# Catalyzing Innovation

## Concurrent Alcohol Recovery and Fermentation Using Pass-Through Distillation

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### Introduction

A fundamental problem in the field of industrial bio-technology is that bio-alcohols—such as ethanol, butanol, and propanol—are toxic to cells and thus contribute significantly to fermentation stress.[1–4] As the solvent concentration increases during an industrial fermentation, the productivity diminishes, limiting broth titer, yield, and substrate feed concentrations. Ultimately, this results in high water throughput, which is associated with large capital expenditure (CAPEX) and operating expense (OPEX). This phenomenon, known as end-product inhibition, can be mitigated by removing product from the broth while fermentation is on-going. Although this strategy, known as in-situ product recovery, has been shown in many research studies to be beneficial, it is not in widespread industrial use.[2,4–8] Few industrially promising product recovery strategies have been evaluated at relevant scale, and all have disadvantages.[1,2,7,9] A practical, low-cost, microbe-compatible separation process is needed to commercialize what in this article is called concurrent alcohol recovery and fermentation (CARAF).

Pass-through distillation, a newcomer to the field of industrial separation, may fill this need because it addresses some of the practical limitations of distillation in CARAF and reduces the otherwise high CAPEX, OPEX, and operating temperature.[10,11] This work explains how pass-through distillation works and how it may contribute to the advancing the biotechnology industry by enabling widespread use of CARAF.

### CARAF

There is a significant body of research spanning from the late 1970s to the present concerning production of bio-alcohols wherein the alcohol separation process functions concurrently with the fermentation process.[1,2,5–9] Various authors have attached differing terms to the concept, including in situ product recovery, instantaneous product removal, continuous extractive fermentation, and many more. In this work we will consolidate these functionally disparate terms under the new label CARAF. Over the years, many separation techniques for CARAF have been studied. They fall into four fundamental categories (and hybrids thereof): vacuum distillation; gas stripping; membrane pervaporation; and liquid-liquid extraction. All of those share one crucial requirement—the recovery process must be conducted at a temperature compatible with the microbes to avoid cell death or negative impact on cell viability. For example, the optimum fermentation temperature for industrial yeast strains in fuel alcohol production is nominally 32°C.[3] Thus, a recovery process operating at substantially higher temperature will risk cell death, negating the sought-after benefits.

While the concept goes back to 1944,[12] the earliest focused research efforts on CARAF used vacuum distillation as the means of alcohol recovery. That work, conducted by Cysewski and Wilke in California in the late 1970s, found that significantly higher alcohol productivities can be achieved compared to conventional fermentation.[5] For example, the fermentor productivities of a typical first-generation ethanol process is reported to be on the order of 2 g/L/h, and application of CARAF could realistically increase that metric by a factor of two or possibly an order of magnitude higher.[3] Although researchers have also found certain specific trade-offs, in the end, what remains is a very promising tool for improving alcoholic fermentations. This tool could facilitate key innovations in economical production of commodity volumes of bio-alcohols. The opportunity is even greater for second-generation fermentation, which involves either lignocellulosic-derived substrates, genetically engineered microbes, or both. Currently, without significant market changes (i.e., higher costs for oil and gas), innovation is needed in order for biobased chemicals to better compete with petrochemicals.

End-product inhibition—the result of solvent toxicity—remains a persistent, unsolved problem for industrial-scale alcoholic fermentations, despite decades of research and development.[4] It factors heavily into practical limitations on titer, volumetric productivity, and yield, carrying with it economic penalties. In first-generation fermentation, however, yeast strains and fermentation management techniques have been improved to such an extent that economically acceptable titers (>10%) and yields (>>90%) are possible.[3,4] However, in the case of corn ethanol production in North America (over 50% of the world capacity) large-volume, long-residence-time batch fermentation is relied upon. For these existing facilities, end-product inhibition contributes to the "ceiling" on increasing throughput and reducing water/energy loads. For second-generation fermentation, the problem of end-product inhibition is significantly more challenging and a major barrier to commercialization, particularly for "advanced biofuels." Microbes are inherently much less tolerant to "advanced" solvents such as butanol and propanol.[4,7] And the use of lignocellulosic feedstocks introduces other compounding complications. Lignocellulosic fermentations must tolerate a range of additional

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inhibiting compounds, including organic acids, phenolics, and furan derivatives.[4] Furthermore, the need to coferment a mixture of C5 and C6 sugars presents a challenge in selecting a suitable microbe.[4] To date, there has been no successful genetic engineering of an industrially relevant microbial strain that can simultaneously ferment mixed sugars and tolerate inhibitors, while delivering acceptable titer, productivity, and yield.[4] It appears that genetic engineering to enable metabolism of multiple sugars worsens tolerance to solvents and other inhibitors.[4] Considerably more attention has been paid to the genetic engineering of strains with special features and tolerances than on CARAF technologies. The ideal industrial microbe has yet to be identified. Until then, perhaps a more holistic approach of integrating genetic engineering efforts with downstream alcohol recovery steps will yield commercial progress.

