010

DEDICATION

This work is dedicated to my beloved wife, Farra Nur Hani for her full support and encouragement during this journey and to my children Haifaa Nur Saffiya, Thaqif Iman Nafis and Hasyaa Nur Saffina for appreciating and understanding me.

ACKNOWLEDGEMENTS

First of all, I would like to express my grateful to Allah S.W.T. for all His gifts that this thesis was completed on time. This thesis also dedicated to my dear family with all their pray, patience and full support that encourage me to go through the obstacle to complete my thesis.

I would like to thank to UniMAP for providing study leave during this study period. I wish to acknowledge my sincere to my supervisor Mr. Khairuddin Md Isa, my co-supervisor Prof. Dr. Khudzir Ismail (Director of UiTM Perlis Campus) and Dr. Khairul Nizar Ismail for their supervision, guidance and encouragement throughout the course of the research.

I also would like to express my gratitude to Dr. Ye Lwin, my ex-supervisor and Mr Saiful Azhar Saad and Pn. Naimah Ibrahim, my ex-co supervisor for many useful discussion and suggestions during early stage of this research. I also would like to express my gratitude to all lecturers, teaching engineers especially Mr. Nazerry, Mr. Zulzikrami, Mr. Roshasmawi and Mr. Munif, technicians especially Mr. Khairul, Mr Shukri and Mr. Andi and management staff at School of Environmental Engineering, UniMAP for their support.

I also wish to thanks all of staff and postgraduate student of Fossil Fuels and Biomass Research Laboratory, Universiti Teknologi Mara, Perlis for their helping during my experiment. Finally, I would like to thank everyone that has been involved in this project directly or indirectly for their help and contribution. Thank you very much.

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A thesis submitted
In fulfillment of the requirements for the degree of
Master of Science (Environmental Engineering)

School of Environmental Engineering
UNIVERSITI MALAYSIA PERLIS

2010

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LIST OF SYMBOLS

%	Percent
wt %	Weight percent
Y	Response
R^2	determination coefficient
T	transmittence
β_o	constant coefficient
β_i,	coefficient for the linear
β_{ii}	coefficient for the quadratic
β_{ij}	coefficient for the interaction effect
χ_i	factors
ε	error.

LIST OF ABBREVIATIONS

ASTM	American Society for Testing and Materials Standard
ANOVA	Analysis of variance
ATR	Attenuated Total Reflection
BET	Brunauer Emmett Teller
$CaCO_3$	Calcium carbonate
CCRD	Central composite rotatable design
CO_2	Carbon dioxide
CV	Coefficient of variation
DOE	Design of Expert
DTG	Differential thermogravimetric
FID	Flame Ionization Detector
FTIR	Fourier Transform Infrared
GC	Gas Chromatography
H_2O	Water
MgO	Magnesium oxide
NO_X	Nitrogen oxide
O_2	Oxygen
RS	Rice straw
RSM	Response surface methodology
SiO_2	Silica oxide
SO_2	Sulfur Dioxide
TGA	Thermogravimetric analysis
XRF	X-ray Fluorescent
ZSM-5	Zeolite Socony Mobile-5

