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PRODUCTION OF MESOXALIC ACID FROM GLYCEROL OXIDATION BY LACCASE/2,2,6,6-TETRAMETHYLPIPERIDINE-1-OXYL (LACASSE/TEMPO) SYSTEM: EFFECT OF PROCESS PARAMETERS AND KINETIC STUDY

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ABSTRAK

Kenaikan harga bahan api fosil telah mendorong industri minyak untuk mencari sumber tenaga boleh diperbaharui, biodiesel. Gliserol, bahan sampingan utama bagi pengeluaran biodiesel wujub sebagai bahan yang berkos rendah dan blok binaan yang sangat serba guna. Nyata sekali, gliserol telah dikanali sebagai sebatian yang menggalakkan dalam mendapatkan bahan kimia berharga melalui pengoksidaan. Dalam kajian ini, pengoksidaan gliserol dengan menggunakan 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) dengan kehadiran laccase untuk menghasilkan satu bahan ubat anti HIV yang berpotensi iaitu asid mesoxalic telah dikaji. Kajian ini dijalankan dengan memberi tindak balas gliserol dengan TEMPO dan laccase dari *Trametes versicolor* dan menukarkan keadaan tindak balas seperti suhu (5 °C – 61 °C), pH (3.5 – 6.15), nisbah molar gliserol kepada TEMPO (1:0 - 100:3) dan nisbah TEMPO kepada laccase (mM: U/ml) (9:0 - 9:4).. Satu eksperimen awal telah dijalankan sebagai pemeriksaan sebelum penyiasatan keadaan tindak balas pada produk pengoksidaan di mana keadaan tindak balas telah ditetapkan pada 25 °C , pH 4.5, nisbah gliserol/TEMPO 10:3 dan nisbah TEMPO/laccase 9: 3. Kajian kinetik telah dilakukan untuk menyiasat kadar tindak balas. Bahan tindak balas pengoksidaan dan produk telah dinilai dengan menggunakan HPLC manakala aktiviti laccase telah ditentukan dengan menggunakan ujian ABTS. Keadaan tindak balas terbaik didapati ialah 19 °C, pH 5.5, nisbah 1:3 bagi gliserol kepada TEMPO dan nisbah 9:3 bagi TEMPO kepada laccase selepas menjalankan eksperimen. Model homogen telah digunakan untuk memadankan data kinetik melalui MATLAB. TEMPO dimangkinkan oleh kuprum-bergantung oxidase, laccase, kepada oxoammonium kation yang terlibat dalam pengoksidaan aerobik. Kehadiran laccases membenarkan pertumbuhan semula kation oxoammonium, dengan itu, proses pengoksidaan dapat diteruskan selagi laccases aktif. Laluan mekanistik yang berbeza ini disebabkan oleh perbezaan dalam potensi redoks antara TEMPO dan laccase. Tiada dihydroxyacetone dikesan dalam pengoksidaan terpilih gliserol dengan laccase/TEMPO. Ia menunjukkan bahawa kumpulan hidroksil primer telah terpilih untuk dioksidakan kepada gliseraldehid. Asid mesoxalic diperoleh adalah 0.0712 M pada keadaan tindak balas suboptimal. Ia adalah kenaikan dua-lipatan daripada keputusan awal. Ini jelas menunjukkan betapa pentingnya keadaan tindak balas ke arah pembentukan produk. Selain itu, kajian ini juga menunjukkan bahawa pembentukan asid mesoxalic mengguanakan tenaga yang kurang dalam keadaan yang terbaik berbanding dengan kaedah konvensional yang memerlukan suhu yang tinggi. Tenaga pengaktifan bagi pembentukan asid mesoxalic daripada asid tartronik adalah 107.17 kJ/mol yang menunjukkan tenaga minimum yang diperlukan untuk ia berlaku adalah yang paling tinggi berbanding dengan langkah-langkah lain. Nilai bagi faktor pra-eksponen dan pemalar kadar tindak balas yang tertinggi untuk langkah tindak balas ini mencadangkan bahawa perlanggaran molekul adalah yang tertinggi. Oleh yang demikian, suhu amat terjejas pada pembentukan asid mesoxalic.

ABSTRACT

The increase of fossil fuel price has prompted the oil industry to look for renewable energy sources, biodiesel. Glycerol, the main by-product of biodiesel production has the potential of being a low-cost and extremely versatile building block. Significantly, glycerol has been touted as a promising compound in obtaining valuable chemicals via oxidation route. In this study, oxidation of glycerol by using 2,2,6,6-tetramethylpiperidine-N-oxyl (TEMPO) in the presence of laccase to produce a potential anti HIV drug ingredient which is mesoxalic acid was investigated. The study was conducted by reacting glycerol with TEMPO and laccase from *Trametes versicolor* and varying the reaction conditions such as temperature (5 °C – 61 °C), pH (3.50 - 6.15), molar ratio of glycerol to TEMPO (1:0 - 100:3) and ratio TEMPO to laccase (mM: U/ml) (9:0 - 9:4). A preliminary experiment in which the reaction conditions was fixed at 25 °C, pH 4.5, 10:3 of glycerol/TEMPO ratio and TEMPO/laccase ratio of 9:3 was conducted as screening before the investigation of reaction conditions on the oxidation products. Kinetic study was performed to investigate the reaction rate. Oxidation reactants and products were quantified by using HPLC whilst laccase activity was determined by using ABTS assay. The best reaction conditions after conducting experiments were found to be 19 °C, pH 5.5, ratio 1:3 of glycerol to TEMPO and ratio 9:3 of TEMPO to laccase. A homogeneous model was used to fit the kinetic data via MATLAB. TEMPO was catalysed by the copper-dependent oxidase, laccase to oxoammonium cations which involved in the aerobic oxidation. The presence of laccases allowed the regeneration of oxoammonium cations, thus, the oxidation process could proceed as long as laccase were active. This different mechanistic pathway was attributed to the difference in redox potential between TEMPO and laccase. The selective oxidation of glycerol by laccase/TEMPO results in no dihydroxyacetone detected. It demonstrated that the primary hydroxyl group had been selectively oxidised to glyceraldehyde. Mesoxalic acid attained was 0.0712 M at the suboptimal reaction conditions obtained. It was two-fold increment from that in the preliminary results. This clearly showes the importance of reaction conditions towards the products formation. Moreover, this study also shows that mesoxalic acid formation consumed less energy in the best condition compared to the conventional method which required high temperature. The activation energy for the formation of mesoxalic acid from tartronic acid was 107.17 kJ/mol which indicated the minimum energy required for it to occur was the highest compared to other steps. The highest in pre-exponential factor and rate constant for this reaction step suggested that the collision of molecules was the greatest. Hence, the temperature affected greatly on the formation of mesoxalic acid.