Lowering the Cost of Alcohol

Energy-efficient alternatives to distillation could make fermented plant materials an attractive source of liquid fuels

New technologies for separating alcohol from water solutions soon may lower significantly the cost of producing ethyl alcohol by fermenting grain, sugar crops, or cellulose. This is possible because the new processes use less energy in recovering the alcohol than does the traditional method of distillation, which was developed primarily to produce beverage-grade alcohol. If laboratory estimates of the energy savings are borne out on an industrial scale, alcohol may become competitive with gasoline. Some fermentation products other than alcohol also can be concentrated efficiently, and show promise as alternative liquid fuels.

Traditional ways of producing and recovering beverage-grade ethyl alcohol require 1.4 to 1.6 times more energy than would be liberated if the alcohol were burned as a fuel,* and the cost of growing and gathering the raw biomass is additional. Including the energy required to remove the last of the water—a step omitted by beverage makers but essential if the alcohol is to be used in gasohol (90 percent gasoline, 10 percent alcohol)—the distillation steps alone require a little more energy than the fuel value of the alcohol. The new processes might halve the total energy cost of alcohol just by making the purification steps more efficient.

In August, researchers at Purdue University announced that the energy used in recovering dry alcohol from fermentation broths—called beer—can be cut to about 10 percent of the fuel value of the alcohol if cellulose or other dry plant materials are used to absorb some of the water (*Science*, 31 August, p. 898). According to Michael Ladisch and Karen Dyck, the Purdue technique for separating alcohol from water solutions is a variant of a much older process. It has been known for years that alcohol can be dried with desiccants such as calcium oxide, which reacts with the water present, forming calcium hydroxide. Ladisch and Dyck's approach is to dry the vapors from an alcohol-water solution that has already been concentrated by distillation to perhaps 85 percent alcohol. They find that desiccants such as cellulose and cornstarch provide greater energy savings than calcium oxide, because less energy is needed to dry cellulose or cornstarch than to drive the water off calcium hydroxide. If cracked corn is used as the desiccant it does not even have to be redried, notes Ladisch, but can be fermented wet to make more alcohol. According to William Scheller of the University of Nebraska, several small industrial plants in Europe dried alcohol with desiccants during and after World War II. But the last of these plants closed down in 1958, a victim of cheap oil.

Another novel technique for separating alcohol from water solutions is a version of gas chromatography. Bernhard Miller of the Textile Research Institute in Princeton says that textile yarns such as rayon retard the movement of water vapor, but allow organic vapors to travel freely. Miller and his co-workers have developed a continuous process for separating alcohol from water based on this principle. An endless loop of yarn fibers is pulled slowly through a tube into which alcohol-water vapors are introduced. The water is removed by the yarn (which is then dried by heating), and pure alcohol vapor is recovered from the other end of the tube. However, the energy requirements for this gas chromatograph have yet to be determined.

Alcohol dissolves readily in some liquids that do not mix with water to any great extent. By exploiting this solubility difference, alcohol can be recovered from aqueous solutions by solvent extraction. One version of the process uses a so-called critical fluid—a gas that has been compressed to the point where the distinction between gas and liquid disappears. At 50 to 80 times atmospheric pressure, carbon dioxide becomes a critical fluid, and can be used to extract alcohol from fermentation beer that has been filtered to remove solids, says Richard de Filippi of Arthur D. Little, Inc. Details of how alcohol is recovered from the carbon dioxide are proprietary, but de Filippi estimates the energy cost of the whole extraction process "conservatively" at 40 to 60 percent of the alcohol fuel value. One advantage of this scheme is that carbon dioxide is a by-product of the fermentation process, so the solvent costs are minimal—an important consideration since some of the solvent inevitably escapes in the alcohol recovery process.

Several other laboratories have different solvent extraction schemes under development. For example, the University of Pennsylvania and General Electric are working together on a process using dibutyl phthalate, a water-immiscible solvent for alcohols. According to Kendall Pye of the University of Pennsylvania, this solvent has a much higher boiling point than fuel alcohols, so the alcohols can be driven off easily in a single distillation step and solvent losses are minimal. Initially the researchers bubbled the dibutyl phthalate through the fermentation liquid, but emulsions of beer and solvent formed. The Penn group is now exploring several different ways to circumvent this problem. One method they have tried with some success is to keep the solvent separate from the beer with a thin membrane.

Harry Gregor, of Columbia University, is optimistic that membranes, without additional solvents, can be used for alcohol purification. He calculates that with membranes, the energy cost of recovering pure alcohol from fermentation beer could be reduced to about 0.6 percent of the alcohol fuel value. This corresponds to an energy expenditure of only about four times the theoretical minimum imposed by the second law of thermodynamics.

Alcohol could be separated from water with membranes that are comparatively impermeable to alcohol but allow the water to pass through. Such membranes already exist, says Robert Riley of UOP Incorporated's Fluid Systems Division in San Diego, but the pressures that would be needed to drive an industrial alcohol separation process are too high to be practical.

Another approach is to use membranes that are permeable to alcohol but not water. Gregor reports that he has such a membrane, one that passes alcohol about twice as fast as water and permits reasonable fluxes of alcohol. But more work is needed to find membranes suitable for commercial use, where high selectivity and high alcohol flux are essential for the overall economics of the

*The energy liberated by burning 1 liter of 100 percent ethyl alcohol is about 23 million joules (85,000 Btu's per gallon).