Pirolisis dan Pirolisis Bermangkin ke atas Jerami Padi

ABSTRAK

Kajian pirolisis bermangkin ke atas jerami padi telah dijalankan di dalam reaktor lapisan terpadat. Objektif penyelidikan ini adalah untuk mengkaji kesan parameter pirolisis iaitu suhu pirolisis, kadar pemanasan dan jangka masa pada suhu capaian pirolisis ke atas taburan hasil produk pirolisis. Proses pengoptimuman telah dianalisis dengan menggunakan CCRD di dalam kaedah permukaan respons. Zeolit ZSM-5 dan dolomit merupakan pemangkin yang digunakan dalam penyelidikan ini. Pirolisis bermangkin telah dilaksanakan berdasarkan keadaan optimum penghasilan minyak bio. Ciri-ciri hasil produk pirolisis diantara tidak bermangkin dan bermangkin telah dikenalpasti melalui kaedah elemen, spekstroskopik dan kromatografik. Analisis termogravimetrik telah dijalankan untuk mengaji penguraian termal terhadap jerami padi. Melalui proses pirolisis, pada kadar pemanasan yang rendah, didapati hasil pepejal adalah tinggi, manakala penghasilan gas adalah tinggi pada suhu yang tinggi dan masa pirolisis yang panjang. Nilai eksperimen penghasilan minyak bio yang optimum adalah 27.62% berbanding nilai simulasi iaitu 27.87% telah diperolehi pada suhu pirolisis 450 ^{o}C, kadar pemanasan 77.63 ^{o}C/min dan jangka masa pada suhu capaian pirolisis selama 2.61 min dengan menggunakan proses pengoptimuman melalui perisian DOE. Kajian ciri-ciri kimia terhadap minyak bio yang tidak melalui proses permangkinan didapati mengandungi kandungan komponen karbonil dan beroksigen dalam kuantiti yang banyak. Ini menyebabkan kandungan oksigen yang tinggi dalam komposisi elemen dan juga mengurangkan nilai pH. Penggunaan zeolit ZSM-5 dan dolomit menyebabkan peningkatan dalam hasil gas dan pengurangan dalam hasil cecair. Kehadiran pemangkin memberi telah memberi kesan terhadap hasil produk dan kualiti minyak bio. Perubahan yang besar terhadap kualiti produk cecair adalah melalui peningkatan kandungan fenol (bahan kimia yang bernilai) dan pengurangan beberapa komponen asid (komponen yang tidak diperlukan) dalam minyak bio. Pemangkin dolomit juga memberi kesan lebih baik berbanding zeolit ZSM-5 ke atas penyingkiran beberapa komponen aldehid dan keton yang memberi kesan dalam kestabilan terma atau penyimpanan. Kesan zeolit ZSM-5 dan dolomit dalam penyelidikan ini adalah ketara dalam aspek kualiti berbanding aspek kuantiti ke atas cecair atau minyak bio yang dihasilkan.

The Direct and Catalytic Pyrolysis of Rice Straw

ABSTRACT

A study of the catalytic pyrolysis on rice straw was carried out in a fixed-bed reactor. The work objectives were to determine the influences of pyrolysis parameters i.e pyrolysis temperature, heating rate and holding time on distribution of product yield. The optimization process was analyzed by employing central composite rotatable design (CCRD) in response surface methodology (RSM). The catalysts used in this research were zeolite ZSM-5 and dolomite. The catalytic pyrolysis was carried out based on optimized condition of bio-oil yield. The characterization of pyrolysis product between non-catalytic and catalytic pyrolysis were investigated, by elemental, spectroscopic and chromatographic techniques. The char yield produced from pyrolysis process was high at low heating rates, while the gas yield produced was high at higher temperature and longer holding time. The experimental value of the optimum bio-oil yield was 27.62% as compared to the predicted value which bio-oil yield was 27.87% at pyrolysis temperature of 450 ^{o}C, heating rate of 77.63 ^{o}C/min and holding time of 2.61 min by using optimization process in the Design Expert (DOE) software. The chemical characterization studies of uncatalysed bio-oil derived from pyrolysis of rice straw contained considerable amounts of carbonyl and oxygenated compound, resulting in higher oxygen content in elemental composition and low pH value. Used of zeolites ZSM-5 and dolomite caused an increase in gas yields and a decrease in bio-oil yields. The product yields and the quality of the produced bio-oil were affected by the used of catalyst. The major improvement in the quality of liquid product with the use of catalyst was the increase of phenol concentration (useful chemicals) and the reduction of some corrosive acids which are undesirable compound in bio-oil. Dolomite catalyst having the most impacts than zeolite ZSM-5 in removing some of aldehyde and ketone compounds which are responsible for the thermal or storage stability. The influence of the zeolite ZSM-5 and dolomite catalyst used in this study caused only enhancement of liquid production in terms of quality but not the bio-oil produced.

CHAPTER 1

INTRODUCTION

1.1 Research Background

In recent years, there is a great concern with the environmental problems associated with the great CO_2, NO_x and SO_x emissions resulting from the rising use of fossil fuels. World wide energy consumption has increased 17 fold in the last century and emissions CO_2, SO_2, and NO_x from fossil fuel combustion are primary cause of atmospheric pollution (Ture et al., 1997). For this reason, biomass energy is being paid more attention for renewable energy. Biomass is abundant in annual production, with a geographically widespread distribution in the world, compared with other renewable energy resources as hydropower, geothermal, solar, wind etc (Kaygusuz, 2004).

