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Coupling chemical and biological catalysis: a flexible paradigm for producing biobased chemicals

Thomas J Schwartz¹, Brent H Shanks² and James A Dumesic³

Advances in metabolic engineering have allowed for the development of new biological catalysts capable of selectively de-functionalizing biomass to yield platform molecules that can be upgraded to biobased chemicals using high efficiency continuous processing allowed by heterogeneous chemical catalysis. Coupling these disciplines overcomes the difficulties of selectively activating C–OH bonds by heterogeneous chemical catalysis and producing petroleum analogues by biological catalysis. We show that carboxylic acids, pyrones, and alcohols are highly flexible platforms that can be used to produce biobased chemicals by this approach. More generally, we suggest that molecules with three distinct functionalities may represent a practical upper limit on the extent of functionality present in the platform molecules that serve as the bridge between biological and chemical catalysis.

Addresses

¹ Department of Chemical and Biological Engineering, University of Maine, 5737 Jenness Hall, Orono, ME 04469, USA

² Department of Chemical and Biological Engineering, Iowa State University, 1140 L BRL, Ames, IA 50011, USA

³ Department of Chemical and Biological Engineering, University of Wisconsin-Madison, 1415 Engineering Drive, Madison, WI 53706, USA

Corresponding author: Dumesic, James A (jdumesic@wisc.edu)

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Introduction

Concerns over the financial, environmental, and societal sustainability of fossil-based feedstocks have motivated research on the production of biofuels and biobased chemicals [1–3]. At the same time, improved recovery of ‘tight resources’ (e.g., shale gas or shale oil) has challenged the need for biomass as a replacement for petroleum. However, the new capacity obtained from such resources consists mostly of C₁ to C₃ species [4^{*}], which requires the development of new methods for producing higher-carbon-number species. Moreover, enhanced petroleum recovery does not mitigate the environmental concerns associated with the use of fossil-based resources.

Biomass, on the other hand, is a renewable feedstock that can potentially supply molecules containing four or more carbons. Any biomass conversion processes must be sufficiently flexible to adapt to the evolving needs of the chemical industry, and in this respect, we suggest that the requisite flexibility can be achieved by using an approach that couples both chemical and biological catalysis.

An effective strategy for the integration of chemical and biological catalysis is to use biological catalysis to selectively de-functionalize biomass to yield platform species that are further upgraded using chemical catalysis [5,6,7,8^{*}]. This strategy is particularly advantageous because it leverages the strengths of both disciplines while avoiding some of their weaknesses. For example, the selective activation of nearly identical bonds (e.g., the C–OH bonds in sugars) is a difficult problem for heterogeneous catalysis, yet it forms the basis of most biochemical transformations. Coupled processing also avoids the challenge of engineering an enzyme or organism to produce petroleum-like molecules, because the final transformations are left to the domain of chemical catalysis, which is well-suited for such reactions.

This review will discuss recent examples of the integration of chemical and biological catalysis to produce biobased chemicals, with a focus on work published since 2013. We will open with an overview of the strategy of combining chemical and biological catalysis, focusing in particular on determining when it is appropriate to pass a molecule from one discipline to the other. Then, we will use examples from the literature to show that the combination of chemical and biological catalysis provides sufficient flexibility to adapt to the evolving needs of the chemical industry to produce both direct replacements for petrochemicals and chemicals with new functional performance not available using fossil-based feedstocks.

Important considerations for coupling chemical and biological catalysis

One of the principal challenges associated with biomass upgrading using solely heterogeneous chemical catalysis is the selective activation of C–OH bonds. While there are examples where high selectivity can be achieved, for example in the isomerization of glucose to fructose [9] or its oxidation to gluconic acid [10^{*}], as a general rule selectivity remains a challenge when upgrading biomass-derived sugars using chemical catalysts alone. In contrast, biological transformations have the advantage of being highly selective for the activation of these bonds,

although biological catalysis is not necessarily well-suited for producing drop-in replacements for petrochemicals. Consequently, we suggest [6,8,11] that biological catalysis can be used as the front-end for biomass upgrading strategies, allowing for the selective de-functionalization of sugars to platform molecules that are suitable for conversion to final products using chemical catalysis. While the toolkit of synthetic biology can be used to directly produce drop-in replacements for petroleum [12], many of the necessary reactions are already practiced by the heterogeneous catalysis community. Moreover, as we will highlight in the examples that follow, the use of platform molecules allows for the more easily diversified production of a variety of species, including both commodity chemicals and high-value building blocks. Some of the most promising future strategies for producing chemicals from biomass, then, may combine the tools of synthetic biology with the potential high efficiency of heterogeneous catalysis.

