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The formate bio-economy

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In this review we discuss the concept of the formate bio-economy: formate can be produced efficiently from various available resources and can be consumed by microbes as the sole carbon source for the production of value-added chemicals, directly addressing major challenges in energy storage and chemical production. We show that the formate assimilation pathways utilized by natural formatotrophs are either inefficient or are constrained to organisms that are difficult to cultivate and engineer. Instead, adapting model industrial organisms to formatotrophic growth using synthetic, specially tailored formate-assimilation routes could prove an advantageous strategy. Several studies have started to tackle this challenge, but a fully active synthetic pathway has yet to be established, leaving room for future undertakings.

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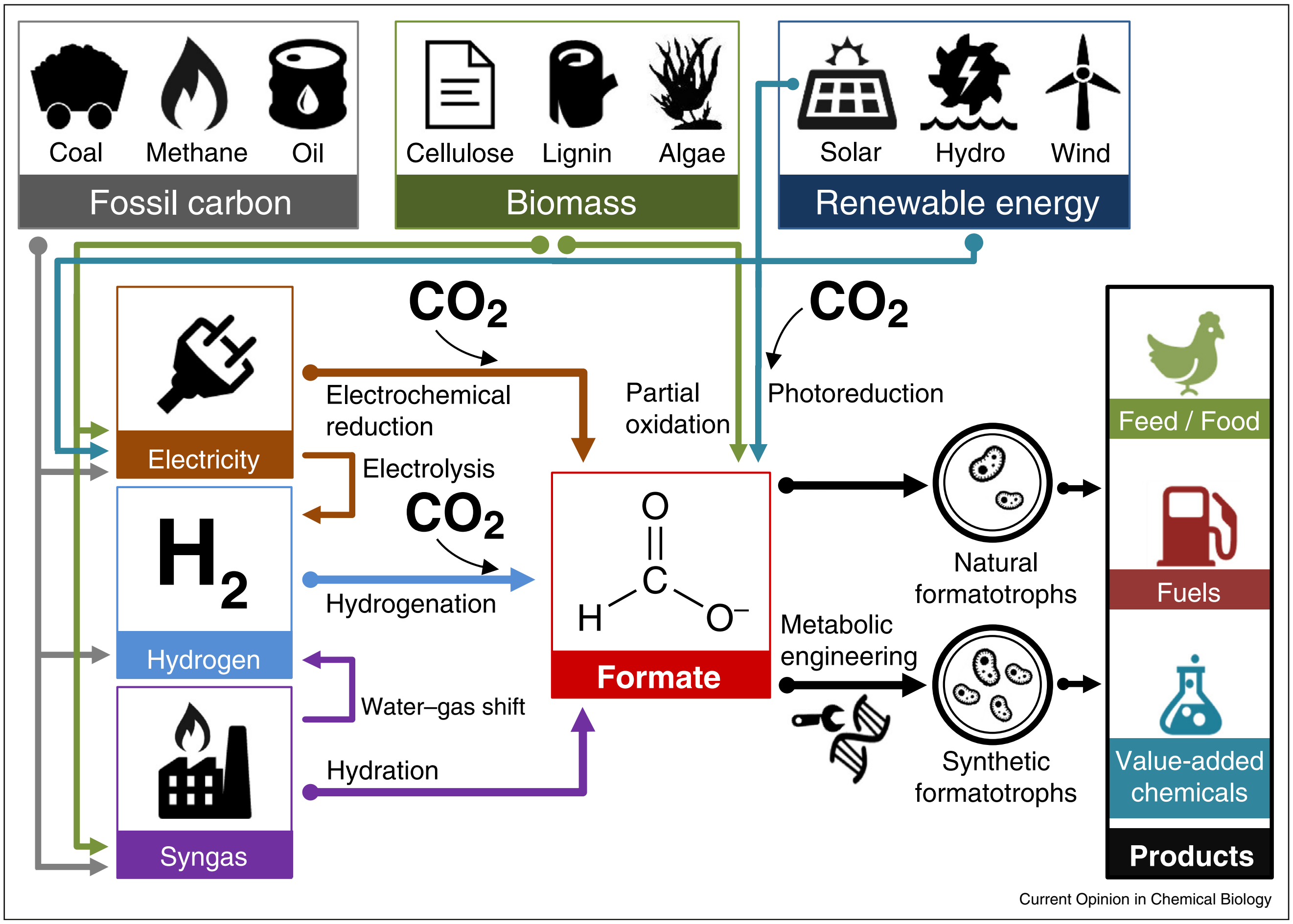
Introduction

