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Ethanol enrichment from ethanol–water mixtures using high frequency ultrasonic atomization

D.M. Kirpalani, K. Suzuki

Institute for Chemical Process and Environmental Technology, National Research Council of Canada[1], M-12 Montreal Road, Ottawa, ON, Canada K1A 0R6

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ABSTRACT

The influence of high frequency ultrasound on the enrichment of ethanol from ethanol–water mixtures was investigated. Experiments performed in a continuous enrichment system showed that the generated atomized mist was at a higher ethanol concentration than the feed and the enrichment ratio was higher than the vapor liquid equilibrium curve for ethanol–water above 40 mol%. Well-controlled experiments were performed to analyze the effect of physical parameters; temperature, carrier gas flow and collection height on the enrichment. Droplet size measurements of the atomized mist and visualization of the oscillating fountain jet formed during sonication were made to understand the separation mechanism.

1. Introduction

High frequency ultrasonic atomization of liquids is an effective way of generating small droplets by subjecting the liquid to a sufficiently high intensity and high frequency ultrasonic field. During high frequency ultrasonic atomization, a piezoelectric crystal, vibrating at frequencies greater than 500 kHz, supplies the energy required for atomizing the liquid. The piezoelectric crystal is typically installed at the bottom of the sonication vessel and focused acoustic energy is transmitted to the atomizing fluid, either directly or via a coupling liquid. When the ultrasonic vibrations are sufficiently intense, a fountain rises from the surface of the liquid due to acoustic pressure waves and breaks up at the apex as a result of gravitational effects. Large liquid ligaments and drops formed as a result of the breakup are commonly returned into the bulk liquid. In addition to the large liquid ligaments, small low inertia droplets are also released periodically from the jet and quickly surround the jet to form a dense fog. Droplet formation during ultrasonic atomization is often considered to be a consequence of the growth of surface waves generated by spreading a thin layer of liquid on the atomizer surface and are reported to be uniform in distribution. In other words, droplets are produced by the large number of air–liquid interfaces generated due to the high frequency oscillation of the surface. The droplets formed travel at very low velocities and hence a carrier fluid such as air is often used to transport the droplets. Ultrasonic atomization has some distinct advantages over conventional atomization processes for the production of small droplets. The droplet size has a very narrow distribution and is inversely proportional to the frequency of ultrasound. The density of the fog generated and the momentum of the droplets can be independently controlled by adjusting the carrier fluid rate past the liquid surface since the amount of liquid suspended in air as a fog is limited only by the rate at which it falls back into the liquid or by the air flow rate at the liquid surface.

Early studies of droplet sizes formed during high frequency ultrasonic atomization concluded that droplets generated using this atomization process were uniform in size and a mono-dispersed spray could be generated by this method. Numerous reports [1–6] have been published on the mechanism of droplet formation by ultrasonic atomization with this limited understanding in the past. However, it has recognized the complexity introduced by an observed acoustic cavitation zone in the liquid and the periodic release of droplets from the capillary wave (fountain) formed at the surface of the liquid. Also, recent observations have noted that the droplet formation and consequent droplet size distribution are not as uniform as previously considered [1]. The formation of satellite droplets, larger than the primary droplets was reportedly observed in recent experiments and uniformity droplet size distributions over a period of time, based on a physical understanding and models of the atomization process, has been discussed [2].

In general, two theories are considered to explain the mechanism of droplet formation during sonication of liquids based on the resonant ultrasound frequency and intensity. The cavitation

Corresponding author. Tel.: +1 613 991 6958; fax: +1 613 941 2529.
E-mail address: deepak.kirpalani@nrc.ca (D.M. Kirpalani).
[1] NRCC No: 52852.

