

## OC-10: The Separation of Azeotropic Mixtures by Ultrasound-Assisted Distillation

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Distillation or rectification are one of the most important thermal separation techniques. Both are applied to separate products from reactants, by-products, impurities and solvents in numerous processes and industrial applications. The thermal processes consume a lot of energy leading to higher operating costs. About 7 % of the total energy consumption in the USA is caused by distillation technologies (Oppenheimer and Sørensen, 1997). Thus, an enhancement of efficiency offers a huge potential to save energy and resources to generate a green and sustainable process.

Distillation is defined as the unique evaporation and condensation of a liquid solvent mixture. Repeated distillation - called rectification - leads to an improved purification due to multiple separation steps. However, there exist some mixtures where the isolation of the components is difficult or not possible. If the vapor pressures of the mixture components are approximately equal, the relative volatility  $\alpha$  approaches to 1. With these close-boiling mixtures the thermal separation becomes more difficult and more energy-consuming, higher technical effort and higher costs are necessary (Hilmen, 2000). When the relative volatility  $\alpha$  is 1 (azeotropic point) the composition in vapor and starting solution is the same and cannot be separated furthermore (Ziegler, 2007). In chemical engineering azeotropic mixtures are separated by multistep processes with the help of additives (Rousseau, 1987), e.g. salts, to change the relative volatility  $\alpha$  of the liquid mixtures (Meranda and Furter, 1974). Moreover this separation can be reached by using azeotropic rectification (Vogel, 2005), vapor permeation (Binning and Lee, 1960) and pressure swing distillation (Modla and Lang, 2010). This offers an additional research and development capability particularly with regard to economy and technology in such proceeding.

The present study focuses on the investigation of the effect of ultrasonic waves on non-ideal, binary mixtures of organic solvents methyl tert-butyl ether (MTBE) and methanol (MeOH) representative for a positive azeotrope. The formation of the azeotrope MTBE/MeOH (70 mol% MTBE) results from the MTBE synthesis (Hilmioglu and Tulbentci, 2004). Acoustic cavitation was used to shift the equilibrium curve and the position of the azeotropic point of the mixture of MTBE and MeOH to enhance the distillative separation. On the one hand ultrasound (US) (24 kHz) was induced directly into the distillation flask via sonotrode, on the other hand indirectly with an ultrasonic bath (thermal energy and US (35 kHz)). Equilibrium diagrams were prepared with analytics conducted by GC/FID.

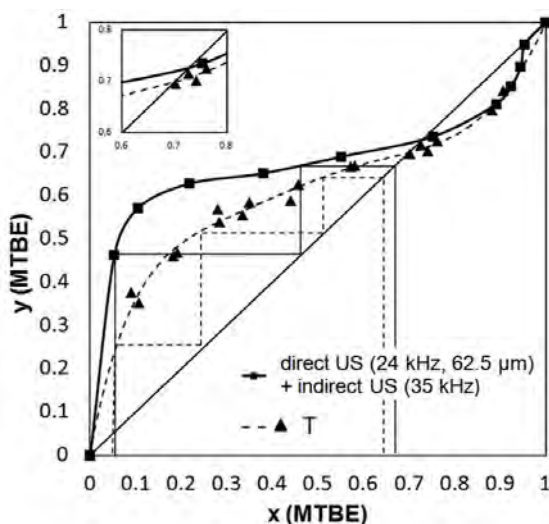


Figure 1: The Comparison of the equilibrium curves of MTBE/MeOH using a combination of direct and indirect US and the common distillation (T) with added theoretical plates. (the mole fraction of MTBE in the bottom solution is applied to the x-axis, the mole fraction of MTBE in the vapor phase, i.e. distillate is applied to the y-axis)

The mechanism of the Ultrasound-Assisted Distillation (UAD) is still unknown. Ripin et al. (2009) who investigated the effects of ultrasonic waves on the vapor-liquid-equilibrium (V-L-E) of MTBE/MeOH justified the improved separation due to an enrichment of the volatile component (MTBE) inside of the bubble compared with common results (thermal V-L-E data). They postulated that, this effect is caused by enhanced mass transport of the volatile compound into the bubble. Further, the simultaneous expulsion of these bubbles leads to an enrichment of MTBE in the vapor phase (Ripin et al., 2008).

However, these cavitative effects are influenced by various parameters. Therefore different parameters like amplitude, frequency, US-input were investigated in this study. An optimisation of the US amplitude resulted in the best effects at 75  $\mu\text{m}$  (22  $\text{Wcm}^{-2}$ ). To onwards gain these effects this setting was combined with indirect US. The best result was obtained with the combination of indirect (35 kHz) and direct US (24 kHz) at 62.5  $\mu\text{m}$  (20.5  $\text{Wcm}^{-2}$ ) and is shown in Figure 1. The alteration of the azeotropic point of MTBE/MeOH was unfortunately marginal, but a decrement of the theoretical plates from three to two plates could be achieved. In the range of low MTBE mole fractions 20 mol% more MTBE in the distillate could be reached. The use of sonotrodes with higher power ranges is conceivable to generate the heat, which is necessary to boil the solution. Furthermore the investigation of the use of salts is supposed to follow.

These results imply, that the innovative UAD affords a huge potential due to the shift of V-L-E-data. Nevertheless the mechanism is unknown and further research is necessary.

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