Storing excess electricity, produced at off-peak hours from renewable and intermittent sources, is a central aim of the energy industry and an essential step towards increasing the share of these sources in electricity production [1]. Similarly, the production of value-added chemicals currently depends almost entirely on fossil carbons or simple sugars, whose utilization directly competes with human consumption and thereby undermines food security [2]. Hence, there is an urgent need to develop methods to utilize available and cheap resources as feedstock for the production of chemicals [3]. Notably, these two challenges may be interwoven: energy might be efficiently stored within stable chemicals, for example, fuels; and, complementarily, available electricity and CO_2 may serve as promising feedstocks for the production of value-added chemicals [4–6]. Such a process can be entirely physicochemical. For example, electrochemical reduction of CO_2 to carbon monoxide alongside hydrogen production via water splitting or water-gas shift [7] can support a downstream Fischer–Tropsch process, producing various hydrocarbons [8]. However, such purely physicochemical processes usually necessitate large infrastructure, tend to require extreme conditions (e.g., high temperature and pressure), and in most cases are not product-specific, leading to the formation of a mixture of compounds [8]. On the other hand, microbial production of chemicals tends to be product-specific, can be carried out under ambient conditions, and can be run economically using a medium-sized apparatus [9]. A sustainable and efficient approach for converting energy into fuels and other chemicals should therefore preferably mix physicochemical and biological strategies [10]. Here, we put forward the case for formate as a mediator between the physicochemical and biological realms, that is, formate can be synthesized efficiently using excess energy and then serve as the sole source for microbial growth (Figure 1). Formatotrophic microbes can then be used to convert formate into a myriad of products, such as fuels, other value-added chemicals (e.g., solvents, plastic monomers, pigments), and even protein meal for animal and human consumption [11] (Figure 1).

Formate production: electrosynthesis and other promising methods

As electricity serves as our main energy currency, electrochemical reduction of CO_2 will likely prove to be the most sustainable way to produce formate. In recent years, the electrochemical reduction of CO_2 to various compounds has gained considerable attention [12]. Yet, out of the wide array of compounds that were shown to be generated by this approach, only carbon monoxide and formate can be produced efficiently [12]. As both compounds require only a two-electron reduction of CO_2, finding a good catalyst for their production is less challenging than for multi-electron products, such as methane, methanol, ethylene, oxalate and acetate [13]. Carbon monoxide is a highly toxic gas of low solubility and low mass transfer rate, which makes its downstream utilization challenging, especially with respect to microbial cultivation [14]. On the other hand, formate is a highly soluble compound that can be handled rather easily, making it a suitable mediator between electricity and microbial cultivation. Supporting this approach, recent studies have demonstrated multiple strategies for the electrochemical reduction of CO_2 to formate — with current Faradaic efficiency of well above 90% — and put

Figure 1



A schematic representation of the formate bio-economy concept. Multiple approaches could support the synthesis of formic acid/formate from available sources. Formate could be then consumed by natural formatotrophic microbes or by microbes engineered to efficiently assimilate formate for the production of fuels, value-added chemicals, and protein meal for animal or human consumption.
Source: All icons are taken from www.icons8.com.

forward the feasibility of an industrial scale-up in the near-future [15•,16•,17,18,19••,20].

Electrochemical reduction of CO_2 to formate circumvents several major shortcomings of other proposed strategies for electricity-dependent microbial cultivation: (1) Direct electron transfer from an electrode to living cells [21] is restricted to a small number of organisms and to low current-density. Conversely, formate can be produced at considerably higher rates and could potentially be assimilated by many biotechnologically engineered organisms (see below); (2) unlike H_2, which can be produced even more efficiently from electricity [22] and serve as a microbial feedstock [23,24•,25], formate is completely soluble and not explosive. Furthermore, unlike H_2, formate can be assimilated directly, rather than being completely oxidized for reducing power; such direct metabolism can support considerably higher biomass and product yields [26••].

A comprehensive economic analysis has put the price of electrochemical production of formate at ~$500 [15•]. This price changes considerably depending on the cost of electricity, the consumables required for the process, the cost of concentrated CO_2, the efficiency of CO_2 reduction (Faradaic efficiency as well as energetic efficiency [22]), the rate of formate production, and the composition and durability of the electrode. A recent study has demonstrated that, from an industrial perspective, current technologies display satisfactory Faradaic efficiencies and quite acceptable current densities; however, the over-potentials currently applied are still too high and the durability and cost of the electrodes are far from optimal [24•]. Improving these factors could substantially reduce the cost of large-scale CO_2 reduction.

Even with current technologies, the use of cheap electricity produced at off-peak hours and concentrated CO_2 from power plants or other industrial factories could