UNIVERSITI PUTRA MALAYSIA

DISSOLUTION OF OIL PALM BIOMASS BY ALKYL-IMIDAZOLIUM IONIC LIQUIDS FOR EFFICIENT ENZYMATIC HYDROLYSIS

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FS 2011 75

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By

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

October 2011

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

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Chairman: Professor Mohd Basyaruddin Abdul Rahman

Faculty: Science

The dissolution of oil palm biomass by ionic liquids (ILs) was comparatively studied. The ionic liquids, 1-ethyl-3-methylimidazolium chloride ([emim]Cl), 1-butyl-3-methylimidazolium chloride ([bmim]Cl) and 1-ethyl-3-methylimidazolium acetate ([emim]OAc) were used to dissolve oil palm biomass and cellulose fibers which are empty fruit bunches (EFB), oil palm frond (OPF) and oil palm trunk (OPT). Dissolution of 5 wt. % (0.1 g) of fibers/ ILs solutions were conducted at 100 °C under inert atmosphere. The heating time for complete dissolution was optimized. It has been shown that [emim]OAc is the best solvent for dissolution of oil palm biomass compared to [emim]Cl and [bmim]Cl. EFB, OPF and OPT fibers dissolved in [emim]OAc shows more than 95 % w/w of dissolution after 16 h of heating, while EFB and OPF fibers dissolved more than 85 % w/w after being heated more than 48 h in [emim]Cl and [bmim]Cl. Cellulose fibers were successfully dissolved after 2 - 3 h of heating in all ILs tested. Fourier-transform infrared spectroscopy (FT-IR)

confirmed the absorbance band at 1729 cm^{-1} and 1512 cm^{-1} which correspond to hemicellulose and lignin, respectively disappeared after regeneration process indicating that they were diminished after the washing step. Regenerated cellulose-rich solids were obtained in amorphous form (cellulose II), thus decreasing the crystallinity index (C*r*I) values. The C*r*I value for regenerated EFB, OPF and OPT fibers decreased after 12 h of dissolution in [emim]OAc which were 79.3, 80.3 and 79.3 % to 39.8, 38.3 and 40.2 %, respectively. The accumulated glucose released was reached to a level approximately 13.8 mg/ml which was at least ten-fold higher than that of untreated fibers samples which only 3.19 mg/ml. From NMR study, the six signals of the unmodified anyhdroglucose unit appear clearly at 102.5 (C-1), 79.67 (C-4), 76.44 (C-5), 75.24 (C-3), 74.19 (C-2) and 60.15 ppm (C-6). Through swelling and dissolution mechanism of fibers, disintegration into rod-like fragments, ballooning followed by dissolution and homogeneous swelling were clearly observed for both oil palm biomass and cellulose fibers. Observation under scanning electron micrograph (SEM) showed that, the loose structures of oil palm biomass fibers and a greater part of the smaller fibrils seemed to be absent in the cellulose-rich solids were observed after regeneration.

Abstrak tesis yang dikemukakan kepada Senat Universiti Putra Malaysia bagi memenuhi syarat bagi mendapatkan Ijazah Master Sains

PEMELARUTAN HASIL BUANGAN KELAPA SAWIT DALAM CECAIR BERION ALKIL-IMIDAZOLIUM UNTUK HIDROLISIS ENZIM YANG CEKAP

Oleh

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Oktober 2011

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Pemelarutan gentian biojisim kelapa sawit oleh cecair berion (ILs) telah dikaji secara perbandingan. Cecair berion iaitu 1-etil-3-metilimidazolium klorida ([emim]Cl), 1-butil-3-metilimidazolium klorida ([bmim]Cl) dan 1-etil-3-metilimidazolium asetik ([emim]OAc) telah digunakan untuk pemelarutan biojisim kelapa sawit dan gentian selulosa termasuklah daripada tandan kelapa sawit kosong (EFB), pelepah kelapa sawit (OPF) dan batang kelapa sawit (OPT). Proses pemelarutan 5 % berat (0.1 g) gentian/ILs dijalankan pada suhu pemanasan 100 °C dan di bawah pengaruh gas nadir. Masa pemanasan untuk pemelarutan lengkap 5 % berat gentian/ ILs yang dipanaskan telah dioptimum dan dicatatkan. [emim]OAc telah membuktikan bahawa ia adalah pelarut yang paling baik untuk tujuan pemelarutan gentian biojisim kelapa sawit berbanding dengan [emim]Cl dan [bmim]Cl. Gentian yang dilarutkan di dalam [emim]OAc menunjukkan lebih daripada 95 % b/b pemelarutan selepas dipanaskan selama 16 jam, sementara gentian EFB dan OPF larut sekitar 85% selepas lebih 48

