INVESTIGATION OF REACTION PARAMETERS AND KINETICS FOR THE SYNTHESIS OF SORBITOL-BRANCHED AZELAIC ACID ESTER

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We hereby declare that we have checked this thesis and in our opinion, this thesis is adequate in terms of scope and quality for the award of the degree of Doctor of Philosophy.

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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

Poliol ester yang boleh diperbaharui dihasilkan melalui proses pengesteran antara isosorbid (ISB) dan asid azelaik (AA), bertujuan mengantikan poliol ester yang diperbuat daripada bahan petroleum. Penghasilan isosorbid-asid azelaik ester (IAAE) ini tidak diselidik secara mendalam dan tidak dilaporkan dalam laporan kajian akademik. Sorbitol (SL) atau anhidrida asid lemak ester (SFAE) biasanya dihasilkan melalui proses yang dimangkin oleh pemangkin homogen. Kelemahan proses ini adalah penghasilan produk yang mempunyai warna yang tidak dikehendaki, penghakisan dan pemprosesan hiliran yang rumit. Faktor penghasilan SFAE diluar spesifikasi adalah reaksi kinetik yang tidak dikenalpasti dan hubungan antara komposisi bahan (SL dan anhidridanya) dengan parameter operasi. Kajian terkini menyiasat kesan operasi parameter dan kinetik terhadap penghasilan IAAE melalui proses jujukan (penghidratan SL dan pengesteran antara ISB dan AA) yang menggunakan pemangkin heterogen. Teknik kromatografi dibangunkan bagi mengenalpasti kuantiti bahan ketika proses penghasilan ester kerana ketiadaan bahan piawai IAAE. Bahan kajian hendaklah melalui proses pengolahan (*silylation II*) sebelum dianalisis. Teknik analisis ini mestilah menggunakan pemanasan yang stabil dan pengurangan aliran gas pembawa, untuk menghasilkan graf yang simetri dan tajam. Teknik kromatografi gas juga menghasilkan keputusan yang terbaik berbanding teknik-teknik yang lain. Sebelum proses pengesteran, penghidratan SL menggunakan pemangkin heterogen (Amberlyst 36 (AM 36)) bagi menghasilkan anhidridanya. Proses penghidratan ini dijalankan mengikut beberapa faktor penting. Peningkatan muatan pemangkin daripada 5 ke 7 wt% didapati tidak memberikan kesan terhadap peningkatan penghasilan ISB. Suhu tinggi akan meningkatkan kadar tindak balas dan pemanjangan masa akan memaksimumkan penghasilan ISB. Prestasi terbaik oleh AM 36 dalam penghasilan ISB berbanding pemangkin yang lain seperti dalam laporan kajian sebelum ini. Selepas 4 jam, penghidratan SL menghasilkan >99% ISB pada suhu 423 K dengan penggunaan 5 wt% pemangkin dan 300 RPM. Tindak balas kinetik bagi proses penghidratan SL di kaji dalam keadaan bebas rintangan pemindahan jisim pada suhu 373 K sehingga 423 K. Data kinetik yang diperoleh menepati model Langmuir-Hinshelwood (LH2) dengan mengambil kira faktor tindak balas sampingan. Tenaga pengaktifan bagi proses penghidratan SL ke sorbitan (ST), ST ke ISB dan ISB ke produk sampingan termasuk humin, masing-masing ialah 109.22, 109.46 dan 104.17 kJ/mol. ISB yang terhasil daripada proses penghidratan SL akan digunakan dalam proses pengesteran bersama AA dengan menggunakan grafit sebagai pemangkin untuk menghasilkan monomer bagi poliol ester yg boleh diperbaharui. Parameter tindak balas kritikal yang mempengaruhi taburan jenis produk disiasat. Antaranya adalah kadar kacauan (0-500 RPM), saiz zarah pemankin (18-120 MESH), muatan pemangkin (0-2 wt%), nisbah molar AA kepada ISB (1:1 ke 1:5 dan 1:1 ke 3:1) dan suhu tindak balas (373-473 K). Pada keadaan bebas rintangan pemindahan jisim, penghasilan maksima ISB monoazelat (ISMA) adalah mengikut keadaan berikut; muatan grafit ialah 1 wt% saiz zarah pemankin iaitu 25-35 MESH, kesamarataan molar antara asid azelaik dan ISB dan kadar kacauan selaju 300 RPM. Manakala, suhu operasi terbaik adalah pada 433 K dengan mempertimbangkan faktor kadar tindak balas dan kualiti produk. Model Langmuir Hinshelwood Hougen Watson (LHHW) dapat meramalkn profil kepekatan ISB dan AA dalam proses pengesteran. Tenaga pengaktifan bagi proses pengesteran ini adalah dianggarkan sebanyak 26.12 kJ/mol. Penyelidikan terkini membuktikan bahawa proses yang dimangkin oleh pemangkin heterogen bagi reaksi berjujukan (penghidratan sorbitol diikuti oleh pengesteran ISB) menjanjikan penghasilan IAAE pada keadaan sederhana.

