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TORREFACTION AND FAST PYROLYSIS OF OIL PALM BIOMASS

by

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DECLARATION OF THESIS

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DEDICATION

To my life partner Rafah....

and our 4 angels....

Rayyan, Rawan, Ali, and Malak

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I would like to thank my supervisor and project leader, Prof. Yoshimitsu Uemura for his guidance and instructions to me, also his belief and patience on me during the course of my research at Universiti Teknologi Petronas. I have learned from him more than the content of this thesis, I have learned values and wisdom that inspired me and will guide me forever. I also acknowledge our MOR director Dr. Suzana Yusup for supporting all of us and serving on my committee.

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ABSTRACT

The present research focuses on torrefaction and fast pyrolysis of Malaysian oil palm residue (empty fruit bunches, palm mesocarp fibre, and palm kernel shell), these biomass types were selected due to their abundant quantity in the country, the current inefficient recycling methods, and the little availability of the decomposition data from few published studies. Torrefaction experiments were carried out in fabricated torrefaction reactor, while fast pyrolysis experiment conducted in newly invented and designed novel drop type pyrolyzer featuring the ability to recover all pyrolysis products with high recover percentage up to 98%.

Catalytic fast pyrolysis was investigated using Pyrolysis-Gas Chromatography/Mass Spectrometry (Py-GC/MS), two groups of commercially available catalysts were investigated (silica and zeolites). The effect of catalyst on the product distribution of the pyrolysis vapors were investigated.

In the torrefaction experiments, both palm mesocarp fiber and palm kernel shell exhibited excellent energy ratio values of 96 and 100%, respectively. EFB, on the other hand, exhibited a rather poor energy ratio of 56%. In the fast pyrolysis experiments, the optimal conditions that were found to maximize bio-oil yield are palm kernel shell as biomass type, 0.235 mm as average particle size, and 500 °C as the pyrolysis temperature. At higher temperature less bio-oil was recovered and more non condensable gases were produced due to the activation of secondary cracking reactions. The same low bio-oil yield was observed for bigger particle sizes as they promotes slow heat transfer and mass diffusion of the pyrolysis vapors resulting in secondary gasification and solidification reaction.

Catalytic Py-GC/MS results showed that the effect of different silica catalysts on improving the product distribution of the pyrolysis vapors is rather limited, they have

no selectivity for aromatics and very low selectivity for esters. Zeolites showed a high selectivity for aromatics. High acidic HZSM-5 was found to be the best zeolite type to produce higher yield of aromatics suggesting that a bio-oil with transport fuel properties is achievable.

The drop type pyrolyzer is proved to be able to achieve high liquid yields (greater than 50 wt.%), and produces bio-oil and bio-char products that are physically and chemically similar to products from other fast pyrolysis reactors and it has the advantage over other reactors (such as fluidized bed) in its superior product recovery which is crucial in mass and energy design calculations. It also can support catalytic fast pyrolysis experiments by feeding a mixture of the biomass and the catalyst or connect it with separate catalytic reactor for online pyrolysis oil upgrading.

ABSTRAK

Kajian ini tertumpu kepada torefikasi dan pirolisis pantas bahan biojisim kelapa sawit Malaysia (tandan kosong, sabut kelapa sawit, dan tempurung kelapa sawit). Biojisim jenis ini dipilih kerana kuantiti mereka yang banyak di negara ini, disamping kaedah kitar semula untuk biojisim sawit yang sedia ada kurang berkesan, dan kekurangan data mengenai pereputan biojisim ini yang telah dilaporkan.

Pirolisis pantas telah dikaji menggunakan pirolisis-gas kromatografi spektroskop jisim (Py-GC/MS) dengan kehadiran mangkin komersil (silika dan zeolite). Kesan kehadiran terhadap taburan hasil tindakan pemangkinan wap pirolisis telah dikaji.

Hasil kajian torefikasi kedua-dua sabut kelapa dan tempurung kelapa sawit menunjukkan nilai nasibah tenaga yang baik iaitu 96 dan 100%. Bagaimanapun torefikasi tandan kosong kelapa sawit menunjukkan nasibah tenaga yang agak rendah pada 56%. Bagi pirolisis pantas, keadaan optima bagi penghasilan minyak-bio tertinggi adalah menggunakan biojisim tempurung kelapa sawit dengan purata saiz partikel 0.235 mm dan suhu 500 C. Sekiranya suhu lebih tinggi digunakan, hanya sedikit minyak-bio yang dapat dihasilkan dan lebih banyak hasil gas akibat tindak balas peretakan sekunder. Begitu juga sekiranya saiz partikel yang besar digunakan, hasil minyak-bio yang rendah diperolehi kerana proses pemindahan haba yang perlahan disamping penyebaran jisim wap pirolisis yang rendah sehingga menyebabkan berlakunya tindakbalas gasifikasi dan pemejalan sekunder.

