Designing Holistic Biorefinery Solutions: Process Optimisation and Technoeconomic Viability of Glycerol derived High Energy-Density Fuel Additives

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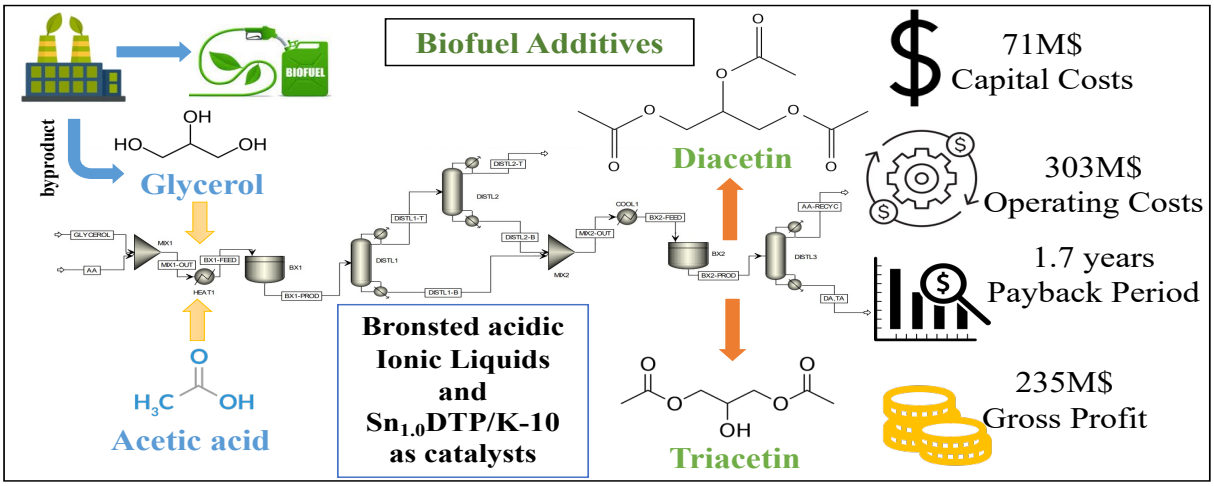
Significance and Relevance

This work presents a comprehensive study aimed at designing holistic solutions for the biorefinery industry, with a particular focus on enhancing both the economic viability and environmental sustainability of biodiesel production. The research emphasizes the integration of innovative catalytic technologies and advanced processes for glycerol esterification. Utilizing Design of Experiment (DoE) methodologies, this study delves into multifaceted approaches that optimize critical process parameters. Furthermore, it conducts kinetic studies based on the Langmuir-Hinshelwood (L-H) dual-site model to better understand the reaction mechanisms involved. To facilitate thorough process simulation, Aspen Plus® is employed, providing insights into operational efficiencies and potential bottlenecks. A detailed techno-economic assessment paired with sensitivity analysis has been conducted for a facility designed to produce di- and tri-acetins via a two-stage process, leveraging an annual feedstock of 100,000 tonnes of glycerol. This rigorous exploration underscores the potential for significant advancements in biorefinery operations by optimizing production pathways that not only reduce costs but also minimize environmental impact by truly embracing the concept of circular economy by blending di- and triacetins into the biodiesel pool effectively.

Introduction and Motivations

With increasing energy demand, decreasing fossil fuel reserves, and climate emergency it is imperative to develop renewable biofuels and fuel additives. One of the potential alternatives is the bio-refinery concept, where biodiesel serves as a replacement of fossil fuels. However, bio-diesel production is associated with formation of up to 10wt% of waste glycerol as a liability. To enhance economic viability of biorefineries, it is essential to add value to glycerol, for instance, glycerol esterification using renewable acetic acid. Glycerol esters have a wide range of applications, both di- and tri-acetins are effective as high energy-density fuel additives, improving the combustion and fuel economy of the biodiesel, whilst also decreasing harmful emissions. Glycerol esters can be directly blended into the biodiesel to enhance the carbon atom economy associated with its production, promoting efficient resource utilization, improving process economics as well as the environmental sustainability.



Results and Discussion

Typically, esterification process requires stoichiometric use of mineral acids or $AlCl_3$ as catalyst. With increased importance placed on green chemistry, catalysts need to be safe, non-corrosive and recyclable. In this work, it has been shown that low-cost and commercially available Bronsted acidic ionic liquids are efficient and reusable liquid acid catalysts for esterification. In particular, using [H-NMP][HSO_4] as catalyst, the glycerol esterification was accomplished with 99% conversion of glycerol within 30 minutes, with 97.6% yield of di- and triacetin fuel additives.[1] For optimisation of the glycerol esterification process, the Design of Experiments (DoE) approach was applied, taking into account the variables such as speed of agitation, reaction temperature, glycerol:acetic acid mole ratio and catalyst loading. Herein, we also compared the efficacy of Bronsted acidic ionic liquids as catalysts with solid acid catalyst, such as tin exchanged tungstophosphoric acid (DTP) supported on montmorillonite K-10. Partially, exchanging the H^+ ion of DTP with Sn (x = 1) increased the acidity of the catalyst and showed an increase in the catalytic activity. Different process parameters were optimised, and a suitable kinetic model was fitted. Langmuir-Hinshelwood (L-H) dual-site model was able to describe the experimental data with high agreement between the experimental and calculated results.[2] Furthermore, we have studied the economic feasibility of a facility producing di- and tri-acetins by a two-stage process using 100,000 tonnes of glycerol per year using Aspen Plus®. The analysis indicates that the capital costs are 71 M$ while the operating costs are 303 M$/year. The gross profit is 60.5 M$/year while the NPV of the project is 235 M$ with a payback period of 1.7 years. Sensitivity analysis has indicated that the product price has the most impact on the NPV.[3]

Materials and Methods

The ionic liquids used in this study were prepared and characterized in QUB. For example [H-NMP][HSO_4] was prepared by adding sulfuric acid (9.8 g, 0.1 mol) dropwise slowly to n-methyl-2-pyrrolidone (9.9 g, 0.1 mol) in an ice bath under stirring. Once completed the reaction is carried out for 4 hr at 40°C. The formed ionic liquid was washed with ethyl acetate (3 x 10 mL), and water was removed under reduced pressure. The ionic liquids were characterized using nuclear magnetic resonance (NMR). All synthesized ionic liquids showed high purity. Esterification of glycerol with acetic acid was conducted in a 100 mL two-necked round bottomed flask. In a typical experiment, the reactor was charged with ionic liquid (2 mol %), glycerol (5 g) and acetic acid (19.56 g) and stirred using a magnetic stirrer at 100°C. The reactions were monitored by taking regular samples and analyzed using gas- chromatography (Agilent Technologies 7820A) equipped with FID detector and HP-5 capillary column. The products were identified by GC-MS.

Tin exchanged tungstophosphoric acid supported on K-10 catalysts (20%w/w Sn_1-DTP/K-10) was prepared by sequential incipient wetness technique using Sn(II)Cl_2 and DTP solutions in methanol as precursors. The as prepared materials were dried at 120°C, followed by calcination at 300°C for 3h in tubular furnace under flowing air.

References

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