376bs - Ultrasound-Mediated Nonequilibrium Separation of Ethanol-Water Solutions, Including Avoidance of the Azeotropic Bottleneck

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Abstract

Title: Ultrasound-mediated nonequilibrium separation of ethanol-water solutions, including avoidance of the azeotropic bottleneck

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Introduction

Separation of liquid mixtures, frequently by distillation, is ubiquitous in the chemical and process industries (CPI). Distillation accounts for ~95% of the energy used in liquid separations, ~25–40% of overall energy used in CPI, and ~3% of global energy consumption.[1-2] The low efficiency of distillation is largely due to two issues. First, there are large irreversible losses due to heat transfer.[3] Second, a significant fraction of energy used in liquid separations is used to separate azeotropic mixtures in azeotrope-forming systems (e.g., ethanol/water). While a number of conventional distillation technologies[4-5] (e.g., pressure-swing, extractive distillation, and azeotropic distillation[6]) and new separation approaches[5] (e.g., dividing-wall columns, membranes, molecular sieves, and bio-absorbance) have been developed for azeotropic systems, these approaches largely rely on thermal separation via phase equilibrium or involve large capital and/or operational costs.

Ultrasound passing through a liquid layer with a free surface above produces droplets that form a mist. Current thinking is that this occurs at crests of capillary waves at the gas/liquid interface, by bursting of cavitating micro-bubbles near the interface, or possibly by both mechanisms.[5] Regardless of the mechanism, it is known that mist formation is accompanied by favorable partitioning of solute between the mist and the mother solution,[7] with studies in EtOH/water solutions showing significant EtOH enrichment in the mist[8-10], including enrichment of EtOH from 0.07 mass fraction in the mother solution to nearly 1.0 in the mist.[9] Current theories attribute enrichment to an excess of ethanol in a thin layer on the liquid side of the interface[10-11], enhanced evaporation due to enlargement of surface area, or to EtOH-rich clusters in the bulk solution, directly brought into the gas phase by bursting cavitation bubbles.

In this study, we propose to develop, test, and demonstrate scalable nonequilibrium liquid separations (including for azeotrope-forming systems), that avoid the heat transfer losses of distillation, as well as the azeotropic bottleneck. Success will result in significant savings in energy and capital costs, for a broad class of systems.

Method

In the first ultrasonic separation prototype, a 2.4 MHz ultrasonic transducer with a diameter of 18 mm and rated power of 13.2 W was installed in the center of the bottom of a custom-designed cylindrical separation unit. The unit (see Figure 1) was made from transparent polyvinyl chloride resin (10 mm thickness), with a height of 305 mm and an inside diameter of 100 mm. The temperature of the bulk liquid (at the bottom of the unit) was kept nearly constant by circulating controlled-temperature water through a volume laterally surrounding the bottom section of the vessel. Mist generated by ultrasonic actuation was carried out of the cylindrical volume by an air flow.

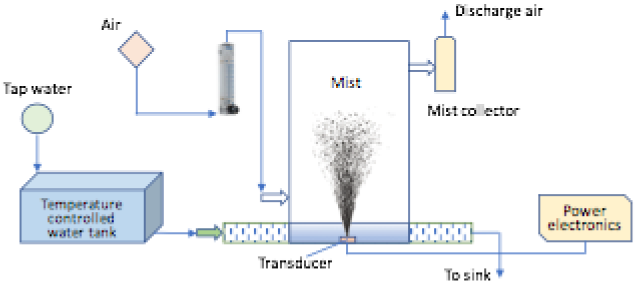

Figure 1. The ultrasonic separation prototype.

