UNIVERSITI PUTRA MALAYSIA

HYDROLYSIS OF OIL PALM EMPTY FRUIT BUNCH USING DILUTE ACID

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By

SHANTI FARIDAH SALLEH

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

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DEDICATED TO

MY BELOVED CHILDREN, HUSBAND AND PARENTS

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

HYDROLYSIS OF OIL PALM EMPTY FRUIT BUNCH USING DILUTE ACID

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SHANTI FARIDAH BINTI SALLEH

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Chairman: Professor Robiah Yunus, PhD

Faculty: Engineering

Extensive research activities have been carried out to identify the best technology to convert biomass to bioethanol and other value added chemicals. This research focuses on the conversion of the hemicelluloses in the Oil Palm Empty Fruit Bunch (OPEFB) fibre to xylose via an acid hydrolysis reaction. The objectives of this study are to investigate a potential pre-treatment method prior to acid hydrolysis, to optimise the reaction conditions and operation modes of the reactor as well as to study the kinetics of the acid hydrolysis of OPEFB fibre in a batch reactor.

A preliminary assessment on the composition of the OPEFB fibre was conducted using TGA analysis and the following composition of the fibre (% dry weight basis) was obtained: cellulose, 44.5%; hemicellulose 26.5%; lignin, 19.1%. Since OPEFB contains more than 70% cellulose and hemicelluloses in its fibre, it is an excellent feed sock of fermentable sugars for bioethanol production. However, the cellulose

and hemicelluloses in the fibre must firstly be converted to fermentable sugars namely glucose and xylose. Consequently, a 1-litre batch reactor was fabricated and commissioned to convert lignocellulosic materials in the fibre to either glucose or xylose. The maximum temperature of the batch reactor was 140 ^{o}C, while the liquid solid ratio was between 20:1 and 30:1. In the preliminary screening of the best acid, three different types of acid were employed; sulphuric acid (H_2SO_4), hydrochloric acid (HCl) and acetic acid (CH_3COOH). The catalyst-screening study was conducted at 100^{o}C and at a liquid solid ratio of 25:1. Sulphuric acid showed the highest catalytic effect, followed by hydrochloric acid and acetic acid. Sulphuric acid was selected and applied for subsequent studies.

The effect of ultrasonic pretreatment on dilute acid hydrolysis of OPEFB was also examined. The experiments were conducted at two temperatures; 100^{o}C and 140^{o}C. The results showed that the exposure of the OPEFB fibre to 20 kHz signal of ultrasonication power at different amplitudes had a marked effect on the efficiency of low temperature (100^{o}C) acid hydrolysis based on the yield of xylose. However, no improvement on yield of xylose was observed for acid hydrolysis at 140^{o}C. SEM analysis showed that OPEFB fibre undergone significant morphological changes due to the effect of ultrasonic pretreatment under different acid hydrolysis conditions.

Optimisation studies were conducted under various conditions; temperatures (80 ^{o}C to 140 ^{o}C), acid concentrations (2%, 4% and 6%), and reaction times (15 min, 30 min, 60 min, 90 min, 120 min and 150 min). The results indicated that the effect of acid concentration on the conversion of xylose was significant at higher temperature.

At temperatures higher than 120^{o}C, acid hydrolysis of OPEFB fibre favoured lower acid concentration and longer reaction time (more than 60 minutes). At lower temperatures (below 120^{o}C), higher acid concentration and shorter reaction time (less than 60 minutes) improved xylose production. The monomeric xylose present in the liquid phase is the key indicator of the extent of the reaction, thus it was used as the basis for the kinetics modelling analysis.

Kinetics study on the dilute acid hydrolysis of OPEFB fibre revealed that the hydrolysis reaction is a first order irreversible reaction. Dilute acid hydrolysis reaction was analysed using kinetics models developed by Saeman. Kinetics constants for Saeman model were analysed using Arrhenius type expansion which includes activation energy and catalyst concentration factors. A general kinetics model for acid hydrolysis of OPEFB fibre in terms of acid concentration and temperature was then developed.