F1    *Figure 1* conceptually illustrates how CARAF might impact the performance of a hypothetical first- or second-generation batch ethanol fermentation. The vertical axis is the degree of substrate consumption and the horizontal axis is fermentation time. The dashed curve represents a typical fermentation while the solid curve shows what might happen if end-product inhibition was eliminated. A typical corn ethanol fermentation, for instance, might see a rise in ethanol concentration from 0 to 80 g/L after 30 h, and then slowly climb to 130 g/L after another 45 h.[3] In practice, the batch is cut off before complete conversion. At the same time, as productivity flattens (~30 h) cell count reaches a maximum. CARAF might alleviate solvent inhibition starting at 10 h, allowing a faster batch, increasing conversion to the desired metabolite, and increasing operational flexibility, with less chance for infections to take hold. But residual substrate limitation will still affect specific growth rate toward the end, and thus the fermentation time, depending on the microbe's affinity for the substrate.[13] It should be noted that enzyme hydrolysis kinetics are not factored in here, but it is

known that ethanol concentrations negatively affect enzyme performance.[14] Also, the impact of ethanol's inhibitory effect on competing organisms is not integrated.

CARAF's ability to increase volumetric productivity could help manage the costs associated with scaling up advanced alcoholic fermentation. Costs for agitation, cooling, and cleaning are a non-linear function of the volumetric capacity of the fermentor and can be a large proportion of a biorefinery's overall CAPEX. OPEX is affected by volume too. For example, power consumption for agitation is sensitive to increasing absolute volume. A recent presentation by Warner Advisors (Sacramento, CA) suggests that the typical installed cost of a fermentor can vary between $1.60 to $16.00/L rates, saving $3.5 million plus the associated OPEX. The opportunity for CARAF to save CAPEX is even greater with advanced fermentations, since there can be the need for aseptic fermentation, or in the case of gas phase fermentation, pressurized vessels.[16]

