UNIVERSITI PUTRA MALAYSIA

CATALYTIC GASIFICATION OF EMPTY FRUIT BUNCH FOR TAR-FREE HYDROGEN RICH-GAS PRODUCTION

MOHAMMED MAHMOUD AHMAD AL-OBAIDI

CATALYTIC GASIFICATION OF EMPTY FRUIT BUNCH FOR TAR-FREE HYDROGEN RICH-GAS PRODUCTION

By

MOHAMMED MAHMOUD AHMAD AL-OBAIDI

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

November 2011

DEDICATION

To my beloved mother, my father, my wife, my sisters, my daughters (Raneia and Reem), and longtime friends

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

CATALYTIC GASIFICATION OF EMPTY FRUIT BUNCH FOR TAR-FREE HYDROGEN RICH-GAS PRODUCTION

By

MOHAMMED MAHMOUD AHMAD AL-OBAIDI

November 2011

Chairman: Salmiaton Ali, PhD

Faculty : Faculty of Engineering

Palm oil industry in Malaysia generates huge quantity of solid biomass every year including trunks, fronds, empty fruit bunches (EFB), shells and fibers as wastes from palm oil fruit harvest and oil extraction processing. These large volumes of wastes represent a big environmental threat for Malaysia. The great potential of oil palm biomass has motivated an increasing interest in the utilization of these wastes (i.e. EFB) as a source of clean energy. Fuel and chemical characteristics of the EFB undertaken in this study confirmed that it is a good candidate for gasification process as it is comparable to other lignocellulosic biomass.

As a thermal process, gasification has been used to treat oil palm wastes due to its high conversion efficiency. This study evaluated the possibility to treat EFB via gasification process for hydrogen-rich gas production. In this study, the EFB

obtained from a local palm oil mill was gasified in an atmospheric bench-scale fluidized-bed gasifier (FBG) using air as gasifying agent. The operating parameters, such as effects of gasifier temperature (700–1000 °C), equivalence ratio (0.15-0.35), feedstock particle size (<0.3, 0.3–0.5, 0.5–1.0 mm), and addition of catalysts (as a primary and secondary) were studied to evaluate the gasification yields and performance so as to reach maximum tar-free hydrogen-rich gas production.

The main gas species generated, as identified by a gas chromatography (GC), were H_2, CO, CO_2 and CH_4. With gasification temperature increases the total gas yield was enhanced greatly and reached the maximum value at 1000 °C with a large fraction of H_2 (38.02 vol.%) and CO (36.36 vol.%). Equivalence ratio (ER) showed a significant influence on the upgrading of hydrogen production and product distribution. The optimum ER value of 0.25 was found to attain a higher H_2 yield. Feedstock particle size showed an influence on the improvement of the gas yield. Smaller EFB particles size produced more H_2, CO, CH_4 and less CO_2.

Tar formation is a major drawback when EFB is converted via gasification to obtain fuel gas. Catalytic cracking is an efficient method to eliminate the tar content in the gas mixture. In this study, three types of Malaysian natural dolomites namely, P1, P2 and P3 in addition to spent mixed metal oxide (SMMO) were used as catalysts to reduce tar contents in the produced gas and for further improvement of hydrogen yield. Various types of analysis techniques such as X-ray fluorescence (XRF), thermogravimetry (TGA), X-ray diffraction (XRD), scanning electron microscopy (SEM) and nitrogen adsorption-desorption isotherm have been used to characterize the catalyst morphology.

The effect of the primary catalyst (dry-mixed with biomass) under different ratios of catalyst to biomass (C/B) varied from 0.05 to 0.3 was carried out in fluidized-bed gasifier. The performance of gasification process is improved by increasing C/B ratio. Malaysian dolomites as primary catalyst showed a better catalytic effect compared to spent mixed metal oxide. With 30% of P1 dolomite, the total gas yield increased by 8%, hydrogen content increased by 18%, and total tar content in flue gas decreased by 78% at gasification temperature of 850 °C.

In the second part of the catalytic experiments, the calcined catalysts were placed in a fixed-bed catalytic cracking reactor located downstream from the fluidized-bed gasifier to investigate the effect of secondary catalyst at different cracking temperatures in the range of 700–900 °C. The results show that raising the temperature in the catalytic bed increases the cracking activity of the catalysts and then significantly improve the gasification yields and performance. As in primary position, Malaysian dolomites showed a stronger catalytic activity as a secondary catalyst compared to spent mixed metal oxide. As cracking temperature increasing to 900 °C, total gas yield increased by 20%, hydrogen increased by 66%, and almost 99% reduction in tar content were obtained with P1 dolomite.

ASPEN PLUS simulation using thermodynamic equilibrium model based on minimization of Gibbs free energy used to predict the EFB gasification yields under selected experimental parameters and to compare the simulation results with experimental data. The analysis of data for product gases and carbon conversion efficiency obtained from the simulation agreed satisfactorily with the experimental data.

As a conclusion, both EFB as untapped waste and Malaysian dolomite as a cheap catalyst that can significantly reduce tar content of the product gas, could greatly contribute to the Malaysian economy in terms of producing clean environmentally renewable energy.