This work highlighted the potential of OPEFB fibre as a feasible feed stock for production of fermentable sugars especially xylose for bioethanol production. This work also demonstrated the ability of the in-house batch reactor to convert OPEFB fibre to xylose with 80% conversion. The breakthrough of this research was the discovery of the ability of ultrasonic pretreatment to physically alter the surface of OPEFB fibre, hence increase the yield of xylose. Ultrasonication of biomass has the potential to be integrated with existing lignocelluloses pretreatment technologies in biomass to bioethanol production to enhance the overall conversion efficiency.

Abstrak tesis ini dibentangkan kepada Senat Universiti Putra Malaysia untuk memenuhi keperluan Sarjana Doktor Falsafah

HIDROLISIS ASID TANDAN KOSONG KELAPA SAWIT DALAM REAKTOR LONGGOK

Oleh

SHANTI FARIDAH BINTI SALLEH

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Pengerusi: Profesor Robiah Yunus, PhD

Fakulti : Kejuruteraan

Aktiviti penyelidikan secara meluas telah dijalankan untuk mengenalpasti pertukaran jisimbio kepada ethanol-bio dan bahan kimia bernilai-tambah. Penyelidikan ini secara spesifik memfokuskan kepada penukaran hemiselulosa dalam fiber tandan kosong kelapa sawit (TKKS) kepada xylosa melalui tindakbalas hidrolisis pemangkin asid. Objektif tesis adalah untuk menjalani ulangkaji terhadap pra rawatan yang berpotensi untuk asid hidrolisis, mengoptima keadaan tindakbalas reaktor dan juga mengkaji kinetik hidrolisis asid cair terhadap fiber TKKS dengan menggunakan reaktor longgok yang telah direkacipta. Satu liter reaktor longgok telah direkacipta, diformulasi dan dikomisenkan untuk mengkaji hidrolisis asid fiber TKKS. Setelah beberapa pengubahsuaian and penambahbaikan, suhu operasi reaktor longgok telah diletakkan pada suhu maksima 140 °C untuk operasi yang stabil. Nisbah cecair-solid telah ditentukan antara 20:1 hingga 30:1 berdasarkan isipadu kecil reaktor dan juga kebolehtahanan terhad bakul `stainless steel' yang menampung fiber TKKS.

Komposisi pecahan utama fiber TKKS yang diperoleh melalui analisis TGA ialah (% berat kering asas): selulosa, 44.5%; hemiselulosa 26.5%; lignin, 19.1%. Keputusan ini adalah selari dengan kajian sebelum ini ke atas komponen asas TKKS menggunakan hidrolisis asid secara kuantiti. Pada permulaan kerja eksperimen, nombor pemangkin asid telah diskrin (H_2SO_4, HCl and CH_3COOH) untuk menentukan asid terbaik untuk digunakan dalam penyelidikan ini. Kajian skrin-pemangkin ke atas hidrolisis asid cair fiber TKKS telah dijalankan pada 100 °C dan nisbah cecair solid adalah 25:1.

Keberkesanan tiga jenis asid telah diuji untuk menentukan pemangkin asid paling optima bagi penghasilan xylosa. Asid paling optima (H_2SO_4) telah dipilih dan diaplikasikan dalam ujikaji yang seterusnya. Kajian terhadap kesan pra-rawatan ultrasonik turut disertakan dalam kerja ini untuk menguji kesan beberapa kaedah pra-rawatan ke atas hidrolisis asid cair fiber TKKS. Ujikaji berkenaan telah dijalankan pada suhu serendah 100 °C dan setinggi 140 °C. Keputusan menunjukkan pendedahan secara terus fiber TKKS kepada kuasa ultrasonik dengan signal 20kHz pada amplitud yang berbeza, mempunyai kesan bertanda ke atas keberkesanan suhu rendah (100 °C) hidrolisis asid berdasarkan kepada hasil keseluruhan xylosa. Walaubagaimanapun, tiada sebarang penambahbaikan terhadap hasil xylose yang dapat diperhatikan melalui hidrolisis asid pada 140 °C mengginakan reaktor longgok. Analisis SEM menunjukkan perubahan ketara morfologi fiber TKKS terhadap kesan pra-rawatan ultrasonik dan perbezaan keadaan hidrolisis asid.

