FUEL FROM PLANTS

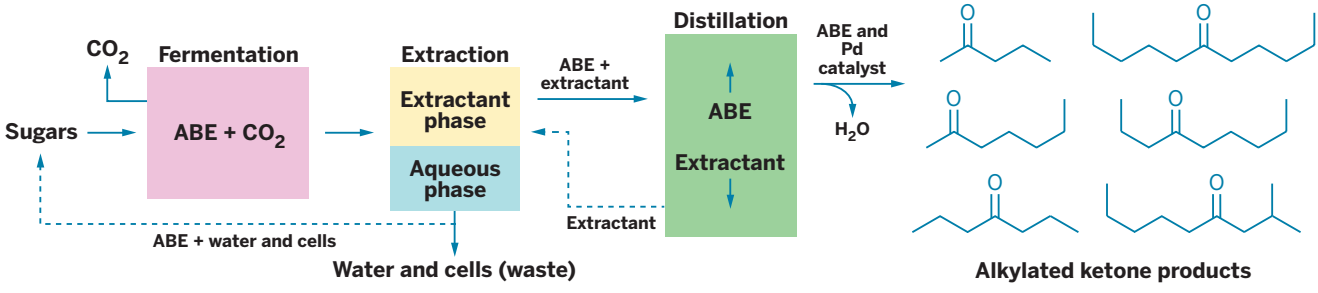
FERMENTATION AND CATALYSIS combine to efficiently convert carbohydrates to fuel

A NEW TECHNIQUE combines fermentation and chemical catalysis into an integrated process for efficiently converting sugars and starches from natural plant sources into ketone precursors of gasoline, diesel, and jet fuel components. The technology could realize a long-sought goal: producing fuels economically from renewable, natural sources to supplement the world's finite sources of petroleum-based fossil fuels.

F. Dean Toste, Douglas S. Clark, and Harvey W. Blanch of the University of California, Berkeley, and coworkers developed the technique, which they report in *Nature* (DOI: 10.1038/nature11594). The researchers have patented the process and believe it could be further refined and commercialized within five to 10 years.

The process uses *Clostridium acetobutyli-*

TRANSFORMATION Acetone, *n*-butyl alcohol, and ethanol (ABE) formed by fermentation are extracted during the process to improve fermentation efficiency and make the ABE product compatible with the catalyst.



ADAPTED FROM *NATURE*

cum bacteria to convert plant lignocellulosic materials, cane sugar, or other natural carbohydrates to acetone, *n*-butyl alcohol, and ethanol, or ABE. Fermentation to form ABE was discovered in the early 20th century by chemist and later Israeli president Chaim Weizmann.

Key to integrating the fermentation and chemical catalysis stages is a glyceryl tributyrate "reactive extraction," which removes ABE and other products from the aqueous bacterial medium as fermentation proceeds. The step boosts the efficiency of fermentation, which is normally inhibited by some of the products the extractant removes. It also isolates ABE while excluding water, enabling ABE to be fed directly to an efficient palladium-based catalyst that is poisoned by water.

The catalyst accelerates C–C bond-forming reactions that convert the ethanol and *n*-butyl alcohol to aldehydes, which react with acetone to produce higher alkylated ketones. The ketones can later be deoxygenated to alkanes similar to those found in liquid fuels.

The technique is not the first to convert renewable plant materials to fuel-like components. Among earlier approaches is one devised by kinetics and catalysis expert James A. Dumesic of the University of Wisconsin, Madison, and coworkers. Dumesic's no-fermentation, all-chemical route dehydrates or dehydrogenates sugars to produce intermediates that are then hydrogenated to yield fuel-like components. The *Nature* paper estimates that the overall carbon yield—the amount of carbon in the raw material that gets converted to products—of Dumesic's all-chemical route is significantly lower than that of the new integrated approach—about 21% versus 38%. Such numbers are necessarily fuzzy, because Dumesic's method may have been improved since it was reported and the new one has not yet been extensively optimized.

UNLIKE OTHER plant-to-fuel methods, Toste notes, the integrated approach can use "dirty" sugars such as molasses and nonfood materials such as grass and field wastes because the fermentation tolerates impurities without reducing yields.

In addition, by varying the reaction temperature or the amount of a key base in the alkylation step, the process can be tuned to produce predominantly gasoline or jet and diesel blends. That ability is "amazing," comments Dionisios G. Vlachos, director of the Catalysis Center for Energy Innovation, a Department of Energy-funded center at the University of Delaware. Furthermore, the process "has the highest ever reported carbon yield from fermentation, does not involve gas-phase catalysis that requires energy-intensive vaporization, and is fairly simple," Vlachos says.

The new technique is "a clever integration of fermentation technology with solvent extraction of products and state-of-the-art nonbiological catalysis," says biofuels expert Eleftherios T. Papoutsakis of the University of Delaware.

James E. Rekoske, vice president and general manager of the renewable energy and chemicals unit at Honeywell's UOP, in Des Plaines, Ill., says, however, that although the work "shows some interesting promise, there is much remaining to be done before we can identify this route as a viable conversion path." He notes that some trace components commonly produced in ABE fermentations weren't included in the study. The technique's yields, "while quite good for an unoptimized process, will need to be higher to make sure expensive carbohydrates are utilized efficiently," he says. "I do worry about the complexity of a combined biochemical and thermochemical process." In addition, metal leaching from the Pd catalyst could cause problems with the process design and its costs, Rekoske says.—STU BORMAN