In spite of its many potential benefits, why is CARAF not more prevalent? Certainly one of the main reasons is economics. Whether real or perceived, CARAF is viewed as expensive.[4] If conventional vacuum distillation is chosen as the separation technology, CARAF's economic advantages are offset by the need for chilled water to cool the condenser. This is an often overlooked, but very practical constraint, to scaling up downstream separation processes. At laboratory- or pilot-scale, this poses no obstacle, but at plant-scale it involves large refrigeration equipment that propel plant CAPEX and OPEX to unacceptably high levels. Gas-stripping technology has a similar issue. For example, in 2010, researchers at the United States Department of Agriculture reported on their work with CARAF using gas stripping, where a continuous pilot plant fermentor was fed liquefied, 40% solids corn mash at 25 kg corn per day for 60 consecutive days.[17] "Nearly complete" conversion of greater than 40% corn mash was completed in a 36-h residence
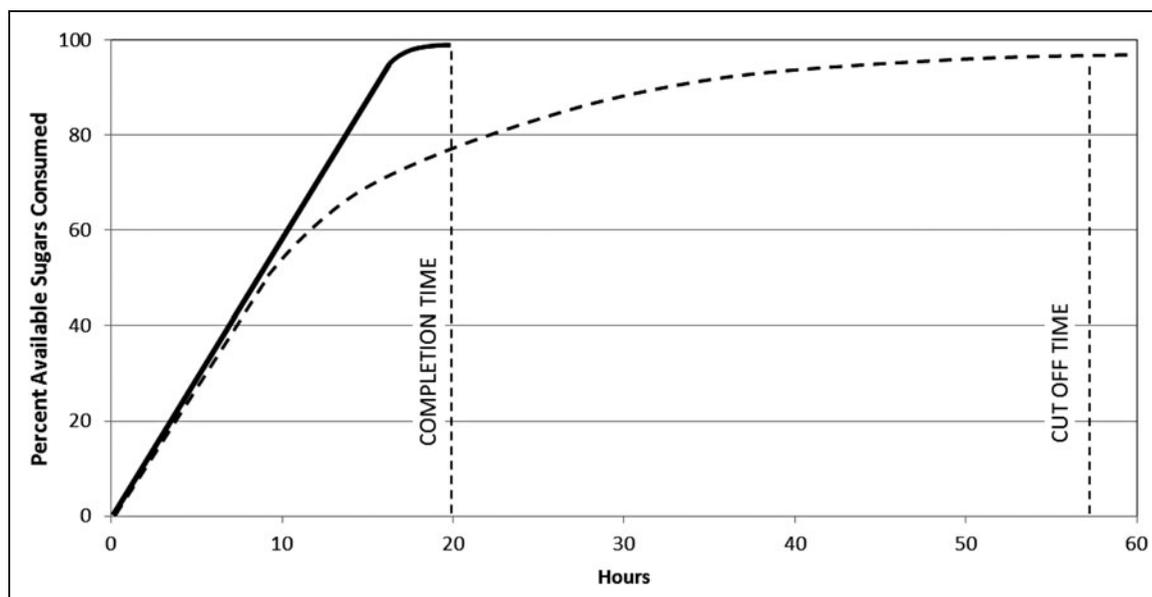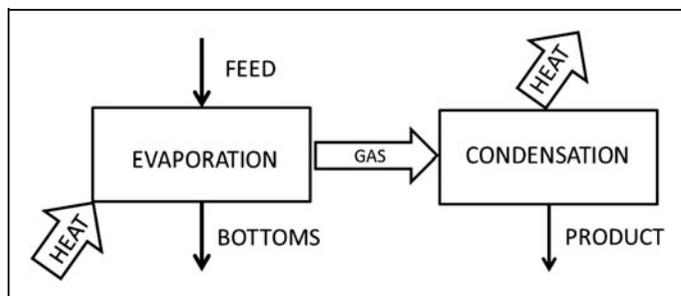


**Fig. 1.** Hypothetical impact of CARAF on batch fermentation.

**Fig. 2.** Ordinary two-step distillation.

time with a steady-state volumetric productivity of 16 g/L/h (nearly 8 times a conventional fermentation), which the authors described as ''an impressive achievement.''[17] This ability to process lower water concentrations is also key to improving a plant's downstream energy costs. But, this is impractical at large-scale, again because the gas-stripping column's condenser is refrigerated (in this case operated at around −1°C).[17]

Several of the concerns raised in the literature regarding CARAF's potential high capital costs are not well-documented, although virtually no large-scale projects or even techno-economic simulations are available to assess cost metrics. The concern about energy intensity is definitely warranted, however. Simple distillation which is reliable and well-understood, is often chosen because it is industry's most mature separation technology.[10] But if distillation is to be the separation method for commercial-scale CARAF, there is a need for a new type of distillation that can provide low-temperature separation without mechanical refrigeration of condensers, while simultaneously minimizing energy requirements.

## Pass-Through Distillation
### DECOUPLING DISTILLATION—SEPARATION OF BOILING FROM CONDENSING

Reduced to its essentials, distillation is a two-step process: evaporation and condensation (*Fig. 2*). These two steps are coupled because they are carried out at the same pressure. The practical consequence is that low evaporator temperature requires an even lower condenser temperature, and that generally involves expensive refrigeration.

Pass-through distillation is a four-step process (*Fig. 3*) that is similar to simple distillation in that it begins by evaporating some feed liquid and ends by condensing it. These steps, however, are decoupled by an absorption step (step 2) and a desorption step (step 3), which involve a recirculating inventory of absorbent fluid. In step 2, this fluid absorbs the gases evaporated in the first step. In step 3, the absorbed material is boiled out of the absorbent fluid. Decoupling permits the evaporator to

operate at very low pressure while the condenser operates at higher pressure, in a regime where water and ethanol will condense using inexpensive cooling means.

### ABSORPTION OF ALCOHOL AND WATER VAPORS INTO BRINE

The absorption fluid must be selected to provide the desired operating conditions. To boil a fermentation broth at 30°C requires an evaporator pressure of roughly 30 Torr, or 1/25th that of the atmosphere. An absorption fluid must therefore be selected that has a vapor pressure of 30 Torr at the chosen operating temperature of the gas absorber.