ABSTRACT

The renewable polyol ester produced from the esterification of isosorbide (ISB) and azelaic acid (AA) is substitute to petro-based polyol ester. The reaction of producing isosorbide azelaic acid ester (IAAE) has not been researched intensively and reported in the open literature. Sorbitol or its anhydrides fatty acid ester (SFAE) is typically produced by a homogeneously catalysed process which suffers with the undesired product colouration, corrosive process environment and complex downstream separation process. The unidentified reaction kinetics and correlation of the composition distribution of the sorbitol and its anhydrides with the operating parameters could render to the off specification SFAE. The present work investigated the effect of reaction parameters and kinetics for the synthesis of IAAE through sequential reactions constituted of heterogeneously catalysed sorbitol (SL) dehydration and ISB esterification with AA. Owing to the unavailability of the IAAE standards, the chromatography techniques to quantify the reactants during the esterification process was developed. The gas chromatography analysis of samples derivatised using silylation II with steady heating and reduced carrier gas flow rate outperformed others, producing identical and sharp peak for AA, SL and its anhydrides. Prior to the esterification reaction, the present study dehydrated SL to its anhydrides using the best heterogeneous catalyst, Amberlyst 36 at different important operating parameters. The increase of catalyst loading from 5 to 7 wt% did not significantly affect the ISB yield. A higher temperature increased the reaction rate, whereas a prolonged reaction time increased the conversion of SL and yield of ISB to the maximum. In terms of giving a higher ISB yield during SL dehydration, Amberlyst 36 was found to outperform the other resin catalysts reported in the literature. Both SL conversion and ISB yield of >99% were recorded after a 4 h reaction at 423 K with a catalyst loading of 5 wt% and stirring speed of 300 RPM. The reaction kinetics was evaluated under a mass transfer resistances free condition at the reaction temperature ranged from 373 K to 423 K. The kinetic data well fitted to the Langmuir-Hinshelwood (LH2) model that took side reaction into account. The activation energy for dehydration SL to sorbitan (ST), dehydration ST to ISB and dehydration of SL to other side products such as humins were 109.22, 109.46 and 104.17 kJ/mol respectively. ISB produced from SL dehydration was reacted with AA catalysed by graphite to synthesis the monomer for renewable polyol ester. The critical parameters that influence the product distributions were investigated. It encompassed the stirring speed (0-500 RPM), catalyst particle size (18-120 MESH), catalyst loading (0-2 wt%), the molar ratio of AA to ISB (1:1 to 1:5 and 1:1 to 3:1) and reaction temperature (373-473 K). The best mass-transfer resistance-free condition that maximising the amount of isosorbide monoazelate (ISMA) was found in the reaction catalysed by 1 wt% of graphite catalyst with the particle size ranged 25-35 MESH and adopted an equimolar of AA and ISB with stirring speed of 300 RPM. Meanwhile, the best reaction temperature was identified as 433 K, considering the trade-off between reasonable reaction rate and product quality. The Langmuir Hinshelwood Hougen Watson (LHHW) model well predicted the concentration profile of the esterification of ISB with AA, estimating activation energy of 26.12 kJ/mol. The current research has proven that the heterogeneously catalysed process, with sequential reactions of the SL dehydration followed by ISB esterification, is promising method to produced IAAE at milder condition.

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