UNIVERSITI PUTRA MALAYSIA

ALKALINE HYDROLYSIS OF OIL PALM EMPTY FRUIT BUNCH FOR ENHANCED FERULIC ACID RELEASE

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2013

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By

FAIROUZ JAHAAN BINTI MOHD AANIFAH

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

July 2013

DEDICATED TO MY PRECIOUS PARENTS AND BROTHERS

Abstract of thesis presented to the Senate of Universiti Putra Malaysia in fulfilment of the requirement for degree of Master of Science

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Chairman : Professor Suraini Abd-Aziz, PhD

Faculty : Biotechnology and Biomolecular Sciences

Malaysia is the second largest producer and biggest exporter of palm oil worldwide. Owing to this fact, the biomass produced is in abundance, namely; oil palm empty fruit bunches (OPEFB), mesocarp fibres, palm kernel shells, oil palm fronds and trunks. Among these, OPEFB is the hugely generated lignocellulosic waste. Accordingly, the National Biomass Strategy 2020 was developed to create wealth through biofuels and bio-based chemicals production from excess biomass. Ferulic acid (FA), a hydroxycinnamic acid, exists in various agricultural residues such as maize bran, corn cob, wheat straw and also OPEFB. FA serves as a raw material for production of pharmaceuticals, cosmetics and flavours. It is mainly utilized in flavour synthesis, especially vanilla flavour, due to its property as a precursor for vanillin, the key ingredient of vanilla aroma. FA from nature provides biovanillin through biotechnological route. In order to obtain FA from the OPEFB fibres for biovanillin production, this study was conducted to examine the methods and conditions of FA release from OPEFB fibres through alkaline hydrolysis. The selected treatment strategy (Treatment B1) that involved autoclaving OPEFB fibres

(120°C, 3 hours) followed by alkaline hydrolysis (90°C, 3 hours, agitated at 120 rpm in water bath shaker), showed significant yield of FA release from OPEFB fibres. Alkaline hydrolysis using 0.5 to 5.0% (w/v) of NaOH, KOH and K_2CO_3 gave both 2.0% (w/v) KOH and NaOH as the best alkalis concentration for better FA release from OPEFB fibres compared to other alkali concentrations. The addition of 98 µL sodium bisulfite ($NaHSO_3$) to KOH treatment yielded 4.23 mg/L higher FA compared to the hydrolysis without $NaHSO_3$ as it reduced re-polymerization and oxidation of FA. It was also observed that the FA release was affected by the different reaction times at high and ambient temperature during alkaline hydrolysis. FA was observed to decrease due to longer hydrolysis time at high temperature and treatment at 37°C for 16 hours yielded only an average of 24 to 42 mg/L FA only. About 66.18 ± 3.24 mg/L and 56.94 ± 3.52 mg/L FA was released using 2.0% (w/v) NaOH and KOH, respectively through Treatment B1 (with the addition of $NaHSO_3$) from the esterified FA in the OPEFB fibres. Fourier transform infrared (FTIR) analysis showed evidence of decrease in aromatic groups, lignin and ester linkages stretching thus showed that FA, the lignin monomer has been released from OPEFB fibres. It was suggested that mild alkaline hydrolysis was sufficient in solubilising FA that is esterified in the OPEFB lignin and hemicellulose.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia sebagai memenuhi keperluan untuk Ijazah Master Sains