The gas absorber relies on a steady supply of regenerated absorption fluid, regardless of where it came from or how it was produced. Steps 3 and 4 furnish that supply in any way the system designer deems appropriate. It might be a single-effect atmospheric distillation if capital cost is the driving consideration or a four-effect system if energy conservation is more important. The condenser may be cooled by evaporative cooling towers where water is abundant or by direct air cooling (fin fans) where it is not. The heat source for the regenerator is another flexible matter. It may be direct-fired, steam-heated, or electrically heated. It might be driven by the waste heat of another process or even be solar powered.

It should be evident at this point that as long as there exists an absorbent fluid capable of absorbing water and ethanol at low absolute pressure, pass-through distillation can be used to carry out CARAF without the use of mechanical refrigeration.[11] However, its economic viability has not yet been made clear. After all, ordinary distillation boils once while pass-through distillation boils the same material twice. How can this possibly result in reduced energy costs? To answer this it is necessary to invoke two basic principles of physical chemistry.

### EQUILIBRIUM VAPOR PRESSURE

In a closed vessel that contains a pure substance in the liquid and gaseous state, molecules are continually moving from the liquid to the gaseous phase and from the gaseous into the liquid phase. When these two take place at equal rates, we say that the system is in a state of equilibrium. For every value of pressure within the vessel, there will be a corresponding unique value of temperature. We call this temperature the boiling point, because
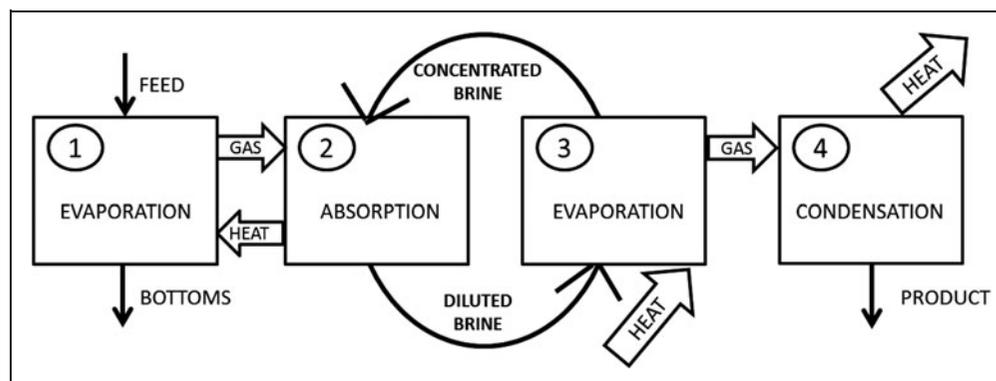


**Fig. 3.** Pass-through distillation.

at this temperature, addition of heat to a system will shift equilibrium and cause the rate of molecules moving from the liquid to the gas phase to exceed the rate at which molecules are going in the opposite direction. However it is equally a ''gas-absorption point'' (dew point), because if heat is withdrawn from the vessel, the net movement of mass is from gas to liquid. Thus boiling and gas absorption are two sides of the same coin. They are both excursions from an equilibrium state; one is caused by the addition of heat, the other by its withdrawal.

### BOILING POINT ELEVATION

When a non-volatile substance (for example, salt) is dissolved in a liquid, the boiling point of that liquid is increased. This phenomenon, known as boiling point elevation (BPE) is well known in the culinary arts. In the kitchen salt concentrations are generally well below 1%, and the resulting BPE is less than 1°C. The effect is far more impressive in industrial settings. Absorption chillers use concentrated lithium bromide brine as a working fluid. At atmospheric pressure, water boils at 100°C, but a 55% solution of lithium bromide boils at 143°C.[18–20] The BPE here is 43°C. Since the salt is non-volatile, the gas generated by boiling the brine is pure water vapor—saturated steam with a temperature of 100°C.

Combining these principles, it is evident that if adding heat to a 143°C salt solution generates a vapor at 100°C, then withdrawing heat from the same 143°C solution will cause it to absorb nearby 100°C water vapor. Albeit counterintuitive, an absorption fluid such as concentrated brine is capable of absorbing a gas cooler than itself.[20]

### RECYCLING HEAT

The first two stages of pass-through distillation may be viewed as an ordinary two-step distillation in which the condenser has been replaced by a gas absorber. Certain things remain the same; heat must be added in step 1 to bring the feed liquid to boil, and heat must be withdrawn from step 2 to bring the gas back to the liquid state. But there are differences. First, the product is no longer a clean, condensed stream, but rather a component of diluted absorption fluid. Second, the temperature profile of the process has altered. In ordinary distillation, the evaporator is the hottest part of the system, but in pass-through distillation, it is the coldest part. This fact opens the door for heat integration opportunity, where the heat removed from the gas absorption stage may be redirected to serve the demand of the evaporator.

