ESTERIFICATION OF FREE FATTY ACID IN USED COOKING OIL USING SULPHONATED HYPERCROSSLINKED EXCHANGE RESIN AS CATALYST

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Thesis submitted in fulfilment of the requirements
for the award of the degree of
Master of Science

Faculty of Chemical and Natural Resources Engineering

UNIVERSITI MALAYSIA PAHANG

JUNE 2017

ABSTRAK

Proses pengesteran adalah proses rawatan yang digunakan untuk mengurangkan asid lemak bebas yang terkandung di dalam minyak berasid. Kebiasaanya, asid lemak bebas yang terkandung di dalam minyak akan menyebabkan pembentukkan sabun dan mengurangkan jumlah asid lemak metil ester yang dihasilkan. Tujuan utama kajian ini adalah untuk mengkaji proses pengesteran asid lemak bebas yang terkandung di dalam minyak masak terpakai buatan menggunakan hypercrosslik resin yang disulfonatkan (SHER) sebagai pemangkin. Kajian ini dibahagikan kepada dua peringkat kajian yang penting. Peringkat pertama membincangkan proses penyediaan SHER melalui teknik sebaran kering diikuti dengan proses sulfonasi. Kesan kepekatan monomer/co-monomer, kepekatan crosslinker, nisbah pemangkin asid Lewis dan reagen sulfonasi ke atas ciri-ciri fizikokimia SHER telah dikaji untuk menghasilkan pemangkin yang terbaik. Pada peringkat ini, pemangkin yang terbaik telah berjaya dihasilkan dengan menggunakan 80% stirena (St), 20% vinilbenzyl klorida (VBC), 1wt% ethylina glikol dimethacrylate (EGDMA), 1:1 nisbah molar $FeCl_3$: CH_2Cl dan 4wt% asid sulfurik. SHER yang dihasilkan mempunyai liang permukaan yang tinggi dengan luas permukaan sebanyak 836 m^2 g^{-1}. Ia juga mempunyai kebolehan untuk bertahan sehingga suhu ke 398°C dan mempunyai keasidan sebanyak 5.1 mmol g^{-1}. Peringkat kedua memfokuskan prestasi SHER di dalam proses pengesteran asid lemak bebas menggunakan minyak masak terpakai buatan sebagai bahan mentah. Proses pengesteran telah dijalankan di dalam sistem kelompok dan beberapa parameter seperti muatan pemangkin, suhu dan nisbah molar telah dikaji. SHER telah berjaya memangkin tindak balas tersebut dan telah mencapai 97% penukaran asid lemak bebas pada kadar kacauan 150 rpm, 5wt% muatan pemangkin, 60°C suhu tindak balas dan 12:1 nisbah molar metanol (MeOH) kepada minyak masak terpakai buatan. Semasa proses guna semula dijalankan, lebih kurang 40% aktiviti pemangkin telah berkurang selepas digunakan sebanyak lima kali. Pengurangan ini adalah disebabkan oleh liang pemangkin telah tersumbat semasa tindak balas berlaku dan telah menghalang reaktan untuk memasuki kawasan yang aktif. Keberkesanan SHER telah dibandingkan dengan beberapa komersial pemangkin (Diaion RCP145H, PK228LH and SK1BH) dan eksperimen tersebut telah dijalankan pada keadaan tindak balas yang sama. Daripada keputusan yang diperoleh, SHER telah menunjukkan penukaran dan kadar tindak balas yang paling tinggi berbanding dengan pemangkin-pemangkin lain. Prestasi SHER yang cemerlang adalah disebabkan luas permukaan, isipadu liang, kandungan sulfur dan keasidan yang tinggi.

ABSTRACT

Esterification reaction is a pretreatment method used to reduce the free fatty acids (FFA) content in acidified oil. Normally, the presence of high FFA content contributes to saponification reaction and thus, decreases the yield of fatty acid methyl ester (FAME) produced. The usage of ion exchange resin (IER) as a catalyst has been widely used to reduce the FFA content because they can catalyse the esterification reaction under mild conditions. However, current IER are having low acidic acid sites, moderate surface area and low thermal stability. This study focuses on the esterification process of FFA in simulated used cooking oil (SUCO) using self-synthesised sulphonated hypercrosslinked exchange resin (SHER) as catalyst. This study was divided into two stages. The first stage focused on the synthesis and characterisation of SHER, prepared via non-aqueous dispersion (NAD) technique followed by sulphonation process. The effect of monomer/co-monomer concentration, crosslinker concentration, Lewis acid catalyst ratio, and sulphonation reagent on the physicochemical characterisation of the resin were investigated to produce the best catalyst beads. From this stage, the best SHER beads has successfully developed at the condition of 80% of styrene (St), 20% of vinylbenzyl chloride (VBC), 1wt% of ethylene glycol dimethacrylate (EGDMA), 1:1 of molar ratio of $FeCl_3$: CH_2Cl, and 4wt% of sulphuric acid. The newly developed SHER possesses a high surface porosity with approximately 836 m^2 g^{-1} surface area. It has the ability to withstand high temperature up to 398°C with the acidity values at 5.1 mmol g^{-1}. The second stage concentrated on the performance of SHER in the esterification of FFA using SUCO as a feedstock. The esterification reaction was carried out in a batch system and the effect of various parameters such as catalyst loading, temperature, and molar ratio were investigated. SHER had successfully catalysed the reaction and achieved 97% of FFA conversion at 150 rpm, 5wt% of catalyst loading, 60°C, and 12:1 of methanol (MeOH) to SUCO molar ratio. During reusability study, the catalyst activity decreased for about 40% after five cycles of reaction. The decrease in FFA conversion was due to the pore blockage during the reaction and hence, blocked the reactants from accessing the active sites. The performance of SHER was compared with selected commercial resins (i.e., Diaion RCP145H, Diaion PK228LH, and Diaion SK1BH) and the experiments were conducted at the same reaction conditions. SHER showed the highest conversion and reaction rate compared to other catalysts. The excellence performance of SHER was due to the high amount of surface area, pore volume, sulphur content, and acidity owned by the SHER.