Penggunaan pelbagai mangkin silica tidak Berjaya memperbaiki taburan produk dari peretakan wap pirolisis menggunakan Py-GC/MS di mana silika tidak mempunyai keselektifan kepada kumpulan hidrokarbon aromatik dan keselektifan yang amat rendah kepada hidrokarbon ester. Mangkin zeolite bagaimanapun menunjukkan

keselektifan yang amat tinggi kepada hidrokarbon aromatik menunjukkan penghasilan cecair yang sesuai sebagai bahan api kenderaan.

Kajian ini menunjukkan pirolizer jenis lepas jatuh mampu mmemberikan hasil cecair yang tinggi (lebih dari 50% jisim) dan menghasilkan produk minyak-bio dan arang-bio yang mempunyai ciri-ciri fizikal dan kimia yang sama seperti produk dari reaktor pirolisis pantas yang lain dan ia memiliki kelebihan dibandingkan dengan reaktor lain (contoh lapisan terbendalir) dalam keupayaan menghasilkan produk yang amat penting dari segi pengiraan rekabentuk jisim dan tenaga. Ia juga boleh menyokong eksperimen pemangkin pirolisis pantas dengan penyuapan campuran biojisim dengan mangkin atau penyambungan reactor pirolisis jenis lepas jatuh ini dengan reaktor pemangkin yang lain untuk penambahbaik kualiti minyak pirolisis.

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LIST OF ABBREVIATIONS

EFB	Empty fruit bunches
PMF	Palm mesocarp fiber
PKS	Palm kernel shell
APS	Average particle size
Py-GC/MS	Pyrolysis gas chromatography mass spectrometry
GC-MS	Gas chromatography mass spectrometry
GC	Gas chromatography
MS	Mass spectrometry
TGA	Thermogravimetric analysis
CHO	Carbon, hydrogen, and oxygen (wt.% or mole.%)
Mtoe	Million ton oil equivalent
NCG	Non condensable gases
GC-TCD	Gas chromatography with thermal conductivity detector
GC-FID	Gas chromatography with flame ionization detector

NOMENCLATURE

Variable	Description	Units
MC	Moisture content	wt.%
W_S	Weight of biomass before experiment	g
W_D	Weight of biomass after drying	G
ASH	Ash content	wt.%
W_A	Weight of biomass and crucible	g
W_E	Weight of dry crucible	g
HHV	High heat value	MJ/kg
LHV	Low heat value	MJ/kg
X_H	Hydrogen mass fraction	
X_W	Free water fraction	
O	Oxygen mass percentage	wt.%
H	Hydrogen mass percentage	wt.%
N	Nitrogen mass percentage	wt.%
C	Carbon mass percentage	wt.%
V_v	Volume of pyrolysis vapours	L
V_{wbv}	Total volume of the water and the Teflon gas bag containing the pyrolysis vapours	L
V_{wb}	Volume of the water and the empty Teflon gas bag	L
SSA	Specific surface area	m ² /g

Si/Al	SiO ₂ to Al ₂ O ₃ molar ratio	mole ratio
Y_{mass}	Mass yield of torrefied biomass	wt. %
$Y_{energy\ ratio}$	Energy ratio of torrefaction	%
$Y_{net\ energy}$	Net energy yield of torrefaction	%
H_S	Sensible heat of torrefaction	MJ/kg
H_{torref}	Heat of torrefaction reaction	MJ/kg
$M_{biomass}$	Mass fraction of dry matter in the fresh biomass	
M_{water}	Mass fraction of moisture in the fresh biomass	
$CP_{biomass}$	Specific heat of biomass	J/g.K
$CP_{water\ vapor}$	Specific heat of water vapor	J/g.K
O/C	Oxygen to carbon molar ratio	
H/C	Hydrogen to carbon molar ratio	
V_{sp}	Specific pore volume of catalyst	ml/g
S_{sa}	Specific surface area of catalyst	m ² /g
D_{pore}	Average pore diameter of catalyst	Nm
$W_{bio-char}$	Weight of bio-char from fast pyrolysis	g
$W_{bio-oil}$	Weight of bio-oil from fast pyrolysis	g
W_{NCG}	Weight of non condensable gases from fast pyrolysis	g
$Y_{bio-char}$	Mass yield of bio-char	wt. %
$Y_{bio-oil}$	Mass yield of bio-oil	wt. %
Y_{NCG}	Mass yield of non condensable gases	wt. %

