RENEWABLE LEVULINIC ACID PRODUCTION CATALYZED BY IRON MODIFIED HY ZEOLITE AND FUNCTIONALIZED IONIC LIQUID

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Verily, with every hardship comes ease (Holy Qur'an 94:6)
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Levulinic acid is a versatile platform chemical that can be derived from biomass as an alternative to fossil fuel resources. In this study, a series of heterogeneous iron modified HY zeolites (Fe/HY zeolite): 5% Fe/HY, 10% Fe/HY, 15% Fe/HY, and homogeneous functionalized ionic liquids (FIL): 1-butyl-3-methylimidazolium tetrachloroferrate ([BMIM][FeCl₄]), 1-sulfonic acid-3-methylimidazolium chloride ([SMIM][Cl]), 1-sulfonic acid-3-methylimidazolium tetrachloroferrate ([SMIM][FeCl₄]), were synthesized, characterized, and tested as a catalyst for glucose conversion to levulinic acid. The properties of Fe/HY zeolite were characterized using x-ray diffraction (XRD), field emission scanning electron microscopy - energy dispersive x-ray (FESEM-EDX), x-ray fluorescence (XRF), Fourier transform infrared spectroscopy (FTIR), nitrogen (N₂) physisorption, thermal gravimetric analysis (TGA), temperature programmed desorption of ammonia (NH₃-TPD), and pyridine-FTIR. The synthesized FIL were characterized using carbon, hydrogen, nitrogen, and sulfur (CHNS) elemental analysis and carbon-13 and proton nuclear magnetic resonance (¹³C and ¹H NMR). The acidic properties of FIL were examined using pyridine-FTIR, Hammett function, and acid-base titration. Experimental results indicated that the selective Fe/HY zeolite and FIL for levulinic acid production from glucose were 10% Fe/HY and [SMIM][FeCl₄], with 62% yield at 180 °C for 3 h, and 68% yield at 150 °C for 4 h, respectively. For Fe/HY zeolite, catalyst with large surface area, high concentration of acid sites and appropriate ratio of Brønsted to Lewis acids seemed suitable for levulinic acid production. It was also discovered FIL which contained both Brønsted and Lewis acid sites, offered a good catalytic performance. Optimization of levulinic acid yield from glucose and oil palm fronds (OPF) were conducted using the response surface methodology (RSM). At optimum conditions, 61.8% and 19.6% of levulinic acid yields were attained from glucose and OPF, respectively, over 10% Fe/HY zeolite. Meanwhile, by using [SMIM][FeCl₄] 69.2% and 24.8% of levulinic acid yields were produced from glucose and OPF, respectively. Both catalysts can be reused without significant loss of catalytic activity. Kinetic studies of glucose conversion to levulinic acid were performed using both 10% Fe/HY zeolite and [SMIM][FeCl₄]. The kinetic parameters obtained were lower and comparable with previous catalysts employed in glucose conversion to levulinic acid. This study demonstrated the potential of proposed catalysts to be used in a biorefinery for processing renewable feedstocks at mild process conditions.
Asid levulinik adalah bahan kimia asas serb pada guna yang dapat dihasilkan daripada biojisim sebagai alternatif kepada sumber bahan api fosil. Dalam kajian ini, satu siri zeolit HY terubahsuai ferum heterogen (zeolit Fe/HY): 5% Fe/HY, 10% Fe/HY, 15% Fe/HY, dan cecair ionik kumpulan fungsian homogen (FIL): 1-butil-3-metilimidazolium tetrakloroferat ([BMIM][FeCl₄]), 1-asid sulfonik-3-metilimidazolium klorida, ([SMIM][Cl]), 1-asid sulfonik-3-metilimidazolium tetrakloroferat ([SMIM][FeCl₄]), disintesis, dicirikan, dan diuji sebagai pemangkin untuk penukaran glukosa kepada asid levulinik. Pencirian sifat-sifat zeolit