Cost-Effective Green Catalysts for Sustainable Hydrolysis of Waste Lignocellulosic Biomass for Platform Chemicals and Drop-in-Biofuel Production

Abstract:

This thesis explores sustainable waste valorization through advanced catalysis, energy-efficient systems, and green technologies to convert lignocellulosic and industrial wastes into high-value chemicals and drop-in-biofuels. Six research activities illustrated the integration of innovative catalysts, advanced reactor designs, and process optimizations for scalable, environmentally friendly production pathways.

Activity 1 focused on developing waste printed circuit board (WPCB) derived Glass fibre-epoxy resin (GFER) framework to prepare cost-effective, reusable Mo-Cu bimetallic Bronsted-Lewis solid acid catalyst through wet-impregnation under near infrared radiation (NIRR) (wavelength 0.75-1.4μm) activation. Efficacy of the prepared catalyst was assessed in synthesis of glucose through hydrolysis of pretreated waste jute fiber (PWJF) and the process parameters were optimized (Mo precursor loading: 1.0 wt. %, catalyst concentration: 5 wt. %, hydrolysis temperature: 80 °C, and hydrolysis time: 10 min) through Taguchi orthogonal design. The GFER support and the prepared catalysts were characterized through TGA, XRD, FTIR, BET–DFT and TPD analyses. The optimal Mo-Cu catalyst and the GFER support possessed 45.377 and 7.049 m^2/g BET area; 0.04408 and 0.02317 cc/g pore volume; 1.9334 and 0.7482 nm modal pore size; surface acidity of 0.48 and 0.40 mmol NH_3/ g catalyst respectively. XPS bands confirmed the co-existence of Mo^{6+} and Cu^{2+} species, XRD and FTIR analyses indicated the presence of MoO_3 and CuO crystalline phases in all prepared catalysts. The optimal catalyst prepared through NIRR activated hydrothermal treatment, resulted significantly greater glucose yield (75.84 mol %) than that achieved (53.64 mol%) using conventionally prepared catalyst. Thus, an energy-efficient application of NIRR (150 W) could significantly improve catalytic properties over conventional hydrothermal treatment (500 W). This investigation provides an innovative application of WPCB derived GFER as a promising cost-effective support for preparation of highly-efficient inexpensive solid catalyst for sustainable synthesis of glucose from low-cost waste jute-fiber.

Activity 2 investigated a hybrid reactor system integrating ultrasonic and far-infrared energy (US-FIRW) for the hydrolysis of PWJF. At optimal 70°C temperature, 2.5 wt. % Amberlyst-15 catalyst concentration, 15 min hydrolysis time and 10 (w/w) water loading; US-

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FIRW rendered significantly greater reducing sugar (RS) yield (74.82 mol%) compared to other reactors provided with far-infrared-wave (69.63 mol%), ultrasonication (50.34 mol%) and conventional thermal system (48.16 mol%). Kinetic models were developed considering non-catalytic-pseudo-homogenous (NCPH) in addition to the combined catalytic-pseudo-homogeneous (CPH) and catalytic heterogeneous (CHE) hydrolysis pathways. The results revealed that pseudo-homogenous-heterogeneous Eley-Rideal (PHHER) model could represent the hydrolysis kinetics most accurately. Remarkably, the lowest activation energy [16.75 $kJmol^{-1}$ (NCPH), 13.82 $kJmol^{-1}$ (CPH), 40.01 $kJmol^{-1}$ (CHE)] required in US-FIRW evidently established its greater energy-efficiency among investigated reactors. The novel reactor and the simulated kinetic models in this study can be applicable to other lignocellulosic biomass conversion for sustainable biorefinery.

Activity 3 presented the development of a $Fe^{3+}/Fe^{2+}/Al_2SiO_5/Ti^{4+}$ nano-photocatalyst (FA_NPC*) employing fly ash (FA) derived nano-Al_2SiO_5 and nano-Fe^{3+}/Fe^{2+} in an innovative assimilated energy-system comprising tungsten-halogen radiation and ultrasound (THUS). The energy-efficient THUS activated optimal FA_NPC* (FA_NPC*^{O}) possessed favourably higher specific surface area (142.11 m^2/g), finer nanoparticles (47.50 nm) and lower band gap energy (2.78 eV) compared (89.72 m^2/g, 62.43 nm, 2.97 eV respectively) to its conventionally prepared analogue (FA_NPC^{CO}). The FA_NPC*^{O} rendered a significantly higher 5-hydroxy methyl furfural (5-HMF) yield (38.37 mol %) from a kitchen waste viz., cooked rice water (CRW) under THUS at 70 °C in only 60 min compared to 21.67 mol % HMF yield provided by FA_NPC^{CO}. DFT study revealed that the CRW conversion process to HMF occurred through water adsorption on FA_NPC* surface for H_3O^+ formation, followed by H_3O^+ induced CRW hydrolysis, subsequent glucose isomerization on -Ti active sites and finally fructose dehydration by H_3O^+. The FA_NPC*^{O} catalysed CRW conversion process could appreciably alleviate harmful environmental parameters, viz. global warming, fossil depletion, human toxicity and metal depletion by 7.65 %, 4.15 %, 8.56 % and 13.57% respectively in comparison with FA_NPC^{CO}. Thus, the THUS promoted systems could favourably demonstrate the efficient and eco-friendly utilisations of two abundant waste resources, viz. fly ash and cooked rice water for a sustainable production of 5-HMF and other allied platform chemicals.