When pass-through distillation is implemented with appropriate heat-exchange equipment, the first two steps operate as a single passive device with

no externally applied heating or cooling. Its net effect is to transfer volatile matter such as water and alcohol from one liquid stream (such as fermentation broth) into a second liquid stream (absorption fluid).

The diluted absorption fluid must be regenerated to be reused in an endless circuit. The volatile substances that were absorbed in the first two steps must be boiled out in steps 3 and 4, using ordinary distillation. But this time, there are no temperature-sensitive components to complicate the process. All the sugars, proteins, enzymes, and microorganisms in the fermentation broth left the system in the bottoms of step 1. Multiple effect distillation (MED), inherently involving high-temperature stages, may be applied with consequent energy savings. For example, a practical three-effect regenerator uses less than half the energy of a single-effect ordinary distillation.

So while it is true that PTD boils the same material twice, the first time costs nothing, as it uses no externally applied heating or cooling. The second time uses nominally half the energy of ordinary distillation through the use of MED.

### PRIOR ART

Although it is a new concept, pass-through distillation is not without technical antecedents. The absorption chiller, first patented in 1860 and in worldwide use today, is almost identical in its operation. Pass-through distillation and absorption chillers are different only because the former is an open system while the latter is a closed system. With minor piping modifications, however, a commercial absorption chiller could be made to operate as a pass-through distillation device.
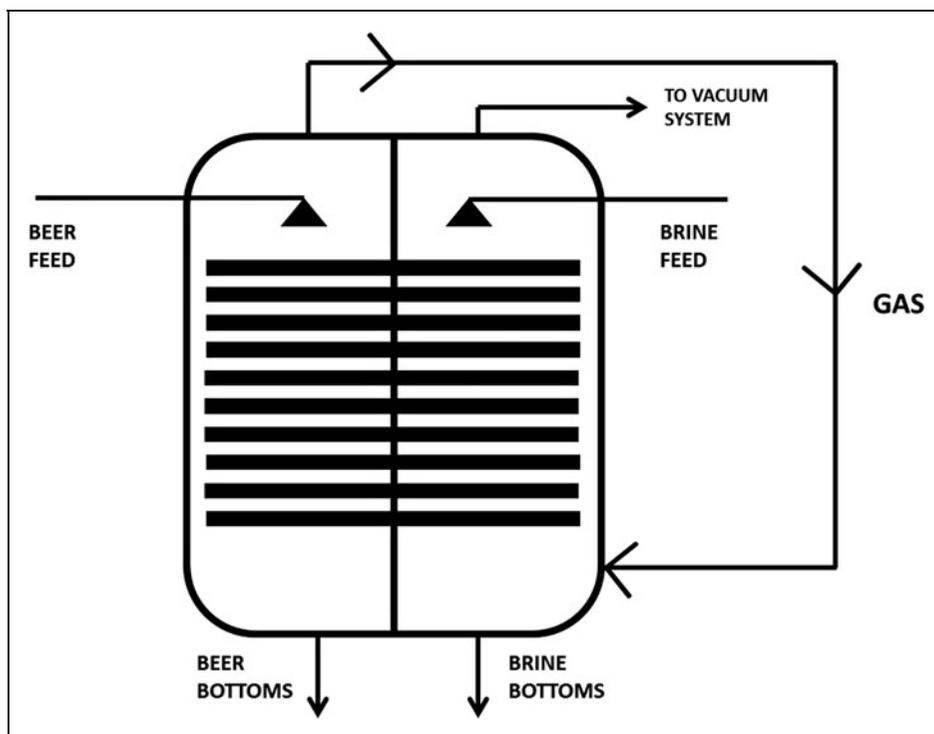


**Fig. 4.** Drystill's patented Stripping Absorption Module (SAM).

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A second pertinent technology is called liquid desiccant air conditioning (LDAC). It circulates indoor air through a brine scrubber to remove humidity, then regenerates the brine in an outdoor device resembling an evaporative cooling tower. It is an inherently open system.[21]

Between these two technologies, there is no aspect of pass-through distillation that is not already in widespread use world-wide.