Biomass feedstock including wood, industrial and agricultural residue and by products (e.g., sawdust, wood chip, bagasse and rice husk) or dedicated energy crops (e.g., fast growing trees, shrubs and grass) usually applied as biomass fuels. There are significant interests because biomass is the fourth largest source of energy in the world, accounting for about 15% of the world's primary energy consumption and about 38% of the primary energy consumption in developing countries (Chen et al., 2003). Biomass offers the attractive advantages of being renewable resources and has the potential to provide high quality fuels and chemicals feedstock. Biomass appears to be an attractive feedstock for three main reasons. First, it is renewable resources that can be sustainable developed in the future. Second, it appears to have significant economic potential provided that fossil fuel prices increase in the future. Third, it appears to have clearly positive environmental properties resulting in no net releases of carbon dioxide and very low sulfur content (Cadenas and Cabezudo, 1998).

The reason interests in using biomass for energy are the net contribution of carbon dioxide to atmospheric pollution is considered to be nil. Combustion of biomass is an example of sustainable technology, as combustion releases carbon dioxide in the atmosphere and therefore does not seem to close the material cycles. While the combustion does release carbon dioxide into the atmosphere, the growth of biomass consumed carbon dioxide. As can be seen from Figure 1.1, the final result of biomass conversion is that there is no net release or consumption of carbon dioxide if the biomass is replenished. Consider the example that a certain unit of active biomass absorbs one unit of carbon dioxide per unit time while growing. If one unit of this biomass is combusted, thus releasing one unit of carbon dioxide, the result is that there is no net increase or decrease in carbon dioxide emission (Arons et al., 2004).

Presently, new technologies for efficient waste utilization have been developed, such as biological process and non-biological conversion. The biological process or the wet process led to the anaerobic methane generation or the ethanol fermentation production. The non-biological, or dry process, is mainly of the thermal processes. Over the past two decades, the thermal conversion technology has gained much attention worldwide due to its potential in the conversion of wastes into energy in a large scale and economical way (Bridgwater, 2004).

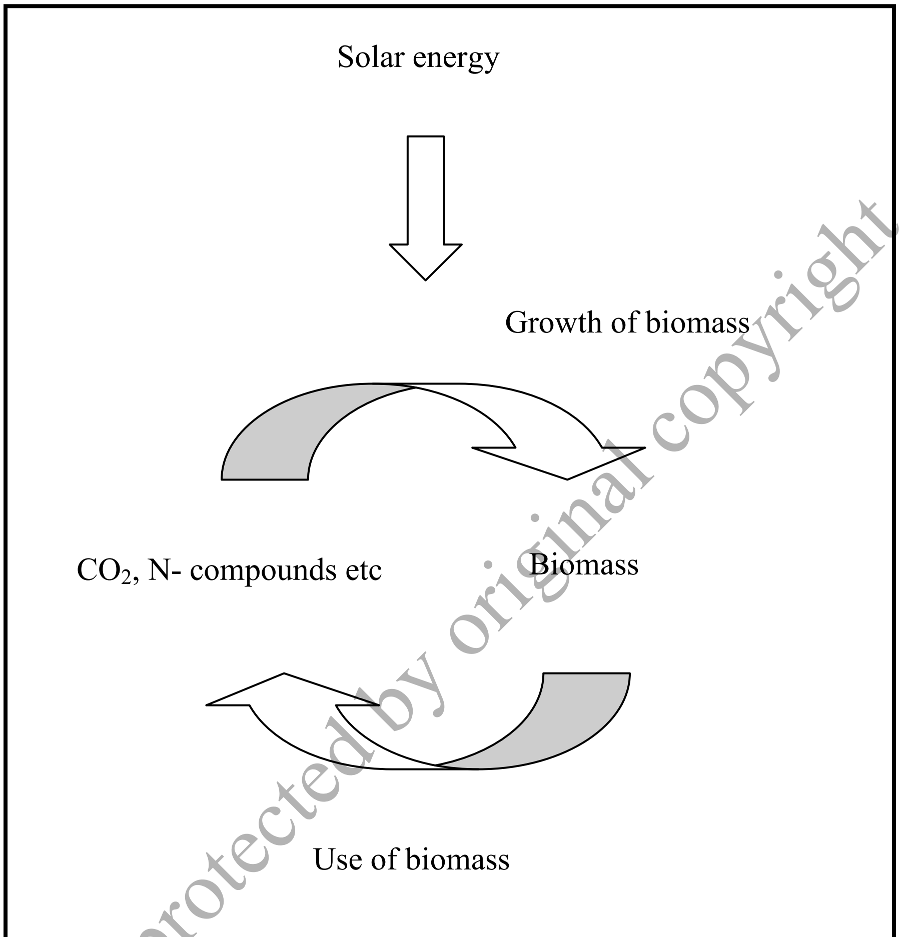

Figure 1.1: Schematic of generation and use of biomass illustrating closed elemental cycles (Arons et al., 2004)