In experiments, the entire set-up was pre-conditioned to a target separation temperature, e.g., 30^{o}C, by water circulation, followed by adding approximately 200 ml of EtOH solution with mass fraction $0.04 \leq w \leq 0.76$ into the separation unit, to a liquid depth of about 25 mm. The ultrasonic transducer was then turned on to produce a mist from the bulk liquid. Then the unit was opened to a flow of carrier air, set at a flowrate between 10 to 30 L/min, to carry the mist to a collector. The collected mist was filtered through a syringe filter into a 1.5 ml capped vial for HPLC analysis. Duplicate samples were analyzed using a Waters e2695 HPLC series system (Waters Associates, Milford, MA, USA) equipped with a Prevail Carbohydrate ES 5 µm column, automatic injector, and a Waters 2414 refractive index detector at 40^{o}C. The mobile phase was 160 µL H_2SO_4/L HPLC grade water, with a flow rate of 1 mL/min. Distilled water and 200 proof ethanol (Decon Labs, King of Prussia, PA) were used.

Results

Enrichment of ethanol was observed in the mist for mother solutions at all initial compositions (see Figure 2). For initial ethanol mass fractions exceeding about $w_{initial} = 0.60$, the ethanol mass fraction in the collected mist exceeded the azeotropic vaalue of 0.956. When $w_{initial}$ exceeded about 0.65, the collected mist was nearly pure ethanol.

The volumetric flow rate of the carrier air had a significant effect on enrichment. For instance, when the air flowrate was increased from 10 L/min to 30 L/min, the ethanol mass fraction in the mist increased from 0.147 to 0.203 and 0.813 to 0.969, for $w_{initial} = 0.040$ and 0.648, respectively (see Figure 3a-b). It can be seen that the air flowrate is even more critical for mixtures with an initial mass fraction $w > 0.25$. We found that the optimal air flowrate for separation at 30^{o}C was between 25 and 30 L/min. Another important parameter for this separation is the collection time. At an air flowrate of 25 L/m, when the sampling time increases, water droplets in the mist tend to reach equilibrium with the surrounding air, which may result in a decrease in the efficiency of separation. As shown in Figure 3c, increasing the sampling time from 2 min to 10 min for samples with $w_{initial} = 0.165$, reduced the EtOH mass fraction in the mist from 0.326 to 0.193. For $w_{initial} = 0.542$, the same change in carrier air flow rate reduced the EtOH mass fraction in the collected mist from 0.871 to 0.675.

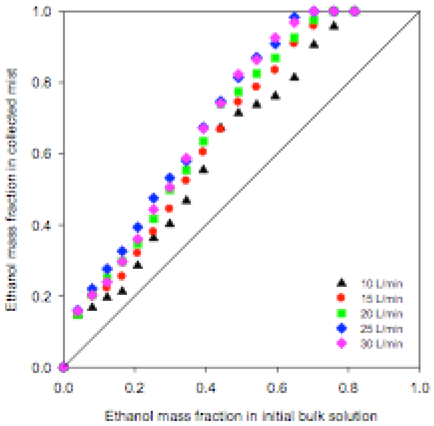

Figure 2. Ethanol mass fraction in the bulk solution and mist at different carrier air flow rates.

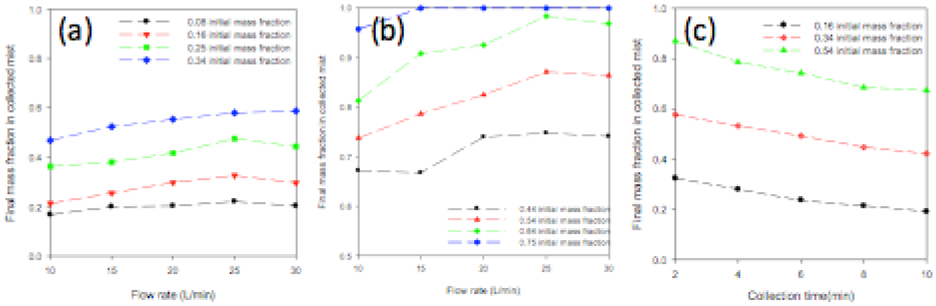

Figure 3. Effect of carrier air flowrate (a & b) and collection time (c) on ethanol mass fraction in the collected mist.

Conclusion

Ultrasound-mediated ethanol separation at low temperature is shown to be effective in enriching ethanol in the ultrasound-generated mist compared to the bulk ethanol-water solution. This nonthermal, nonequilibrium separation method is able to break the ethanol-water azeotrope, showing promise to reduce energy consumption in ethanol production.

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