Tiga jenis kepekatan asid iaitu 2%, 4% dan 6% telah dipilih untuk kajian ini. H_2SO_4 menunjukkan kesan pemangkinan paling tinggi, diikuti oleh HCl dan CH_3COOH. Pengoptimuman hidrolisis asid cair telah dijalankan menggunakan H_2SO_4 sebagai pemangkin. Tindakbalas telah dijalankan di bawah suhu yang berbeza (80 ^{o}C hingga 140 ^{o}C), kepekatan asid (2%, 4% dan 6%), dan masa tindakbalas (15 min, 30 min, 60 min, 90 min, 120 min dan 150 min). Secara keseluruhannya, keputusan bagi hidrolisis asid fiber TKKS menunjukkan bahawa kesan kepekatan asid terhadap penukaran xylosa adalah lebih kritikal pada suhu yang tinggi. Pada sebarang kepekatan asid dalam kajian ini (2%, 4% dan 6%), suhu optima untuk penghasilan xylosa telah diperhatikan pada 120 ^{o}C. Kepekatan asid mempunyai kesan yang lebih dominan ke atas penghasilan xylosa pada suhu rendah (bawah 120 °C) dan masa tindakbalas pendek (kurang dari 60 minit). Dengan kata lain, hidrolisis asid TKKS adalah lebih sesuai pada kepekatan asid yang rendah bagi suhu lebih dari 120 °C dan masa tindakbalas melebihi 60 minit. Monomer xylosa yang berada dalam fasa cecair merupakan kunci penunjuk kepada pemanjangan kepada tindakbalas, seterusnya menjadi matlamat untuk analisis model kinetik. Kajian kinetik ke atas hidrolisis asid fiber TKKS menunjukkan bahawa tindakbalas yang terlibat adalah tindakbalas berbalik pertama. Kinetik tindakbalas utama telah ditentukan dan keadaan tindakbalas optima telah didefinisikan atas asas kepada model kinetik berkenaan.

Tindakbalas hidrolisis asid cair telah dianalisa menggunakan model kinetik dengan mengaplikasikan model yang diperkenalkan oleh Saeman.

Pemalar kinetic untuk model Saeman telah dianalisa menggunakan jenis perluasan Arrhenius yang melibatkan tenaga pengaktifan dan factor kepekatan pemangkin.

Persamaan yang baik antara model anggapan dan data ujikaji dengan pembolehubah penentuan melebihi 90%. Kinetik umum yang ditunjukkan dari segi kepekatan asid dan suhu telah dibina. Akhirnya, walaupun pertukaran tinggi hemiselulosa kepasa xylosa adalah ketara, aras rendah pertukaran selulosa adalah diberi perhatian. Beberapa cadangan penambahbaikan telah diusulkan untuk kajian masa hadapan bagi menambahbaik kajia ini. Walaubagaimanapun, kajian ini menunjukkan bahawa penggunaan fiber TKKS berkemungkinan menjadi pilihan yang praktikal sebagai bahan mentah untuk penghasilan gula bagi sintesis bahan api bio, berdasarkan kos yang murah dan hasil gula yang tinggi.

Kajian ini menekankan potensi serat TKKS sebagai bahan mentah bagi pengeluaran gula fermentasi terutama xylose untuk penghasilan bioetanol. Kajian ini juga menunjukkan kemampuan reaktor kelompok dalaman untuk menukar serat TKKS xylosa dengan keberkesanan sebanyak 80%. Penemuan kajian ini adalah penemuan keupayaan prarawatan ultrasonik untuk mengubah fizikal permukaan serat TKKS, justeru meningkatkan hasil xylose. Ultrasonikasi biomass mempunyai potensi untuk diintegrasikan dengan teknologi prarawatan lignocelluloses yang sedia ada dalam biojisim untuk pengeluaran bioetanol untuk meningkatkan kecekapan penukaran secara keseluruhan

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I certify that a Thesis Examination Committee has met on 13th November 2011 to conduct the final examination of Shanti Faridah Salleh on her thesis entitled "**Acid Hydrolysis of Oil Palm Empty Fruit Bunch in A Batch Reactor**" 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 degree.

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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.

SHANTI FARIDAH SALLEH

Date:

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