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Introduction to green chemistry and reaction engineering

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The emerging circular economy requires the development of new routes for re-introduction of molecules into industrial supply chains from various waste products, or coupling of natural carbon cycles with the proposed industrial carbon cycle. Although there is an increasing number of papers on new chemical transformations to support the transition to circularity, there are few studies on engineering the new process concepts. This issue focuses on *reaction engineering* for circular use of molecules,

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deliberately leaving the applications scope very wide. The reaction engineering methods are frequently agnostic to specific chemistry, and this issue is highlighting both the traditional methods of reaction engineering, as well as the emerging methods of data science and machine learning.

Lignocellulosic biomass is notorious for its recalcitrance to chemical and enzymatic degradation. The 2nd generation biological biorefinery process relies on physical and chemical treatment of raw biomass followed by enzymatic hydrolysis, which takes a few days to accomplish. A competing route is chemical hydrolysis employing H₂SO₄ at elevated temperatures. The main limitations of the latter include high corrosiveness and severe degradation of sugars into humins. Adding a polar aprotic solvent can alleviate these is-

issues, but earlier reports^{1,2} based on the addition of γ -valerolactone suffer from the high cost of the organic co-solvent, and the difficulty to recover γ -valerolactone. To overcome these issues, Brown and co-workers developed an 80:20 tetrahydrofuran (THF)-water binary system with low H₂SO₄ concentration to break down red oak (DOI: 10.1039/D0RE00192A). In a two-stage operation process, involving a pretreatment step at 120 °C to extract lignin and hemicellulose, and a reaction step at 220–270 °C to hydrolyse cellulose, an impressive fermentable carbohydrate yield of up to 65% was achieved. The space-time productivity is drastically enhanced, while the yield is comparable with the enzymatic hydrolysis pathway.

The obtained sugars from biomass hydrolysis have to be upgraded *via*



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either biological fermentation or catalytic conversion. In the catalytic pathway, several chemicals, such as furfural, 5-hydroxymethylfurfural, levulinic acid and its derivatives, have been identified as top platform bio-based chemicals with a broad range of end products. Ethyl levulinate is one such candidate and can further be transformed into fuels, solvents or value-added chemicals. Smith Jr and co-workers developed a hybrid Ni/NiO-carbon nanofiber material bearing metal and acid bifunctional sites to promote one-pot transformation of both C5 and C6 sugars into ethyl levulinate (DOI: 10.1039/D0RE00153H). The catalyst was synthesised *via* a solvothermal approach using 5-sulfosalicylic acid and NiSO₄ in *N,N*-dimethylacetamide at 120 °C, before undergoing pyrolysis at 500 °C. The effectiveness of the catalyst lies in the smart choice of the organic acid precursor, 5-sulfosalicylic acid, which contains -OH, -COOH, and -SO₃H groups, resulting in enriched acid functionalities on the catalyst surface. The metal and acid sites, together, promote a tandem dehydration-ethanolysis sequence to convert 5-hydroxymethylfurfural into ethyl levulinate. This approach avoids the use of noble metals, mineral acids and expensive solvents as used previously.

Another powerful multiple functional catalytic system was established by Tomishige and co-workers to convert 1,4-anhydroerythritol into 1,4-butanediol in one-pot (DOI: 10.1039/D0RE00085J). Erythritol is a commercially manufactured C4 sugar alcohol that can be used to produce C4 chemicals. 1,4-Butanediol is used in the production of paints, coatings and a wide variety of other polymer applications. The conversion of 1,4-anhydroerythritol into 1,4-butanediol, however, is not an easy task and has not been thoroughly investigated. The reaction requires deoxydehydration, isomerization, hydration, ring opening and a hydrogenation step to occur in tandem. In this work, a ReO_x/WO₃-ZrO₂ catalyst was combined with a ReO_x-Au/CeO₂ catalyst to enable the transformation. The ReO_x-Au/CeO₂ catalyst is responsible for the deoxydehydration in the first step,

whereas the ReO_x/WO₃-ZrO₂ catalyst catalyzes the other steps, reaching a 1,4-butanediol yield of 55%. The previous work³ in this area used carbon supports which cannot be regenerated, while this catalyst can be regenerated by calcination.

