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Editorial
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ACS Sustainable Chemistry & Engineering Virtual Special Issue on Hydrogen Transfer Strategies for Biomass Valorization

Lignocellulosic biomass and the platform chemicals derived from it contain a plethora of structural motifs that can replace many petrochemicals and provide inherently more benign and less persistent building blocks for fuels and chemicals. However, the upgrading of biomass derivatives to biofuels and chemicals typically requires a reduction of oxygen content, which varies from approximately 30% in lignin to 50% in cellulose. The oxygen-to-hydrogen ratio can be reduced by addition of hydrogen equivalents via hydrodeoxygenation (HDO), hydrogenation of carbonyls, and hydrogenolysis.

While addition of hydrogen in the above processes has historically been dominated by the use of direct hydrogenation, a few disadvantages in direct hydrogenation when applied to biomass have slowly become evident. Although safety concerns surrounding the use of high hydrogen pressures may have been minimized by advances in reactor engineering, the high infrastructure cost associated with such reactors poses an economic barrier, especially in the third world. In addition, the relatively harsh reaction conditions required in direct hydrogenation can lead to decomposition and thus low selectivity for desired products from biomass-derived platform chemicals.

The use of alternative sources of hydrogen via catalytic transfer hydrogenation (TH) has the potential to both minimize the complexity of such hydrogenation processes (thus lowering infrastructure cost) and to allow the use of milder reaction conditions. Milder conditions are better suited for achieving high selectivity for reducing particular bonds, such as for C═O over C═C, as well as reducing operational costs.

Although early examples of homogeneous TH were not considered practically useful because they were relatively slow, this changed once a base was found to accelerate reaction rates nearly 1000-fold by serving as a catalyst promoter. At around the same time, a number of heterogeneous catalysts for TH were also developed, which operated via the Meerwein−Ponndorf−Verley (MPV) mechanism. Heterogeneous catalysts typically have a clear cost advantage over precious metal homogeneous catalysts, and significant strides were made to enhance their activity and selectivity. These developments, together with increased efforts to design processes consistent with the principles of green chemistry, led to the rapid growth of the field in the last three decades.

However, the application of TH processes, originally developed for synthetic applications, to biomass substrates is not straightforward and poses a number of specific challenges. For one, the structural motifs, and thus properties, of biomass-derived substrates are vastly different from those of fine-chemical substrates; for example, the oxygen-rich nature of biomass substrates renders them much more hydrophilic, requiring use of polar solvents. In turn, the use of polar or aqueous solvents calls for development of homogeneous catalysts that have suitable solubility profiles. The change in solvent polarity may be associated with a different catalytic mechanism compared to that in organic solvents, thus requiring new investigations. In a development aimed at this goal, in this Virtual Special Issue (VSI) on Hydrogen Transfer Strategies for Biomass Valorization, Crabtree highlights some of the effects that polar media pose on catalyst homogeneity and decomposition for glycerol TH, and Chaudhari et al. elucidate the kinetics of aqueous-phase glycerol catalysis, where H_2 is generated *in situ* rather than directly transferred.

Another challenge associated with TH for biomass substrates is the application of lifecycle considerations. In most cases, lifecycle considerations favor the use of renewable H-donors, such as glycerol, ethanol, and 2-butanol. However, these H-donors can necessitate vastly different reaction conditions compared to those optimized for petroleum-based alcohols. Lifecycle considerations also apply to the catalyst, which should not deplete precious metal reserves, as well as to the byproduct formed from the H-donor. The fate of the byproduct also directly influences green chemistry metrics applied to the process. If the byproduct can be separated and constitutes a value-added chemical, as in the case of lactic acid generated from glycerol, the overall atom economy can be optimized, and the economics of the process can be improved. In an eloquent analysis by Li and Moores in this VSI, carbonyl TH is used as a case study to discuss the contributions of catalyst lifecycle, alternative energy sources, solvents, and green metrics in a systematic comparison of TH processes.

Hydrogen borrowing also has an important role to play in facilitating atom-economical functionalizations in both synthesis and biomass applications. This approach has been applied to N-alkylation of alcohols and, more recently, N-alkylation of amines to form secondary amines. However, methods to form primary amines by this method are rare. In an elegant example by Barta et al., the formation of primary amines is achieved by amination of biomass-derived benzylic and aliphatic alcohols. The method uses readily available base metal (Ni) catalysts and easy-to-handle ammonia sources. In another interesting example of quasi-catalytic transfer hydroamination in this issue, Li and Yang et al. report an atom-economical synthesis of N-unprotected lactams from formamide and keto acids, such as biobased levulinic acids.

In addition to reducing oxygen content, it would be highly advantageous if TH processes for biomass applications can also target selective depolymerization. In a timely example in this VSI involving ether hydrolysis in lignin, Mauriello et al. and Luque et al. demonstrate the use of transfer hydrogenolysis to target biphenyl ethers (4-O-5 linkers) in lignin. In yet another important advance toward selective depolymerization of lignin, Deuss et al. apply an innovative hydrogen-neutral catalytic route involving oxidation and decarbonylation to strategically modify lignin and facilitate cleavage of *β*-O-4 motifs.

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Lastly, TH for biomass applications must be held to a high standard in terms of addressing the principles of green chemistry and circular economy. New processes should have a niche in a circular flow of materials, given the shifting paradigm from linear to circular processes in future economies. Energy efficiency should also be part of our process design, with the application of alternative energy sources, including microwave, photochemistry, mechanochemistry, sonochemistry, and continuous flow reactions (an elegant example of flow chemistry is presented in this VSI by Tabanelli and Mauriello et al.).

In sum, we believe that the articles featured in this VSI provide a timely snapshot of the progress toward development of catalytic transfer hydrogenation, hydrogenolysis, and hydrogen-neutral functionalization that will form a critical part of the toolbox of future biorefineries. We thank all the authors and reviewers whose efforts made it possible to produce this VSI and the editorial team of *ACS Sustainable Chemistry & Engineering* for their continuous support. The fact that the articles in this VSI represent both homogeneous and heterogeneous catalysis is a reminder that the field of biomass valorization breaks the barriers between the two fields and inspires us to train future chemists and engineers to understand how to apply both. We hope these advances will seed further developments toward the design of economically viable biorefineries.

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