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theory assumes that when a liquid is subjected to ultrasound, small cavitating bubbles formed in the liquid oscillate and collapse implosively close to the surface of the liquid generating high intensity hydraulic shock waves and eject droplets from the liquid surface. This hypothesis was postulated for low frequency ultrasonic atomization. The second theory, based on capillary effects or known as the capillary wave theory [3], was postulated for high frequency ultrasonic atomization (>800 kHz) and hypothesizes that atomization occurs by the breakup of the capillary waves formed at the surface of the liquid due to unstable oscillations that release droplets from the crests of the capillary waves. Hence atomization takes place away from the bulk liquid in the surface capillary waves and the droplets produced at the crests of the capillary wave are proportional to the wavelength of the capillary instability. The capillary wavelength decreases with increasing frequency and produces finer droplets at higher frequencies. For sonically generated capillary waves, whose wavelength can be calculated using Kelvin's equation, the surface wave frequency is equal to one-half of the exciting sound frequency. Hence the droplet size produced by atomization must be approximately one-half the capillary wavelength. A comparison of the number mean diameter with the capillary wavelength indicated that the mean droplet size was a constant fraction of the capillary wavelength. This fraction was determined to be 0.34. Hence Lang [3] proposed the correlation shown below:

$$d_p = 0.34\left(\frac{8\pi\sigma}{\rho f^2}\right)^{\frac{1}{3}}$$

The strong correlation between capillary wavelength and measured droplet size formed favors the capillary wave theory. However, the influence of liquid vapor pressure, amount and type of dissolved gas in the liquid, sonoluminescence and observed droplet breakup on ultrasound induced atomization shows the dependence of the atomization process on acoustic cavitation [4–6].

Boguslavskii and Eknadiosyants [4] extended the capillary theory for high frequency ultrasonic atomization and proposed a "conjunction" theory that attributes droplet formation to be an effect of periodic shocks generated by the implosive collapse of cavities in the capillary waves leading to the breakup of capillary wavelength scale droplets. The cavitational disturbances are assumed to be responsible for the broadening of the droplet size distribution. Due to the random nature of cavitation, limited experiments that show the effect of cavitational disturbances have been reported and majority of research has relied on the capillary wave theory and Lang's equation [3] for the estimation of mean droplet size.

Selective separation of ethanol from ethanol–water mixtures using ultrasound was first introduced by Sato et al. [7]. They subjected ethanol–water mixtures of 10–90 mol% ethanol at 10 °C to high frequency ultrasound at 2.4 MHz. The atomized mist was reported to be pure ethanol and a mechanism based on parametric decay instability of the capillary wave, in which local accumulation of the acoustic energy occurs and this leads to the formation of an atomized mist of pure ethanol was proposed. Remarkably, unlike distillation processes, much less heat is required since phase change is less important in the process. In our previous reported work [8], an alternate mechanism based on the conjunction theory has been postulated for the process of ultrasonic atomization. This mechanism involves the formation of micro-bubbles in the liquid during sonication and the growth of the bubbles as they travel through the liquid mixture and collapse at the liquid surface into a cloud of micro-bubbles moving upwards in a capillary fountain jet and releasing the alcohol vapor diffused in the bubbles. The selective separation of alcohols was explained as a corollary effect of the physical mechanism whereby a surface excess of alcohol molecules formed at the surface of the micro-bubbles. The alcohol molecules at the walls of the bubbles were expected to diffuse into the bubbles and fill the bubbles with alcohol vapor until their collapse in regions of high accumulation of acoustic energy. However, this theory limits the ethanol concentration of the mist to the surface excess over the bulk concentration.

In this study, our previous work on evaluation of ethanol enrichment [9] was extended with experiments conducted in a continuous enrichment system to evaluate ethanol enrichment and also develop a reliable process with a constant enrichment quality for a given feed ethanol concentration. In addition, droplet size measurements of the enriched ethanol mist and local temperature measurements of the ultrasonic jet formed were also performed.