For any system that combines chemical and biological catalysis, there is a question of how to decide at what point in the selective de-functionalization of biomass the molecule should be passed from the biological process to the chemical process. We consider this problem from a perspective analogous to that taken by the petrochemicals industry: for a particular molecule, what degree of oxidation is most useful for subsequent upgrading? We consider first the most reduced form of carbon, alkanes, which are also the ultimate products of deep hydrodeoxygenation (HDO) of biomass-derived molecules. The selective functionalization of these fully-saturated species to useful

chemicals is difficult because of their low reactivity, leading to the need to operate at demanding reaction conditions. However, slightly more oxidized forms of carbon, alkenes in particular, are highly useful as platform species in petrochemical facilities. Having the functional group in the terminal position is perhaps most useful, as in the case of α -olefins. However, processes for producing alkenes from biomass already involve both chemical and biological catalysis [13–15] and do not necessarily proceed at high yields. Focusing on increasingly oxidized species, we arrive at, in increasing order of oxidation state, alcohols, aldehydes, ketones, and acids, each of which can be upgraded using the common reactions shown in Table 1. Notably, the production of acids and alcohols is relatively straightforward using biological catalysis [16,17], although often these species contain more than one functional group.

In the case of bifunctional species, one must address the selectivity for upgrading one group in the presence of another. Molecules containing two identical groups, such as dienes, diols, or diacids present the greatest challenge. In this case, the molecular structure often drives the selectivity. For example, selectivity in diol oxidation is governed largely by chain length [18]. However, sometimes it may be possible to design catalysts with active sites that are highly selective for converting only one of the functional groups in a symmetric bifunctional molecule, as in the case of butadiene reduction to butene [19]. This problem can be simplified if the bifunctional molecule contains two unique functional groups, as in the case of hydroxyacids such as lactic acid or glycolic acid.

Table 1

Common uses of heterogeneous catalysts for biomass-conversion reactions

Reaction	Common catalysts
$\text{R}-\text{CH}=\text{CH}-\text{R}' \xrightarrow{+\text{H}_2} \text{R}-\text{CH}_2-\text{CH}_2-\text{R}'$	Transition metals: Pt, Pd, Ni, Rh, Ru
$\text{R}-\text{C}(=\text{O})-\text{R}' \xrightarrow{+\text{H}_2} \text{R}-\text{CH}(\text{OH})-\text{R}'$	Transition metals: If R' is CH _x : Pt, Ni, Ru, Cu, Co, CuCr If R' is OH: Ru, CuCr If R' is aromatic: Pd, Ni, Co, Cu
$\text{R}-\text{CH}_2-\text{OH} \xrightarrow{+\text{O}_2} \text{R}-\text{CH}_2-\text{CHO}$	Certain transition VIII metals: Pt, Pd, Au
$\text{R}-\text{CH}_2-\text{CHO} \xrightarrow{+\text{O}_2} \text{R}-\text{CH}_2-\text{COOH}$	Certain transition VIII metals: Pt, Pd, Au
$2\text{x R}-\text{CH}_2-\text{COOH} \xrightarrow{-\text{CO}_2} \text{R}-\text{CH}_2-\text{CO}-\text{CH}_2-\text{R}$	Metal oxides: CeO _x , La ₂ O ₃ , CeZrO _x , CeO _x -Mn ₂ O ₃
$\text{R}-\text{CH}_2-\text{OH} \xrightleftharpoons[+\text{H}_2\text{O}]{-\text{H}_2\text{O}} \text{R}-\text{CH}=\text{CH}_2$	Brønsted acids: Sulfonic acid resins, amorphous silica-alumina, zeolites
$\text{R}-\text{CH}_2-\text{COOH} + \text{R}'-\text{CH}_2-\text{OH} \xrightleftharpoons[+\text{H}_2\text{O}]{-\text{H}_2\text{O}} \text{R}-\text{CH}_2-\text{CO}-\text{O}-\text{CH}_2-\text{R}'$	Brønsted acids: Sulfonic acid resins, amorphous silica-alumina, zeolites

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