UNIVERSITI PUTRA MALAYSIA

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By

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Thesis Submitted to the School of Graduate Studies, Universiti Putra Malaysia, in Fullfilment of the Requirements for the Degree of Doctor of Philosophy

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For my beloved Hafizul, Hanz and Dayana

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for the degree of Doctor of Philosophy

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Chair: Azni Idris, PhD

Faculty: Faculty of Engineering

Agriculture waste such as oil palm empty fruit bunch (EFB) is an environmental concern to our country as one of the world's biggest oil palm producers. Pyrolysis has been used as a thermal process to treat biomass wastes due to its flexibility in producing solid, liquid and gas products. This study evaluated the possibility to treat EFB via microwave pyrolysis. In this study, the EFB taken from a local oil palm mill was directly placed inside a fixed-bed quartz reactor which was placed in a modified household microwave oven, where both drying and pyrolysis took place simultaneously. Microwave absorbers were added to elevate the reaction temperature so as to reach the required temperature for a pyrolysis reaction to take place. Parameters, such as effects of residence time, addition of inorganic materials (catalysts) and pre-treatment of the EFB, were studied. Meanwhile, a comparison experiment with a conventionally heated reactor was also conducted.

Fuel, chemical and dielectric characterization of the EFB undertaken in this study confirmed that it is a good candidate for a microwave pyrolysis process as it is

comparable to other biomass. However, dielectric properties of the EFB indicated that it is almost a transparent material to microwave, and for this reason, addition of microwave absorber is required. Studying several microwave absorbers, namely SiC, activated carbons (coconut and palm kernel shell) and char which were produced from a previously conducted experiment, concluded that 5% coconut activated carbon in a granular form was enough to maintain a reaction temperature above 500^{o}C within 15 minutes (60.8^{o}C/min) with highest productivity of 5.1 mol% syngas per g EFB per g absorber.

Two types of common pre-treatment, namely cutting and drying, were also studied. Reduction of the EFB size without drying seemed to favor gas production; however, untreated sample was found to give the highest H_2 composition but with a similar CH_4 concentration as in the other treatments. A slow release of volatile matters in the untreated sample might have provided the opportunity for secondary reaction to produce more H_2. Nevertheless, the addition of inorganic materials for tar minimization and syngas enhancement ($NaCO_3$, HSZM5, CaO and $CaCO_3$) did not influence the product distribution. On the other hand, the composition of gas was found to be greatly influenced by the addition of HSZM5, especially H_2. Meanwhile, increasing residence time (0.02 - 0.10 s) of volatiles within the reactor was shown to have increased gas composition (increment of 68.4% for H_2), particularly for the production of CH_4 which resulted in a higher calorific value of the gas.

Liquid product (bio-oil) and solid product (char) were also characterized for their potential end use. The char produced in this study has high carbon content (68%), giving it a moderate calorific value at 21.5 MJ/kg, which is similar to that of the

commercially produced EFB char, rendering it a good candidate for solid fuel substitute. The EFB char is characterized as mesoporous with highest pore size distribution around 4 nm. The BET surface area is modest at 14.2 m^2g^{-1} and has high mesopore area of 28.3 m^2g^{-1}. These characteristics present microwave pyrolysis of EFB as a superior alternative for the carbonization step for activated carbon preparation. Also, EFB char produced from this study is suitable for soil amendment. Highly oxygenated, acidic and viscous bio-oil produced from pyrolysis of EFB has high heating value (30.8 MJ/kg) which is higher than wood tar. Palmitic acid is the most abundant chemical component (12.0-36.4%) in bio-oil.

A shorter time was needed in the microwave pyrolysis of EFB compared to the conventional one, and this gives a higher gas production with four times better calorific value (7.6 MJ/m^3) but lower calorific value as compared to pyrolyzed coffee hulls and rice straw. The energy cost to produce twelve times higher energy products in the EFB microwave pyrolysis is lower, i.e. at 1.90 cent/MJ as compared to 49.90 cent/MJ in conventional heating. These findings reflect the potential of microwave pyrolysis as an alternative method to both treat waste and produce energy.

In summary, EFB was successfully pyrolyzed using microwave as heating source. The bio-oil product has better quality compared to wood oil therefore it has potentially for fuel oil substitute. The char also has the potential for activated carbon or solid fuel. EFB pyrolysis using microwave produced better syngas and cost cheaper compared to conventional heating. Further study is needed to optimize the parameters as to produce product of choice.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk ijazah Doktor Falsafah

PENILAIAN PIROLISIS GELOMBANG MIKRO TANDAN KELAPA SAWIT KOSONG

Oleh

ROZITA OMAR

Julai 2010

Pengerusi: Azni Idris, PhD

Fakulti: Fakulti Kejuruteraan

Bahan buangan pertanian seperti tandan kelapa sawit kosong (TKSK) adalah kerisauan alam sekitar kepada negara kita yang merupakan antara pengeluar minyak kelapa sawit terbesar dunia. Pirolisis merupakan proses terma yang telah digunakan untuk merawat bahan buangan biojisim kerana fleksibilitinya untuk menghasilkan produk pepejal, cecair dan gas. Kajian ini menilai kemungkinan untuk merawat TKSK menggunakan pirolisis gelombang mikro untuk menghasilkan gas sintesis (singas) yang tinggi. Di dalam kajian ini, TKSK yang diperoleh dari sebuah kilang pemprosesan minyak kelapa sawit tempatan telah diletakkan ke dalam reaktor lapisan tetap yang diperbuat daripada kuarza yang ditempatkan di dalam ketuhar gelombang mikro domestik, yang mana proses pengeringan dan pirolisis berlaku secara serentak. Sementara itu, bahan penyerap gelombang mikro telah ditambah untuk menaikkan suhu tindakbalas sehingga mencapai suhu yang diperlukan untuk membolehkan tindakbalas pirolisis berlaku. Parameter-parameter seperti kesan masa mastautin, penambahan bahan tak-organik (pemangkin) dan pra-rawatan TKSK telah

dikaji. Ekperimen perbandingan dengan reaktor yang dipanaskan secara konvensional juga dijalankan.