Activity 4 explored a heterogeneous catalytic system for the first time in the synthesis of 5-(chloromethyl) furfural (5-CMF). A reusable dual catalytic system comprising Smopex-101 and TiO_2 was effectively utilized for energy-efficient and eco-friendly synthesis of 5-CMF

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from soluble starch (SS) under synergistic photo-thermal effect of UV-ultrasound (US) irradiations. At mild optimal operating conditions (80°C, 60 min), both batch (UVUS-BR) and continuous-flow rectangular packed bed reactor (UVUS-RPBR) resulted in maximum 5-CMF yields of 60.54 mol% and 58.75 mol% respectively. Significantly, the first-ever heterogeneous surface reaction kinetic model was formulated for 5-CMF synthesis process, which revealed that activation energies needed for different reaction steps involved in the consecutive reaction pathway were 79.04 kJ/mol (SS hydrolysis), 61.55 kJ/mol (glucose dehydration), and 52.2 kJ/mol (5-hydroxymethylfurfural chlorination) respectively. RTD analysis and ANSYS fluent simulation study revealed that utilization of US energy significantly reduced the non-ideal behaviour of UVUS-RPBR (63 % reduction in dispersion number). Moreover, the efficacy of the UVUS-RPBR in 5-CMF synthesis process was evaluated employing the experimentally validated heterogenous kinetic model parameters. Furthermore, based on comparative LCA analysis, cyclohexane was identified as the most favourable solvent for in-situ 5-CMF (purity: 96 %) extraction due to its potential environmental advantages over other solvents. The outcomes of the present study can be useful for scale-up of such reactor for industrial application.

Activity 5 demonstrated the synthesis of ethyl levulinate (EL) from pretreated sugarcane bagasse (PSCB) in presence of photoactive ternary acidic deep eutectic solvents (TADES) under microwave-xenon (MWXE) irradiation under mild process conditions (90 min, 90°C). The Taguchi orthogonal designed optimized conditions (20 W/cm^3 of MW specific irradiation power input, 1 mol/mol of $FeCl_3$ to citric acid ratio, 90 min of reaction time, 150 W of XE specific power input) rendered maximum 61.3 mol % of EL yield (selectivity: 87.70±0.5 %). Remarkably, synergistic effect of MW and XE irradiation significantly enhanced the EL yield (61.3 mol %) compared to the individual MW (34.52 mol %) and XE (22.67 mol %) irradiation at otherwise optimized reaction conditions. Moreover, the MWXE irradiated reactor exhibited a significant 79.10% increase in EL yield compared to the conventional thermal reactor, at the expense of 10% less energy consumption. The ethyl levulinate could be recovered efficiently through green protocol from reaction mix resulting in high purity (97±0.5 %) and TADES was sustainably reused in the process.

Activity 6 utilized an innovative microwave-visible irradiated continuous stirred slurry reactor (MWVIS-CSSR) for sustainable continuous production of a drop-in-biofuel, namely, ethyl levulinate (EL), from pretreated sugarcane bagasse (PSCB). Besides, a novel realistic kinetic model, considering MWVIS intensified EL production through parallel non-catalytic

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and homogeneous-heterogeneous catalytic pathways in the presence of magnetic $Ni_{0.5}Zn_{0.5}Fe_2O_4$ (NZF) photocatalyst in conjunction with oxalic acid-choline chloride based acidic deep eutectic solvent was also formulated and validated (R2 adj. ≥ 0.95). The 5-litter volume MWVIS-CSSR could render maximum 54.7 mol% of EL yield (selectivity: 97.85%) at feed flow rate of 35 ml/min under optimized conditions (temperature: 100°C, NZF loading: 6 wt.% of PSCB, stirring speed: 500 rpm). Remarkably, the synergistic impact of MW and VIS irradiations substantially elevated the EL yield (54.7 mol%) compared to the individual MW (29.45 mol%) and VIS (20.1 mol%) systems. The optimally produced EL when blended at 5 vol% with B10 and B20 (10% and 20% biodiesel-diesel blends), could enhance the break thermal efficiency (1-2%) besides mitigating 21-22% HC and 7.5-20% CO engine exhaust emissions in comparison with reference blends (B10 and B20). Notably, the reactor scale-up study based on penetration depth of MW and VIS energy of NZF and DES2, showcased the potential to upscale the 5-liter MWVIS-CSSR to a 1 m3 volume, allowing EL production to reach 689 kg/h with a sugarcane bagasse processing capacity of 2000 kg/h. Moreover, the process simulation conducted in Aspen Plus software, utilizing COSMO-based property estimation with DFT calculation, alongside the techno-economic analysis, revealed a robust internal rate of return (IRR) of 54.25% and a net present value (NPV) of 8.22E+05 US$ with a payback period of 4.91 years. Additionally, the environmental impacts analysis study for the scaled-up EL production process in MWVIS-CSSR revealed a reduction of 40-60% in marine ecotoxicity and 39-61% in human toxicity compared to the separate MW-CSSR and VIS-CSSR reactor systems.

Through these six activities, this thesis addresses critical challenges in waste management, renewable energy, and climate change mitigation. By repurposing waste materials like waste printed circuit boards, fly ash, waste cooked rice water, and sugarcane bagasse, this research demonstrates a sustainable framework for converting waste into high-value products. The integration of advanced catalysis, innovative reactor systems, and green chemistry offers scalable solutions for resource-efficient industrial applications, contributing to the broader goals of sustainable development and environmental conservation.

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