jam dipanaskan di dalam [emim]Cl dan [bmim]Cl. Sementara itu, gentian selulosa telah berjaya dilarutkan selepas 2-3 jam pemanasan. Spektroskopi infra-merah (FT-IR) jelas menunjukkan jalur penyerapan pada 1729 cm^{-1} and 1512 cm^{-1} yang merujuk kepada ketiadaan hemisellulosa dan lignin selepas proses penghasilan semula iaitu semasa proses pembasuhan. Proses penghasilan semula telah menghasilkan bahan kaya selulosa yang bersifat amorfos (selulosa II), sekaligus merendahkan nilai indeks kristal (C*r*I). Nilai C*r*I untuk bahan kaya selulosa yang telah terhasil semula daripada gentian EFB, OPF dan OPT menurun daripada 79.3, 80.3 dan 79.3 % kepada 39.8, 38.3 dan 40.2 % selepas 12 jam pemelarutan di dalam [emim]OAc. Glukosa terhasil adalah sebanyak 13.8 mg/ml, iaitu kira-kira sepuluh kali ganda lebih tinggi berbanding sampel yang tidak dirawat yang hanya 3.19 mg/ml. Daripada analisis NMR, enam isyarat unit anhidroglukosa tidak diubahsuai muncul dengan jelas pada 102.5 (C-1), 79.67 (C-4), 76.44 (C-5), 75.24 (C-3), 74.19 (C-2) dan 60.15 ppm (C-6). Melalui mekanisma pembengkakan dan pemelarutan gentian, penceraian secara memanjang kepada ceraian berbentuk rod yang besar, bengkakan membelon diikuti dengan pemelarutan dan pembengkakan setara jelas diperhatikan untuk kedua-dua gentian kelapa sawit dan sellulosa. Pemerhatian menerusi mikroskopi pengimbas elektron (SEM) menunjukkan struktur gentian biojisim kelapa sawit adalah sedikit longgar dan sebahagian besar gentian yang lebih kecil didapati tidak wujud di dalam bahan kaya selulosa selepas melalui proses penghasilan semula.

ACKNOWLEDGEMENTS

Alhamdulillah, praises to ALLAH s.w.t., for giving me the strength to endure all challenges and complete this study.

Firstly, I would like to extend my heartfelt thanks to my supervisor, Prof. Dr. Mohd Basyaruddin Abdul Rahman, who gave me the opportunity to conduct his research, for the great concern, help, advices, persistence encouragement and directed me through nearly two years of thesis work. His supportive discussions and enthusiasm for chemistry always replenished my energy to work. I'm also indebted to my co-supervisor, Prof. Dr. Dzulkefly Kuang Abdullah and Dr. Astimar Abdul Aziz for their invaluable guidance, encouragement and criticism, which kept me in a right track. Without these people, this thesis would not have been possible.

To my research group, Enzyme and Microbial Technology Research Group UPM (EMTECH), especially thanks to Prof. Dato' Dr. Abu Bakar Salleh, Prof. Dr. Mahiran Basri and Prof. Dr. Raja Noor Zaliha Raja Abd Rahman for their valuable advice and suggestions during weekly meeting. I would also like to thank Dr. Emilia Abdul Malek, Dr. Bimo Ario Tejo, and Dr. Naz Chaibakhsh for their opinion, support and discussion during completion of this thesis.

A special thanks to the staff members of the Microscopy and Microanalysis Unit, Institute of Bioscience UPM especially En. Mohd Hafizad Rahmat and En. Rafiuz Zaman Haroun, staff of Nuclear Magnetic Resonance (NMR) instrument, En. Johadi Iskandar and En. Mohd Zahid and also all the staff of Malaysian Palm Oil Board (MPOB), Bangi Lama, especially Cik Nik Fadzilah, Pn. Suchirah, Pn. Azizah, Pn.

Siti, Pn. Ina, Cik Rahayu, En. Mahadi and En. Mohd. Hafiz who were so helpful and cooperation in many ways during the course of the study.

I want to thank all of my lab mates in lab 401 especially to Emmy Maryati, Noraini, Nur Fariza, Uswatun Hasanah, Nursyamsyila, Norazlinaliza, Hanim, Mahashanon, Devandran, Khairulazhar, Mohd Rizal, Asrul Farrish, Peter Chang Ngi Lee, Brian Teo, Casey, Siti Safrina, Shamsul Hana and Nahrul Hayawin, master student from MPOB for the bond of friendship and for making my stay in UPM a bearable one with many sweet memories and experiences. Without all of you, I would not have made it this far.

Love and thanks to my family, especially my mom and dad, there is no way I can adequately express my gratitude in words, for the support, love and encouragement you have shown me throughtout the years and for many sacrifices that you have made for me. Last but not least, thank to Ministry of Science, Technology and Innovation Malaysia (MOSTI) for scholarship *National Science Fellowship* (NSF) and Universiti Putra Malaysia for financial support and facilities.

This 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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DECLARATION

I declare that the thesis is based on 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 currently, submitted for any other degree at Universiti Putra Malaysia or other institutions.

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Date: 10 OCTOBER 2011

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