There are three main thermal processes of converting solid wastes into energy; pyrolysis, gasification and combustion. Each process gives different range of products. The primary products from thermal conversion processes can be either gas, liquid or solid. These products can be used directly as raw fuel, or they can be subjected to further treatment and processes to produce secondary products such as higher value and quality fuel or chemical products. In pyrolysis process, when the components were quickly quenched, the volatile components condensed to bio-oil. Xiu et al. (2005) reported that the bio-oil can be alternative for fuel oil in many static applications including boilers, combustion engines and turbine for the generation of electricity. Table 1.1 shows the conversion of biomass with different thermal conversion technology.

Table 1.1: Biomass conversion with different thermal conversion technology

Biomass	**Type of thermal conversion**	**Products**	**References**
Herb residue	Pyrolysis	Bio-oil, char, gas	Wang et al. (2010)
Birch	Gasification	Gas, tar	Yu et al. (2009)
Wood	Combustion	Heat	Bridgwater, 2004
Wheat straw	Liquefaction	Liquid products	Liang et al. (2006)

Past and current economic growths of Malaysia have been primarily energized by fossil fuels. Malaysia has very substantial potential for biomass energy utilization given its equatorial climate that is ideal for dense tropical forest growth and agricultural vegetation. There are six major sectors contributing wastes to biomass energy in Malaysia: forestry (wood products), rubber cultivation, cocoa cultivation, sugar cane cultivation, paddy cultivation and oil palm cultivation (Chuah et al., 2006).

1.2 Abundance of Rice Straw in Malaysia

Rice straw is one of the abundant lignocelluloses waste materials in the world. Ninety percent of the world's production is in the developing countries of East and Southeast Asia where the straw is a main feed for ruminants (Soest, 2006). Rice straw is a lignocelluloses agricultural by-product containing cellulose (37.4%), hemi-cellulose (44.9%), lignin (4.9%) and silicon ash (13.1%) (Hills and Roberts, 1981). The estimation on annual production of rice by Food and Agriculture Organization (FAO) points to about 600 million tones per year in 2004. On the other hand, Maiorella (1985) reported that every kilogram of grain harvested is accompanied by production of 1 to 1.5 kg of rice straw. Lee et al. (2005) reported that more than 90% of the world's rice is produced and consumed in Asia. Therefore, the global rice require in 2020 is planned to rise by 35% over the 1995 level.

In Malaysia, paddy was planted in area of approximately 650 000 to 680 000 hectares and it grows 2.2 million ton annually (Department of Agriculture, 2009). As it is expected after huge amount of production, huge amounts of residue remain as can be seen from Table 1.1. Thus rice straw causes a lot of environmental problems since it exists with enormous quantities and is not easy to handle or transport. As such, direct open burning in the fields is a common practice for disposal. This practice causes serious air pollution, hence new economical methods for rice straw disposal and utilization must be developed.

Table 1.2: Planted Area and Production of Paddy and Paddy Straw in Malaysia for All Seasons (Department of Agriculture, 2009)

Year	Planted Areas (Hectares)	Paddy Production (Tonnes)	Paddy Straw Production (Tonnes)
2003	671 820	2 257 000	902 800
2004	667 310	2 291 000	916 400
2005	666 781	2 181 000	872 400
2006	676 034	2 202 000	880 800
2007	676 111	2 375 604	n.a
2008	670 524	2 384 143	n.a

Although rice straw may contain valuable compounds, or retained in the field to prevent soil erosion, converting the organic matter in the residue into more valuable and concentrated forms of energy will be beneficial to developing countries. Pyrolysis is an advantageous method to obtain liquid fuels from agriculture residues that are distributed widely (Putun et al., 2007).