More bang for the biofuel buck

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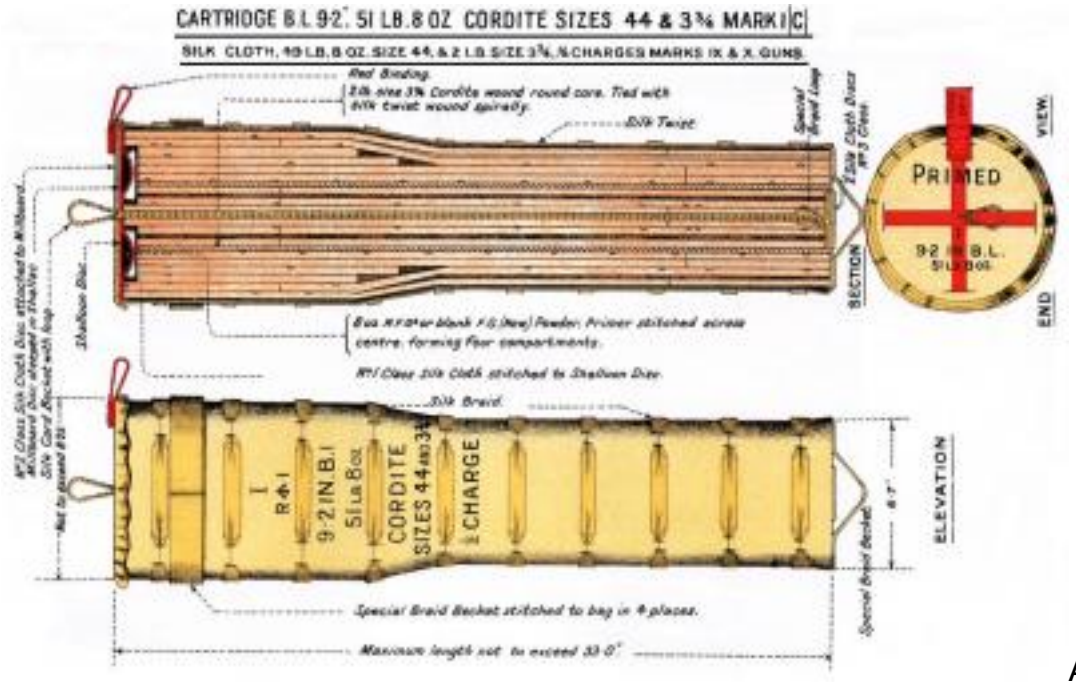

A fermentation technique once used to make cordite, the explosive propellant that replaced gunpowder in bullets and artillery shells, may find an important new use in the production of advanced biofuels. With the addition of a metal catalyst, researchers at the U.S. Department of Energy (DOE)'s Lawrence Berkeley National Laboratory (Berkeley Lab) have shown that the production of acetone, butanol and ethanol from lignocellulosic biomass could be selectively upgraded to the high volume production of gasoline, diesel or jet fuel.

Using the bacterium Clostridium acetobutylicum, the Berkeley Lab researchers fermented the sugars found in biomass into the solvent acetone and the alcohols butanol and ethanol, collectively known as "ABE" products. They then catalyzed these low carbon number products with the transition metal palladium into higher-molecular-mass hydrocarbons that are possible precursors to the three major transportation fuel molecules. The specific type of fuel molecule produced – whether a potgasoline, diesel or jet - was determined by the amount of time the ABE products resided with the palladium catalyst.

"By catalytically upgrading ABE fermentation products we're able to exploit highly efficient metabolic pathways and achieve near theoretical yields of transportation fuel precursors," says Dean Toste, a chemist who holds joint appointments with Berkeley Lab and the University of California (UC) Berkeley. "With our technique, we can obtain about a gallon of fuel from 16 pounds of the sugars that can be derived from lignocellulosic biomass."

Toste is the corresponding author of a paper published in the journal Nature titled "Integration of chemical catalysis with extractive fermentation to produce fuels." Co-

authoring this paper were Pazhamalai Anbarasan, Zachary Baer, Sanil Sreekumar, Elad Gross, Joseph Binder, Harvey Blanch and Douglas Clark. The work was supported by the Energy Biosciences Institute (EBI), a collaborative partnership between UC Berkeley, Berkeley Lab and the University of Illinois at Urbana Champaign. EBI is funded by the BP energy corporation.