In the early 21st century the main focus was on producing sugars from biomass/cellulose, with little work on producing other chemicals. Thanks to the pioneering work from Fukuoka,⁴ Liu⁵ and Zhang,⁶ we see an increasing number of reports on one-pot conversion of lignocellulosic biomass into commodity chemicals. Alginic acid is a biopolymer that widely exists in the cell walls of algae, consisting of two C6 sugar acid monomers with their carbon-6 oxidized in the form of -COOH. Kim and co-workers converted alginic acid into ethylene glycol, 1,2-propanediol, and other glycols (DOI: 10.1039/D0RE00224K). Unlike earlier studies on cellulose which was conducted in neutral conditions, they identified that NaOH with Ru or Ni catalysts provided the highest carbon efficiency. Starting from sorbitol, mannitol, lactic acid, and glycolic acid, glycols did not form with comparable yield, suggesting the reaction pathway does not involve these polyols and acids as intermediates, but occurs *via* a retro-aldol reaction. In addition to glycols, several organic acids were also obtained.

'No matter how technologies for bio-fuels and biorefining evolve, catalysis is sure to be an important part of the mix'.⁷ This quote highlights the critical role of catalyst development for biomass refineries. While the identification of new and/or improved catalysts still heavily rely on semi-empirical wisdom as well as trial and error approaches, experimental and theoretical tools for the thorough understanding and rational design of catalysts has been long sought after by the catalysis community. Vlachos and co-workers communicated a new methodology to establish quantitative synthesis-structure-property relations (DOI: 10.1039/D0RE00243G). The approach is based on data driven experimental design using Bayesian optimization, which correlates catalytic performance with a range of catalysts'

properties that are traced back to the synthesis conditions. Further optimization *via* active learning enabled the development of better catalysts with preferred structures and improved properties. The work illustrates the power of active learning in capturing and disentangling the contribution of multiple parameters in catalysis. These parameters are coherently and profoundly linked with each other, which is difficult to perceive, and are individually optimized using static methods.

There are two major tasks for the future biomass refinery and use of bio-waste in the emerging circular economy. The first task is to improve the synthetic pathways of known chemicals, in an attempt to reduce their reliance on non-renewable resources, and to decrease the carbon footprint during production. The second one is to identify new chemicals that are bio-based to replace fossil-based chemicals without compromising performance. For the latter purpose, Hunt and co-workers evaluated the replacement of toxic polar aprotic solvents such as *N*-methyl pyrrolidinone, *N,N*-dimethylformamide and *N,N*-dimethylacetamide, by green solvents (DOI: 10.1039/D0RE00174K). In the Baylis-Hillman reaction between 4-nitrobenzaldehyde and methyl acrylate, dihydrolevoglucosenone (Cyrene) was demonstrated to be the most suitable due to its high initial reaction rate, quantitative transformation of substrate and relatively easy solvent recovery. Cyrene is a cellulose derived molecule that is being produced at the pilot scale with plans to scale this to the commercial level.

Along a similar line, Watanabe and co-workers reported the use of citric acid for the continuous leaching of LiCoO₂ under hydrothermal conditions (DOI: 10.1039/D0RE00286K). As a widely used cathode material in lithium-ion batteries, the amount of discarded LiCoO₂ in spent batteries has increased substantially. A known method to recover metal components in batteries is through hydrometallurgy, in which metal ions are transformed into an aqueous solution using mineral acids and other chemical reagents. Biomass

feedstock readily offers a range of organic acids. Among them, the relatively strong acidity of citric acid ($pK_a = 3.1$) and the chelating property of citric ions make it a viable substitution to the mineral acids. In the industrially preferred continuous operation 81.3% of Li and 92.7% Co were transferred into citric acid solution after 1 h residence time in this work.

The spread of applications of reaction engineering tools in developing green chemistry solutions with the specific focus on the emerging bio- and cir-

cular economies, demonstrates the importance of the core field. At the same time, studies in this themed issue demonstrate the transformation of the field into the digital R&D workflow.

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