## Process Intensification—The Stripping Absorption Module

As described above, pass-through distillation is a fairly obvious consequence of well-known scientific principles. One might wonder then why it is not already in use. The answer may be that until very recently there has been no appropriate heat and mass exchange equipment with which to carry out steps 1 and 2. Drystill (Toronto, Canada)'s Stripping Absorption Module (SAM) uses a bundle of low-cost heat pipes to conduct the heat generated in an absorption chamber into an evaporation chamber.[23]

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Modern heat pipes, with very low thermal resistance, were invented by NASA in the 1960s as a means to move heat for aerospace applications. Since then, they have found use in products ranging from air conditioners to laptop computers. But they are only beginning to find acceptance in the field of chemical process equipment.[22] Their use profoundly simplifies the construction of a SAM. It makes the equipment easy to tear down for cleaning and maintenance. It also makes a more robust system; if a heat pipe develops a leak it stops working, but if it is one heat pipe among hundreds, the impact on system performance is negligible.

*Figure 4* shows Drystill's SAM, where an external passageway conducts vapors from the evaporator chamber to the bottom of the absorption chamber. 

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## Testing and Validation

Drystill has built and tested proprietary SAMs at bench- and pilot-scale. Lithium bromide and lithium chloride solutions have both been successfully used as absorbent fluids.

Drystill constructed a pilot plant (*Fig. 5*) in 2014. It feature a SAM with 100 copper heat pipes that were 25 mm in diameter by 55 cm in length. It could boil water at a temperature as low as 20°C and a rate of 50 kg/h. A companion, single-effect brine regenerator was able to maintain continuous operation indefinitely. Feed streams included both watery and high-solids aqueous slurries.

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More recently, the bench-scale apparatus shown in *Fig. 6* was used to explore low-temperature separation of water and ethanol
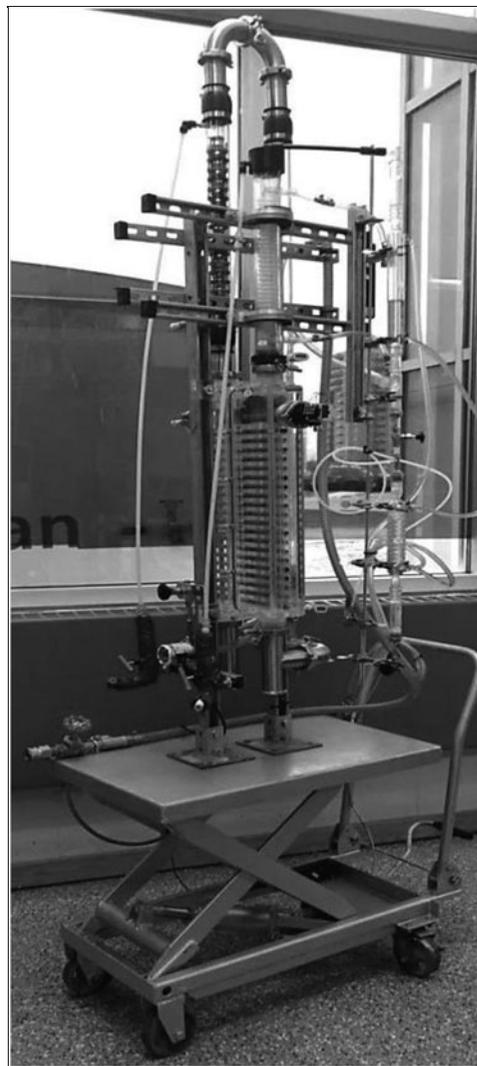
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**Fig. 5.** Pilot-scale SAM.



**Fig. 6.** Bench-scale SAM.

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from synthesized fermentation broth. The SAM comprised 20 heat pipes 12 mm in diameter by 20 cm in length. Brine was regenerated off-line in a single-effect glass still.

This study, conducted at Sheridan College (Brampton, Canada) won first place in a Project of the Year competition held by the York chapter of the Professional Engineers of Ontario. Drystill now plans to team with a local first-generation fuel ethanol company to conduct CARAF tests on a slip stream of fermentation broth.

## Conclusion

Pass-through distillation is a low-energy, low-temperature separation technique that can, in principle, implement CARAF without the cost burden of mechanical refrigeration. The development of Drystill's SAM technology makes pass-through distillation practical, affordable, robust, and easy to maintain. It may be the catalyzing innovation that brings CARAF into the mainstream of the industrial biotechnology revolution.

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