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

PENGGASAN BERMANGKIN TANDAN KELAPA SAWIT KOSONG UNTUK PENGELUARAN GAS KAYA HIDROGEN BEBAS TAR

Oleh

MOHAMMED MAHMOUD AHMAD AL-OBAIDI

November 2011

Pengerusi: Salmiaton Ali, PhD

Fakulti : Fakulti Kejuruteraan

Industri minyak kelapa sawit di Malaysia menghasilkan kuantiti biojisim pepejal yang besar setiap tahun termasuk sesalur, pelepah, tandan buah kosong (EFB), kelompang dan gentian sebagai sisa daripada penuaian buah kelapa sawit dan pemprosesan pengekstrakan minyak. Isipadu sisa yang amat besar ini merupakan ancaman alam sekitar yang besar untuk Malaysia. Potensi bagus biojisim kelapa sawit telah mendorong minat meningkat dalam penggunaan sisa ini (iaitu EFB) sebagai sumber tenaga bersih. Ciri-ciri bahan bakar dan kimia EFB yang digunakan dalam penyelidikan ini mengesahkan yang EFB adalah calon yang baik untuk proses penggasan kerana ianya standing dengan biojisim lignoselulosa yang lain.

Sebagai proses terma, penggasan telah digunakan untuk merawat sisa kelapa sawit kerana kecekapan penukaran yang tinggi. Dalam penyelidikan ini, EFB yang

diperolehi daripada kilang kelapa sawit tempatan telah digaskan dalam penggas lapisan terbendalir skala makmal atmosfera (FBG) dengan menggunakan udara sebagai agen penggaskan. Parameter kendalian seperti kesan suhu lapisan penggas (700–1000 °C), nisbah kesetaraan (0.15-0.35), saiz zarah suapan (<0.3, 0.3–0.5, 0.5–1.0 mm), dan penambahan mangkin (sebagai primer dan sekunder) telah diperiksa untuk menilai hasil dan prestasi penggasan dalam mencapai pengeluaran gas kaya hidrogen bebas tar yang maksima.

Spesies gas utama yang dihasilkan, seperti yang dikenalpasti oleh kromatografi gas (GC), adalah H_2, CO, CO_2 dan CH_4. Dengan kenaikan suhu penggasan, jumlah keseluruhan hasil gas telah bertambah dengan jayanya dan mencapai nilai maksima pada 1000 °C dengan bahagian besar H_2 (38.02 %isipadu) dan CO (36.36 %isipadu). Nisbah kesetaraan (ER) menunjukkan pengaruh bermakna terhadap peningkatan pengeluaran hidrogen dan taburan keluaran. Nilai ER optima 0.25 didapati mencapai hasil H_2 yang lebih tinggi. Saiz zarah suapan juga menunjukkan pengaruh ke atas peningkatan hasil gas. Saiz zarah EFB yang lebih kecil menghasilkan lebih gas H_2, CO, CH_4 dan kurang CO_2.

Formasi tar merupakan kelemahan utama apabila EFB ditukarkan melalui penggasan untuk memperolehi gas kaya hidrogen dengan sasaran untuk penggunaan di loji penjanaan kuasa atau untuk pengeluaran bahan kimia. Keretakan bermangkin merupakan satu kaedah yang cekap dalam penyingkiran kandungan tar dalam campuran gas. Dalam penyelidikan ini, tiga jenis dolomit Malaysian asli iaitu P1, P2 dan P3, disamping campuran logam beroksida terpakai telah digunakan sebagai mangkin untuk pengurangan kandungan tar dalam gas keluaran.

Pelbagai jenis teknik analisis seperti pendarkilau sinar-X (XRF), termogravimetri (TGA), belauan sinar-X (XRD), kemikroskopan elektron imbasan (SEM) dan isoterma jerapan-nyaherapan nitrogen telah digunakan untuk mencirikan morfologi mangkin.

Kesan mangkin primer (campur-kering dengan biojisim) di bawah berlainan nisbah mangkin kepada biojisim (C/B=0.05–0.30) telah dilaksanakan dalam penggas lapisan terbendalir. Prestasi proses penggasan telah diperbaiki dengan meninggikan nisbah C/B. Dolomit Malaysian sebagai mangkin primer menunjukkan kesan mangkin yang lebih baik berbanding dengan campuran logam beroksida. Dengan 30% dolomit P1, jumlah keseluruhan hasil gas telah meningkat sebanyak 8%, dan kandungan hidrogen sebanyak 18%, manakala jumlah keseluruhan kandungan tar telah menurun secara dramatik sebanyak 78% pada suhu penggasan 850 °C.