Ciri-ciri bahan api dan kimia TKSK telah memastikan bahawa ia ialah kandidat yang sesuai untuk proses pirolisis gelombang mikro yang sebanding dengan biojisim lain. Sifat dielektrik TKSK telah membuktikan bawa ia merupakan bahan yang telus gelombang mikro, dan oleh itu penambahan bahan penyerap gelombang mikro adalah diperlukan. Kajian beberapa bahan penyerap gelombang mikro seperti SiC, karbon-karbon teraktif (tempurung kelapa dan kelompang kepala sawit) serta arang yang dihasilkan dari eksperimen terdahulu menyimpulkan bahawa 5% karbon teraktif dari tempurung kelapa berbentuk butiran adalah cukup untuk mengekalkan suhu tindakbalas di atas 500^{o}C didalam masa 15 minit (60.8^{o}C/min) dengan produktiviti tertinggi iaitu 5.1 mol% singas per g EFB per g penyerap.

Dua jenis pra-rawatan am iaitu pemotongan dan pengeringan juga telah dikaji. Pengurangan saiz TKSK tanpa dikeringkan didapati telah membantu produksi gas tetapi sampel tanpa rawatan memberikan komposisi H_2 yang tertinggi walaupun kepekatan CH_4 adalah sebanding dengan pra-rawatan lain. Pembebasan jirim meruap oleh sampel tidak dirawat yang lambat mungkin telah memberi peluang tindakbalas sekunder untuk menghasilkan lebih banyak H_2. Bagaimanapun, penambahan bahan tak-organik untuk mengurangkan penghasilan tar dan penambahan singas ($NaCO_3$, HSZM5, CaO dan $CaCO_3$) tidak mempengaruhi taburan produk. Walau bagaimanapun, komposisi gas adalah sangat dipengaruhi oleh penambahan HSZM5, terutamanya H_2. Kenaikan masa mastautin (0.02 - 0.10 s) jirim di dalam reaktor telah membantu menaikkan komposisi gas (kenaikan 68.4%

untuk H_2), terutamanya penhasilan CH_4 yang telah menyebabkan gas berkalori tinggi dihasilkan.

Produk cecair (bio-minyak) dan produk pepejal (arang) juga dicirikan untuk menilai potensi kegunaan bahan-bahan ini. Arang yang dihasilkan dari kajian ini didapati mengandungi kandungan karbon yang tinggi yang telah memberikan nilai kalori sebanyak 21.5 MJ/kg iaitu sebanding dengan arang TKSK yang dihasilkan secara komersil, dan dapatan ini telah menjadikan ia kandidat yang baik untuk bahan api pepejal gantian. Arang daripada TKSK telah dicirikan sebagai berliang-meso dengan agihan liang tertinggi bersaiz 4 nm. Luas permukaan BET adalah sederhana pada 14.2 m^2g^{-1} dan keluasan berliang-meso yang tinggi pada 28.3 m^2g^{-1}. Ciri-ciri ini membuatkan pirolisis gelombang mikro satu alternatif yang lebih baik untuk langkah karbonisasi untuk penyediaan karbon teraktif. Arang daripada TKSK dari kajian ini sesuai untuk pengubahsuaian tanah. Bio-minyak yang dihasilkan adalah beroksigen tinggi, berasid dan likat yang mempunyai nilai pemanasan yang tinggi (30.8 MJ/kg), lebih tinggi dari tar daripada kayu. Asid palmitik ialah bahan kimia yang terbanyak (12.0-36.4%) di dalam bio-minyak yang mungkin diwarisi dari buah kelapa sawit.

Hanya masa yang singkat diperlukan dalam pirolisis gelombang mikro TKSK berbanding dengan cara konvensional dengan memberikan hasil produk gas yang tinggi dengan nilai kalori empat kali lebih tinggi (7.6 MJ/m^3) sesuai untuk digunakan sebagai bahan api pemanasan sederhana tetapi nilai kalorinya adalah kurang berbanding gas pirolisis kulit kopi dan jerami padi. Kos tenaga untuk menghasilkan dua belas kali lebih tinggi tenaga produk dalam pirolisis gelombang mikro TKSK adalah kurang iaitu 1.90 sen/MJ berbanding 49.90 sen/MJ. Hasil penyelidikan ini

menunjukkan bahawa pirolisis mikro gelombang adalah satu metod alternatif untuk merawat bahan buangan dan juga penghasilan tenaga.

Kesimpulannya, TKSK telah berjaya dipirolisis menggunakan gelombang mikro sebagai sumber pemanas. Produk bio-minyak adalah lebih berkualiti berbanding minyak kayu oleh itu ia berpotensi untuk dijadikan bahan bakar gentian. Produk arang juga berpontensi sebagai karbon teraktif atau bahan bakar pepejal. Pirolisis EFB menggunakan gelombang mikro menghasilkan produk syngas yang lebih baik dan lebih murah berbanding pemanasan konvensional. Walaubagaimana pun, kajian mendalam diperlukan untuk mendapatkan parameter optimum untuk menghasilkan produk yang dipilih.

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I certify that a Thesis Examination Committee has met on 2 July 2010 to conduct the final examination of Rozita Omar on her thesis entitled "**Evaluation of Microwave Pyrolysis of Oil Palm Empty Fruit Bunch**" 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 be awarded the Doctor of Philosophy.

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

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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 concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institution

ROZITA OMAR

Date: 2 July 2010

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