0036-8075/79/1005-0041$00.50/0

separation process. Harold Lonsdale of Bend Research, Inc. in Bend, Oregon, a firm that specializes in membrane research and development, believes that alcohol-permeable membranes will become industrially practical only when carrier molecules are developed to selectively transport alcohol molecules across membranes. "The day might come when someone finds a carrier," says Lonsdale, "but it won't come in a decade." Gregor, on the other hand, feels it is only a matter of time before practical membranes are found, provided funding is available for a sustained research effort.

Zeolites—molecular sieves—selectively absorb molecules smaller than a certain size. These porous rocks might be useful in alcohol recovery, notes Garry Baughman of the Colorado School of Mines Research Institute. A promising candidate is clinoptilolite, a naturally occurring zeolite with holes that water, but not alcohol, should fit into. Clinoptilolite has yet to be tested for its selectivity in absorbing water, but if it works, the relative abundance of clinoptilolite could make its use economically attractive at least in some parts of the country. According to Joseph Gelo of Union Carbide Corporation's Linde Division, researchers there are exploring the use of synthetic zeolites for the final purification step. Gelo says that such a process can compare favorably with distillation in terms of cost and energy consumption.

Although traditional beverage distillation technology requires almost ten times more energy than the Purdue drying technique, a number of commercial modifications have been developed that improve the energy efficiency of distillation. By recycling much of the heat needed for distillation, industrial designers have been able to cut substantially the energy required for producing ethyl alcohol.

Engineers at Raphael Katzen Associates International have designed plants that incorporate heat-recouping schemes and use in total about 65 percent of the fuel value in producing a given amount of alcohol. Says George Moon, only about 22 percent of the fuel value is needed for the distillation steps. One of the tricks used by Katzen Associates, a Cincinnati-based firm that specializes in designing industrial processes, is to run two separate distillation steps at different pressures so that the waste heat from the higher-pressure distillation can be used again in the lower-pressure procedure. Traditional distillation technology requires three or more separate distillations to recover pure alcohol from fermented beer.

Another successful energy-saving strategy is to use entraining substances that do not have to be recycled to help distill the last bit of water from the ethanol. Normally a separate distillation step is required to eliminate the last of the water because ethanol and water form a mixture, called an azeotrope, that cannot be separated by distillation without the addition of a third substance. Traditionally benzene is the additive. But in fuel alcohol plants made by the ACR Process Corporation in Champaign, Illinois, gasoline is substituted for benzene as the entraining substance. Since the alcohol is intended for use as fuel, there is no need to remove the gasoline that remains in the end product, so one step in the purification is eliminated. Robert Chambers of ACR says that the total energy cost of their process is equivalent to about 53 percent of the alcohol fuel value, but this does not include the cost of drying the solids left over after fermentation—in this case a protein-rich grain product that can be fed wet to cattle.

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Several different laboratories have been working on vacuum distillation procedures to remove alcohol from beers that are still producing alcohol. While this requires a fair energy investment, it produces only slightly concentrated alcohol (17 to 18 percent alcohol would be obtained from 6 to 7 percent brew in one scheme). But when the alcohol is removed before it inhibits fermentation, the yeast (or bacteria) can produce alcohol much faster than it could in a normal beer: a significant advantage, notes Charles Wilke of the University of California, Berkeley.

Although much attention has been focused on lowering the energy cost of producing pure alcohol, some research has been done on producing other useful fuels and chemicals from fermented plant materials. By reacting alcohol or other products in the broth to form substances that are insoluble in water, a variety of useful products can be obtained.

Polyphosphoric acid not only removes all the water from an aqueous solution of alcohol, but also removes two hydrogens and an oxygen atom from each alcohol molecule, according to Donald Pearson of Vanderbilt University. Dehydrated alcohols other than ethanol polymerize to form gasoline-like hydrocarbons that rise to the top of the solution and can be skimmed off. At atmospheric pressure, ethyl alcohol is converted to ethylene gas, a valuable chemical feedstock, but Pearson hopes to produce gasoline from ethanol by changing the reaction pressure. Polyphosphoric acid can be reconstituted by heating it to drive off the water, but the heat required is rather high, so the energetics may be unfavorable.

In another process, decane, a diesel fuel substitute, can be skimmed off the top of the solution, says Donald Wise of Dynatech R/D Company in Cambridge. Wise manages a project to produce liquid fuels by fermenting marine algae with bacteria. If the normal production of methane is suppressed, fermentation can be made to produce caproic acid, a six-carbon carboxylic acid. This acid is extracted from the fermentation brew with kerosene and converted electrolytically to decane, which floats to the top of the electrolysis vessel. Wise estimates that the total processing cost is less than 45 cents per gallon of decane, so this process could be economically attractive.

Carboxylic acids also can be used to make ketones, notes Edward Lipinsky of Battelle's Columbus Division. The acid can be precipitated as a salt, which is then heated to drive off a ketone. For example, a salt of butyric acid might be "roasted" to produce 4-heptanone. Besides being useful solvents, says Lipinsky, ketones could be used as motor fuels.

While there is little doubt that distillation is the technology of choice for the immediate future, less conventional separation methods may prove more energy-efficient in the long run. But with such a wide variety of techniques under investigation, it is unclear which, if any, will displace distillation for the recovery of alcohol or other fermentation products. In the end, choices may be made on the basis of fringe benefits or capital investment costs that affect the economics of the whole process, rather than on the basis of energy efficiency of the purification step alone.

—Frederick F. Hartline