INVESTIGATION ON THE EFFECT OF REACTION PARAMETERS TO THE PALM OIL CROSS-METATHESIS USING 1-OCTENE AND RUTHENIUM BASED CATALYST

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SUPERVISOR'S DECLARATION

I hereby declare that I have checked this thesis and, in my opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Master of Science.

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STUDENT’S DECLARATION

I hereby declare that the work in this 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 or concurrently submitted for any other degree at Universiti Malaysia Pahang or any other institutions.

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ABSTRAK

Penggunaan poliol terbitan minyak sawit untuk penghasilan poliuretana adalah terhad kerana nilai hidroksilnya yang rendah yang menyebabkan rangkaian poliuretana tidak sempurna. Poliol dengan nilai hidroksil yang dikehendaki boleh dihasilkan daripada minyak sawit jika ia diubah secara kimia menggunakan metatesis silang (CM) kepada produk olefin dan ester dengan ikatan berganda terminal sebelum penghasilan poliol. Proses CM minyak tumbuhan menggunakan etilena telah dihalang oleh kepilihan yang lemah dan hasil yang rendah disebabkan penyahaktifan mangkin dan perantaraan pemangkinnya (ruthenium methylidene), sebagai tambahan kepada tindak balas metatesis kendiri yang tidak diingini. Kajian itu bertujuan untuk mengenal pasti keadaan operasi terbaik CM minyak sawit menggunakan 1-octene, yang dipercayai dapat menyekat pembentukan produk sampingan dan perantara pemangkin yang tidak diingini, membenarkan pemangkin generasi kedua Hoveyda Grubbs berasaskan rutenium (HGC ke-2) mengekalkan aktiviti dan kestabilannya. Kesan parameter yang berbeza terhadap prestasi oktenolisis minyak sawit telah dijalankan menggunakan satu faktorial pada masa (OFAT) dalam sistem kelompok. Perubahan dalam parameter seperti masa tindak balas, suhu, nisbah molar bahan tindak balas 1-oktena kepada minyak sawit ($M_{OC/PO}$)/nisbah molar 1-oktena kepada triolein ($M_{OC/TR}$) dan beban mangkin HGC ke-2 dikaitkan dengan penukaran triolein, hasil 1-decene dan kepilihan 1-decene dikira berdasarkan jumlah hasil tindak balas. Produk seperti 1-decene dan glyceryl tri-9-decenoate telah dikira menggunakan Gas Chromatography-Mass Spectrometry (GC-MS). Analisis Resonans Magnetik Nuklear Proton (1H NMR) digunakan untuk mengesahkan perubahan struktur trigliserida minyak sawit kepada olefin lain dalam campuran tindak balas. Penukaran maksimum, hasil dan kepilihan diperoleh apabila metathesis silang minyak sawit dengan $M_{OC/TR}$ sebanyak 8 dan pemuatan mangkin 5 ppm berlaku pada 343 K selama 2 jam yang menghasilkan 97.78% penukaran triolein, 293.36% daripada hasil 1-decene. Selepas tiga ujian pemangkin berturut-turut dijalankan pada keadaan operasi terbaik, penurunan yang tidak ketara dalam prestasi tindak balas membuktikan bahawa pemangkin HGC ke-2 masih kekal aktif dan stabil. Ia juga didapati bahawa model undang-undang kuasa meramalkan profil kepekatan metatesis silang minyak sawit menggunakan 1-oktena, menganggarkan tenaga pengaktifan sebanyak 22583 J/mol.

ABSTRACT

The use of palm oil-derived polyol for the production of polyurethane is restricted because of its low-hydroxyl value that causes imperfect polyurethanes network. The polyol with desired hydroxyl value could be produced from palm oil if it is chemically transformed using cross metathesis (CM) into olefin and ester products with terminal double bonds prior to the production of polyols. The plant oil CM process using ethylene has been hampered by its poor selectivity and low yield due to the catalyst deactivation and its catalytic intermediate (ruthenium methylidene), in addition to the undesired self-metathesis reaction. The study aimed to identify the best operating condition of the palm oil CM using 1-octene, which is believed to supress the formation of side products and unwanted catalytic intermediate, allowing the ruthenium-based Hoveyda Grubbs second generation catalyst (2nd HGC) to maintain its activity and stability. The effect of different parameters on cross-metathesis of palm oil performance was carried out using one factorial at time (OFAT) in a batch system. The changes in parameters like reaction times, temperatures, reactant molar ratios of 1-octene to palm oil ($M_{OC/PO}$)/molar ratio of 1-octene to triolein ($M_{OC/TR)}$ and 2nd HGC catalyst loadings were correlated to the triolein conversion, 1-decene yield and selectivity of 1-decene calculated based on the amount of the reaction products. The products such as 1-decene and glyceryl tri-9-decenoate were quantified using Gas Chromatography-Mass Spectrometry (GC-MS). Proton Nuclear Magnetic Resonance (1H NMR) analysis was used to verify the structural changes of palm oil triglyceride to other olefins in the reaction mixture. The maximum conversion, yield and selectivity were obtained when the palm oil was cross-metathesised with $M_{OC/TR}$ of 8 and catalyst loading of 5 ppm occurred at 343 K for 2 h which resulted in 97.78% of triolein conversion, 293.36% of 1-decene yield. After three consecutive catalytic tests carried out at best operating condition, the insignificant decline in the reaction performance evidenced that the 2nd HGC catalyst still remained active and stable. It was also found that the power-law model well predicted the concentration profile of the cross-metathesis of palm oil using 1-octene, estimating activation energy of 22583 J/mol. This study developed a new technically feasible process for adding value to palm oil, enable the use of palm oil as a feedstock for the production of polyol with required hydroxyl value.

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