HIDROLISIS BERALKALI TANDAN KOSONG BUAH KELAPA SAWIT BAGI MENINGKATKAN PENGEKSTRAKAN ASID FERULIK

Oleh

FAIROUZ JAHAAN BINTI MOHD AANIFAH

Julai 2013

Pengerusi : Profesor Suraini Abd-Aziz, PhD

Fakulti : Bioteknologi dan Sains Biomolekul

Malaysia merupakan negara penghasil kedua terbesar dan pengeksport utama minyak kelapa sawit di dunia. Berdasarkan fakta ini, banyak biomas yang terhasil seperti tandan kosong buah kelapa sawit (OPEFB), sabut mesokap, tempurung isirong sawit, pelepah sawit dan batang sawit. OPEFB merupakan penyumbang utama kepada kuantiti sisa lignoselulosik yang terhasil. Oleh yang demikian, Strategi Biomas Kebangsaan 2020 dibentuk untuk membina kekayaan melalui penghasilan biotenaga dan biokimia daripada biomas. Asid ferulik (FA) adalah asid hidroksisinamik yang wujud dalam pelbagai sisa pertanian seperti dedak jagung, tongkol jagung, jerami gandum dan juga OPEFB. FA bertindak sebagai bahan mentah dalam pembuatan bahan farmaseutikal, kosmetik dan perisa. FA digunakan secara meluas dalam sintesis perisa, terutamanya perisa vanila kerana sifatnya sebagai prekursor kepada vanilin, sebatian penting yang memberi aroma vanila. FA yang diekstrak dari sumber semulajadi boleh menghasilkan biovanilin melalui kaedah bioteknologi. Kajian ini bertujuan menyelidik kaedah dan keadaan pengekstrakan FA daripada sabut OPEFB melalui hidrolisis beralkali untuk

dijadikan bahan mentah bagi penghasilan biovanillin. Strategi rawatan terpilih (Rawatan B1) yang terdiri daripada mengautoklaf sabut OPEFB (120°C, 3 jam) dan diikuti dengan hidrolisis beralkali (90°C, 3 jam, dicampurkan pada 120 rpm dalam penggoncang rendaman air), menunjukkan penghasilan FA yang bagus daripada sabut OPEFB. Hidrolisis beralkali menggunakan NaOH, KOH dan K_2CO_3 dengan kepekatan 0.5 hingga 5.0% (berat/isipadu) menunjukkan bahawa 2.0% (berat/isipadu) KOH dan NaOH adalah kepekatan alkali yang dapat mengekstrak kuantiti FA yang lebih tinggi berbanding alkali dan kepekatan yang lain. Tambahan 98 µL natrium bisulfite ($NaHSO_3$) dalam rawatan menggunakan KOH, menyumbang kepada peningkatan FA sebanyak 4.23 mg/L berbanding hidrolisis tanpa $NaHSO_3$ kerana sebatian ini bertindak mengurangkan kadar polimerisasi semula dan oksidasi FA. Selain itu, pengekstrakan FA juga dipengaruhi oleh jangka masa rawatan pada suhu tinggi dan ambien. Kajian menunjukkan konsentrasi FA berkurangan disebabkan oleh masa hidrolisis yang lama pada suhu tinggi dan hidrolisis pada 37°C untuk 16 jam menghasilkan 24 hingga 42 mg/L FA sahaja. Melalui Rawatan B1, sebanyak 66.18 ± 3.24 mg/L dan 56.94 ± 3.52 mg/L FA berjaya diekstrak menggunakan 2.0% (berat/isipadu) NaOH dan KOH masing-masing (dengan penambahan $NaHSO_3$), daripada FA yang terester dalam OPEFB. Analisis infra merah transformasi Fourier (FTIR) menunjukkan pengurangan regangan pada kumpulan aromatik, lignin dan ikatan ester, sekaligus membuktikan pembebasan monomer lignin (FA) dari sabut OPEFB. Dengan itu, dicadangkan bahawa keadaan hidrolisis beralkali yang sederhana mencukupi untuk membebaskan FA yang teresterifikasi dalam lignin dan hemiselulose OPEFB.

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I certify that a Thesis Examination Committee has met on 29th July 2013 to conduct the final examination of Fairouz Jahaan Bt. Mohd Aanifah on her thesis entitled "Alkaline Hydrolysis of Oil Palm Empty Fruit Bunch for Enhanced Ferulic Acid Release" 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 Master of Science.

Members of the Thesis Examination Committee were as follows:

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

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Date:

DECLARATION

Declaration by graduate student

I hereby confirm that:

- this thesis is my original work
- quotations, illustrations and citations have been duly referenced
- this thesis has not been submitted previously or concurrently for any other degree at any other institutions
- intellectual property from the thesis and copyright of thesis are fully-owned by Universiti Putra Malaysia
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- there is no plagiarism or data falsification/fabrication in the thesis, and scholarly integrity was upheld as according to Rule 59 in Rules 2003 (Revision 2012-2013). The thesis has undergone plagiarism detection software.

Signature: _____ Date: _____

Name and Matric No.: _____

Declaration by Members of Supervisory Committee

This is to confirm that:

- the research conducted and the writing of this thesis was under our supervision;
- supervision responsibilities as stated in Rule 41 in Rules 2003 (Revision 2012-2013) were adhered to.

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Signature : _____
Name of Member
of Supervisory Committee: _____

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