2. Experimental setup

A schematic of the experimental arrangement used in this study is shown in Fig. 1. A high frequency ultrasonic transducer, operating at 2.4 MHz and 18 mm diameter, was installed in the bottom of a glass cylindrical column, of 0.5 m diameter and 1 m (height), with a stainless steel bottom. Ethanol–water solutions with concentrations up to 90 mol% ethanol were subjected to ultrasound in this column fed from a 1-L beaker during the study. During sonication, sonic energy is imparted to the feed liquid and a fountain is formed at the surface of liquid in the column and a droplet mist is released from the fountain. Ultrasound irradiation of the liquid combined with acoustic cavitation in the fountain increases the temperature of the fountain. The column incorporates an opening to allow the fountain to pass through and fall into the bulk solution thereby avoiding avoid temperature and concentration changes during the process as shown in Fig. 1. Feed liquid level in the column was kept constant at 3 cm above the transducer level by adding fresh feed liquid from the beaker to compensate for the amount of liquid atomized and the ultrasonic fountain re-circulated to the beaker. The input power for the transducer was maintained at 20 W. Air is introduced in the system at a very low velocity (0.086–0.271 L/min) as a carrier gas to collect the mist produced by atomization to a series of condensers. Mist collection outlets were provided at different elevations (at 0.3, 0.5, 0.9 m) above the surface of the transducer in the column. Time to the collect a condensate sample was typically 1 h to ensure that a large enough sample was made in analysis and the concentrations, quantity of mist and temperature distribution in the solution were measured. The ethanol concentration in the feed mixtures and condensate

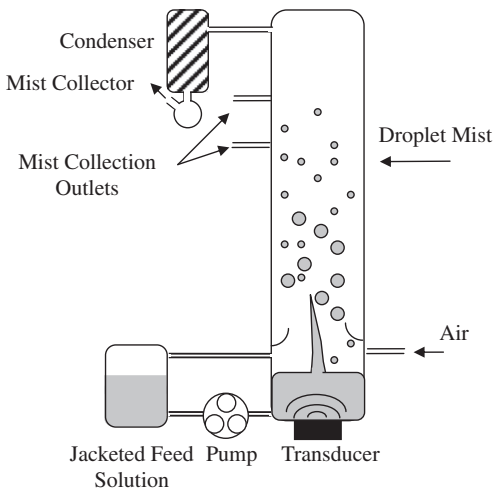

Fig. 1. Schematic representation of experimental apparatus used for ultrasound studies on ethanol–water mixtures.

products were analyzed by using an Abbe refractometer and a gas chromatograph (Hewlett Packard HP6890G series). Mist collection rate was also recorded by weighing the collected sample on an hourly basis. To visualize the atomization process, a high frame rate digital video camera (Red Lake PCI 8000-S) was used to record images at 2000 frames per second. The experimental setup was backlit using a 500 W halogen lamp as shown in the experimental arrangement and the light was diffused to provide a uniform concentration of light across the liquid jet formed and the mist. Close up and far field images were captured by a combination of close-up and telephoto lenses. A sequence of images showing the mist formation is shown in Fig. 2. Intermittent formation of micron sized bubbles was first observed as the power input to the transducer was increased above 7 W. The bubble formation was correlated visually to the collapse of large ligaments from the oscillating surface wave. An increase in the rate of atomized mist and bubble formation in the liquid was recorded as the power input to the transducer was increased. At threshold conditions for atomization, droplet size measurements were conducted using a laser diffraction system (Sympatec LDI) that provides droplet size distributions. During the atomization process, the droplets generated pass through the outlet port and are crossed by a parallel beam of light emitted from a He–Ne Laser (l = 632 nm and power output = 5 mW.) and the light scattered in the near forward direction is measured using a Fourier Transform lens and focused on a detector consisting of 30 concentric semi-annular diodes (Sympatec – R7 optical module) The maximum droplet size measured using this arrangement is 175 mm. Droplet size measurements were made at least three (3) times for the different fluid mixtures to ensure consistency of results. Droplet size measurements for the laser diffraction experiments are shown in Fig. 3.