Fe/HY dilakukan menggunakan pembelauan sinar-x (XRD), mikroskopi elektron pengimbas pancaran medan - sebaran sinar-x (FESEM-EDX), pendarfluor sinar-x (XRF), spektroskopi inframerah transformasi Fourier (FTIR), penjeraapan fizik nitrogen (N₂), analisis gravimetri terma (TGA), penyahjerapan berprogram suhu ammonia (NH₃-TPD), dan FTIR-piridina. FIL yang telah disintesis dicirikan menggunakan analisis unsur karbon, hidrogen, nitrogen, dan sulfur (CHNS) dan resonans magnet nukleus karbon-13 dan proton (¹³C dan ¹H NMR). Sifat berasid bagi FIL dikaji menggunakan FTIR-piridina, fungsi Hammett, dan pentitratian asid-bes. Keputusan eksperimen menunjukkan bahawa zeolit Fe/HY dan FIL yang selektif bagi penghasilan asid levulinik daripada glukosa adalah 10% Fe/HY dan [SMIM][FeCl₄], masing-masing dengan hasil sebanyak 62% pada suhu 180 °C selama 3 j, dan hasil sebanyak 65% pada 150 °C selama 4 j. Untuk zeolit Fe/HY, pemangkin dengan luas permukaan yang besar, kepekatan yang tinggi bagi tapak asid dan nisbah yang sesuai untuk asid Lewis hingga Brønsted tampak sesuai untuk penghasilan asid levulinik. Kajian juga menemukan FIL yang mengandungi kedua-dua tapak asid Lewis dan Brønsted memberikan prestasi pemangkin yang baik. Pengoptimuman hasil asid levulinik daripada glukosa dan pelepah sawit (OPF) telah dilakukan menggunakan kaedah gerak alas permukaan (RSM). Pada keadaan optimum, hasil asid levulinik sebanyak 61.8% dan 19.6% masing-masing telah dicapai daripada glukosa dan OPF, menggunakan 10% zeolit Fe/HY. Sementara itu, dengan menggunakan [SMIM][FeCl₄], sebanyak 64.2% dan 24.3% asid levulinik masing-masing telah dihasilkan daripada glukosa dan OPF. Kedua-dua pemangkin dapat digunakan semula tanpa kehilangan aktiviti katalitik yang signifikan. Kajian kinetik penukaran glukosa kepada asid levulinik telah dilakukan menggunakan kedua-dua 10% zeolit Fe/HY dan [SMIM][FeCl₄]. Parameter kinetik yang diperoleh adalah lebih rendah dan setanding dengan pemangkin sebelumnya yang digunakan dalam penukaran glukosa kepada asid levulinik. Kajian ini menunjukkan potensi pemangkin yang dicadangkan sesuai digunakan dalam loji biopenapisan minyak untuk memproses stok suapan boleh diperbaharu pada keadaan proses yang sederhana.
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XRD patterns (a), FTIR spectra (b), and FESEM images (c) of fresh and regenerated 10% Fe/HY zeolite catalyst.

Parity plot of levulinic acid yield from glucose conversion using 10% Fe/HY zeolite catalyst.

Pareto chart of levulinic acid yield from glucose conversion using 10% Fe/HY zeolite catalyst.

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<td>5-HMF</td>
<td>5-hydroxymethyl furfural</td>
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<tr>
<td>[BMIM][Cl]</td>
<td>1-butyl-3-methyl imidazolium chloride</td>
</tr>
<tr>
<td>[BMIM][FeCl₄]</td>
<td>1-butyl-3-methyl tetrachloroferrate</td>
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<tr>
<td>[SMIM][Cl]</td>
<td>1-sulfonic acid-3-methyl imidazolium chloride</td>
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<td>[SMIM][FeCl₄]</td>
<td>1-sulfonicacid-3-methylimidazolium tetrachloroferrate</td>
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<td>HY</td>
<td>Faujasite type zeolite</td>
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<td>FESEM</td>
<td>Field emission scanning electron microscopy</td>
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levulinic acid in a concentrated aqueous solution of betaine hydrochloride. \textit{RSC Advances}, 4(55), 28836-28841.