Dalam bahagian kedua ujikaji bermangkin, mangkin berkalsin telah diletakkan di dalam reaktor pemecahan bermangkin lapisan tetap bertempat di hilir daripada penggas lapisan terbendalir untuk menyiasat kesan mangkin sekunder pada suhu pemecahan yang berlainan dalam julat 700–900 °C. Keputusan tersebut menunjukkan bahawa dengan menaikkan suhu di dalam lapisan bermangkin, aktiviti pemecahan oleh mangkin telah meningkat menyebabkan hasil dan prestasi penggasan telah diperbaiki dengan jayanya. Serupa dengan keputusan oleh mangkin primer, dolomit Malaysia menunjukkan aktiviti bermangkin yang lebih kuat sebagai mangkin sekunder berbanding dengan campuran logam beroksida. Apabila suhu pemecahan meningkat kepada 900 °C, jumlah keseluruhan hasil gas dengan dolomit

P1 telah meningkat sebanyak 20%, pengeluaran hidrogen sebanyak 66%, manakala hampir 99% tar telah terdegradasi.

Simulasi ASPEN PLUS menggunakan model keseimbangan termodinamik berdasarkan peminimuman tenaga bebas Gibbs telah digunakan untuk meramalkan hasil penggasan EFB di bawah parameter uji kaji terpilih dan untuk mengesahkan keputusan simulasi terhadap data uji kaji. Analisis data untuk gas keluaran dan kecekapan penukaran karbon diperolehi daripada simulasi bersetuju dengan memuaskan dengan data uji kaji.

Secara kesimpulannya, kedua-dua EFB sebagai sisa terpendam dan dolomit Malaysia sebagai mangkin murah yang dapat mengurangkan dengan nyata kandungan tar di dalam gas keluaran, boleh menyumbang dengan banyak ke atas ekonomi Malaysia dari segi pengeluaran tenaga boleh dibaharui persekitaran bersih.

ACKNOWLEDGEMENTS

Thank Allah to Almighty for giving me the patience and perseverance to finish this thesis to the end.

I hereby convey my sincere gratitude and appreciation to my venerable supervisor Associate Prof. Dr. Salmiaton Ali, how gave me invaluable and worthwhile advice on this thesis, and gave me a panorama of observance into knowledge in my field.

I also would like to appreciate the efforts of my co-supervisors Prof. Dr. Fakhru'l-Razi Ahmadun, Prof. Dr. Taufiq Yab, Dr. Wan Azlina and Dr. Mohamad Amran for their support, advice, recommendation and comments through my research.

I would like to extend my appreciation to former head of department Prof. Dr. Azni Idris and the entire staff of the Department of Chemical and Environmental Engineering, UPM.

My special appreciation is extended to Prof. Dr. Robiah Yunus and Dr. Rozita Omar for providing me with fruitful information. My appreciation also goes to the technicians, research officers and science officers at Department of Chemical Engineering, Department of Civil Engineering, Department of Food Engineering, Department of Physical and Chemistry, Center of Excellence for Catalysis Science and Technology how have helped me at the experimental stage.

My heartfelt gratitude to have helping hands of my fellow friends Dr. Ali Riza, Dr. Azahari, Maziyar, Ahmad, Baba, Shehab, Riza, Mustika, Baiti, Taha, Amir and others that I might have forgotten to mention their names.

Finally, thanks to beautiful Malaysia for giving me the care and tenderness to achieve my dreams and finish my study.

I certify that a Thesis Examination Committee has met on 22 November 2011 to conduct the final examination of Mohammed Mahmoud Ahmad Al-Obaidi on his thesis entitled "Catalytic gasification of empty fruit bunch for tar-free hydrogen rich-gas 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 be awarded the Doctor of Philosophy.

Members of the Thesis Examination Committee were as follows:

Dayang Radiah Binti Awang Biak, PhD
Lecturer
Faculty of Engineering
University Putra Malaysia
(Chairman)

Robiah Binti Yunus, PhD
Professor
Faculty of Engineering
University Putra Malaysia
(Internal Examiner)

Thomas Choong Shean Yaw, PhD
Associate Professor
Faculty of Engineering
Universiti Putra Malaysia
(Internal Examiner)

John R. Grace, PhD
Professor
Faculty of Engineering / Chemical and Biological Engineering (CHBE)
The University of British Columbia
Canada
(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 fulfilment of the requirement for the degree of Doctor of Philosophy. The members of the Supervisory Committee were as follows:

Salmiaton Binti Ali, PhD
Associate Professor
Faculty of Engineering
University Putra Malaysia
(Chairman)

Wan Azlina Binti Wan Ab Karim Ghani, PhD
Associate Professor
Faculty of Engineering
University Putra Malaysia
(Member)

Mohamad Amran Bin Mohd. Salleh, PhD
Lecturer
Faculty of Engineering
University Putra Malaysia
(Member)

Fakhru'l-Razi Bin Ahmadun, PhD
Professor
Faculty of Engineering
University Putra Malaysia
(Member)

Taufiq Yap Yun Hin, PhD
Peofessor
Faculty of Science
University Putra Malaysia
(Member)

BUJANG BIN KIM HUAT, PhD
Professor and Dean
School of Graduate 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 concurrently, submitted for any other degree at Universiti Putra Malaysia or at any other institutions.

MOHAMMED MAHMOUD AHMAD AL-OBAIDI

Date: 22 November 2011

TABLE OF CONTENTS