Clostridium acetobutylicum is also known as the Weizmann organism after Chaim Weizmann, the chemist who first used the bacterium to ferment ABE products from starch. The bacterium rose to prominence during World War I when it was used by the British to ferment acetone for the production of cordite. C. acetobutylicum and the ABE fermentation process continued to be widely used until the 1950s when they were replaced by cheaper petrochemical-based processes.

With rising concerns about the release of excess carbon into the atmosphere as the result of burning fossil fuels, there is a renewed scientific effort to develop advanced biofuels for transportation energy. Synthesized from the sugars in the lignocellulosic biomass of grasses and other non-food plants, and produced in a sustainable manner, advanced biofuels could be carbon-neutral, meaning their use would not add excess carbon to the atmosphere. In addition, they would be renewable and non-polluting and represent a huge potential source of domestic jobs and revenue. Furthermore, unlike ethanol made from corn starch or sugarcane, advanced biofuels, if they could be successfully developed and produced cost-effectively, could be dropped into today's vehicles with presumably with no impact on performance, and used in today's infrastructures with no modifications required.

"In some ways, this work is a step back in time in which a very old fermentation process is being used with some new engineering and chemistry," says co-author Harvey Blanch, one of the nation's deans of biofuels research who also holds joint appointments with Berkeley Lab and UC Berkeley. "While there has been some progress in engineering microbes to produce advanced biofuels, the quantities produced thus far - technically, the solution's titer - tend to be very limited. A hybrid method, combining microbial production with chemical catalysis, might provide a pathway to more efficient production of these advanced biofuels."

C. acetobutylicum ferments the sugars in lignocellulosic biomass into a product that is three parts acetone, six parts n-butanol, and one part ethanol, similar to how yeast ferments the sugars in grapes and hops into wine and beer. From a transportation energy perspective, the two-carbon chains of ethanol, three-carbon chains of acetone and four-carbon chains of butanol are mainly useful as additives to gasoline. However, the production of acetone in combination with the alcohols makes it possible to build longer hydrocarbons chains of gasoline, diesel and jet fuel.

"The key to our technology is the ability of C. acetobutylicum to produce acetone," Toste says. "Acetone harbors a nucleophilic alpha-carbon, which is amenable to the formation of carbon bonds with the alcohols produced in ABE fermentation."

To catalyze the build-up of these shorter carbon chains into longer fuel chains – a process called "alkylation" - Toste and his co-authors tested a number of transition

metal catalysts, the workhorses of modern industry that are used to initiate virtually every industrial manufacturing process involving chemistry. The best performer they tested was palladium.

"In the first reactor, we remove the low-boiling ABE products from the fermentation broth using a high-boiling extractant, such as glyceryl tributyrate," Toste says. "This removes toxic products from the organism, allowing for higher yields of ABE and a clean stream of product for chemical catalysis, which takes place in a second reactor. While palladium on carbon was the best catalyst in these tests, we have already identified other transition metal catalysts that could be even better."

Toste believes that the integrative biological/chemical approach he and his colleague are reporting should be relatively simple to scale-up and implement on a commercial scale.

"The ABE fermentation process was established and scaled nearly a century ago," he notes, "and while the chemistry portion is less proven on scale, it relies on heterogeneous catalysis, a mainstay of industrial chemistry today."

Toste believes the combination of biological fermentation and chemical catalysis has important potential applications beyond the conversion of lignocellulosic biomass into transportation fuels and could become a powerful new technology-enabling tool.

"Many technologies today rely on either fermentation or chemical catalysis," he says. "The idea of building integrated fermentation processes involving networks of catalysts is an exciting prospect."

Adds co-author Blanch, " Integrating chemistry and fermentation is a useful way to capitalize on the best of both worlds. The chemistry described in our Nature paper is exciting because new carbon-carbon bonds are being formed between molecules and oxygen is being rejected without the need of hydrogenation. This results in very high yields."

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