3. Results and discussion

3.1. Video analysis of ultrasonic jet

Experiments conducted using this arrangement showed that the jet formed at the surface of the liquid during ultrasonic atomization at 2.47 MHz has a milky appearance indicating the presence of bubbles in the fountain. Video taken with the high frame rate camera confirmed that the droplet breakup mechanism could be envisaged as an accumulation of energy in the oscillating capillary jet, leading to the eventual breakup of the jet and release of a droplet mist and larger secondary droplets. The location of mist release for the constant power supplied and feed solution concentration was not constant but always occurred from the surface of the capillary jet. Droplet mist formation was observed only when ethanol water mixtures of 10–30 mol% ethanol concentration were subjected to ultrasound. At feed concentrations higher than 30 mol%, droplets could not be visualized or measured. However, product condensate was collected for all feed concentrations indicating that if droplets are formed during the atomization process at higher feed concentrations, they tend to vaporize instantaneously.

Video records of the oscillating ultrasonic jet formed at the surface of the liquid under sonication were analyzed to gain an understanding of the effect of feed concentration on the ultrasonic jet formed. For this, jet heights at different feed concentrations, analyzed from video records, are reported in Fig. 4. As shown in Fig. 4, liquid jet height increases with increasing feed concentration and peaks at 30 mol% ethanol feed concentration. The jet height gradually decreases above this feed concentration. Interestingly, the velocity of sound for different ethanol–water mixtures was reported by Blitz [10] to peak at 35 mol% and decrease gradually at higher ethanol concentrations as shown in Fig. 4.

3.2. Droplet size measurements

Sato et al. assumed that small droplets, with high concentration of ethanol not visible, are formed during sonication. In this work, droplet size measurements of the mist formed during ultrasonic atomization at 2.47 MHz were made using the SYMPATEC laser diffraction instrument described earlier. From video records, it was shown that droplet mist was not generated while sonicating ethanol–water mixtures with concentrations greater than 30 mol% at 24 °C. Fig. 3 shows the droplet size distribution of the mist formed from the ultrasonic jet obtained by sonicating water at 24 and 10 °C. Also, droplet size measurements were made for mist generated at low concentrations of ethanol – 10 and 25 mol% and are shown in Fig. 4(a) and (b), respectively. The droplet statistics, provided in Table. 1, indicate that the droplet mist formed, while sonicating water and ethanol water mixtures at low concentrations, has the same droplet statistics for 10 and 24 °C but the selective separation curve from Fig. 5 shows that the condensate concentration increases with ethanol concentration in the feed. Hence, it can be inferred that the size distribution of droplets cannot be the primary mechanism for the physical separation process reported.

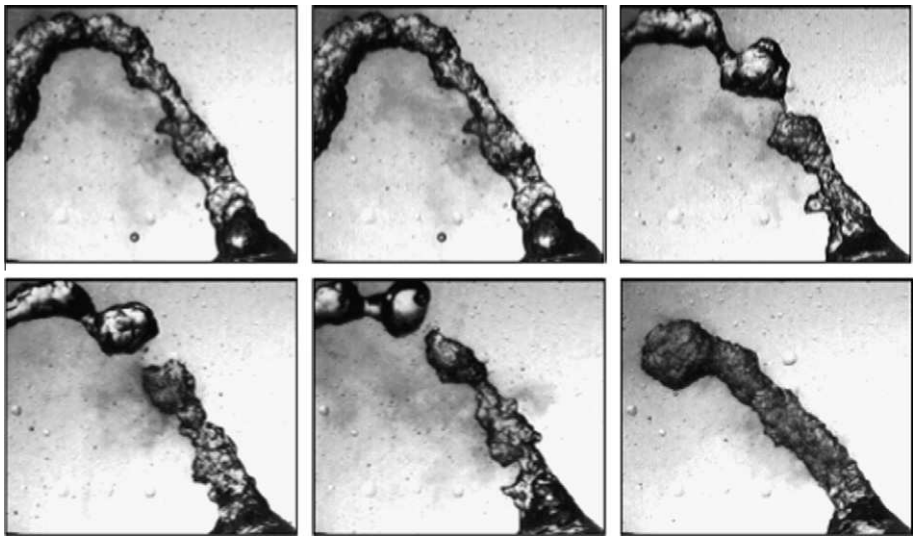

Fig. 2. A sequence of images captured by high frame rate video showing periodic breakup of the jet and fine droplet mist formation during high frequency ultrasonic atomization.

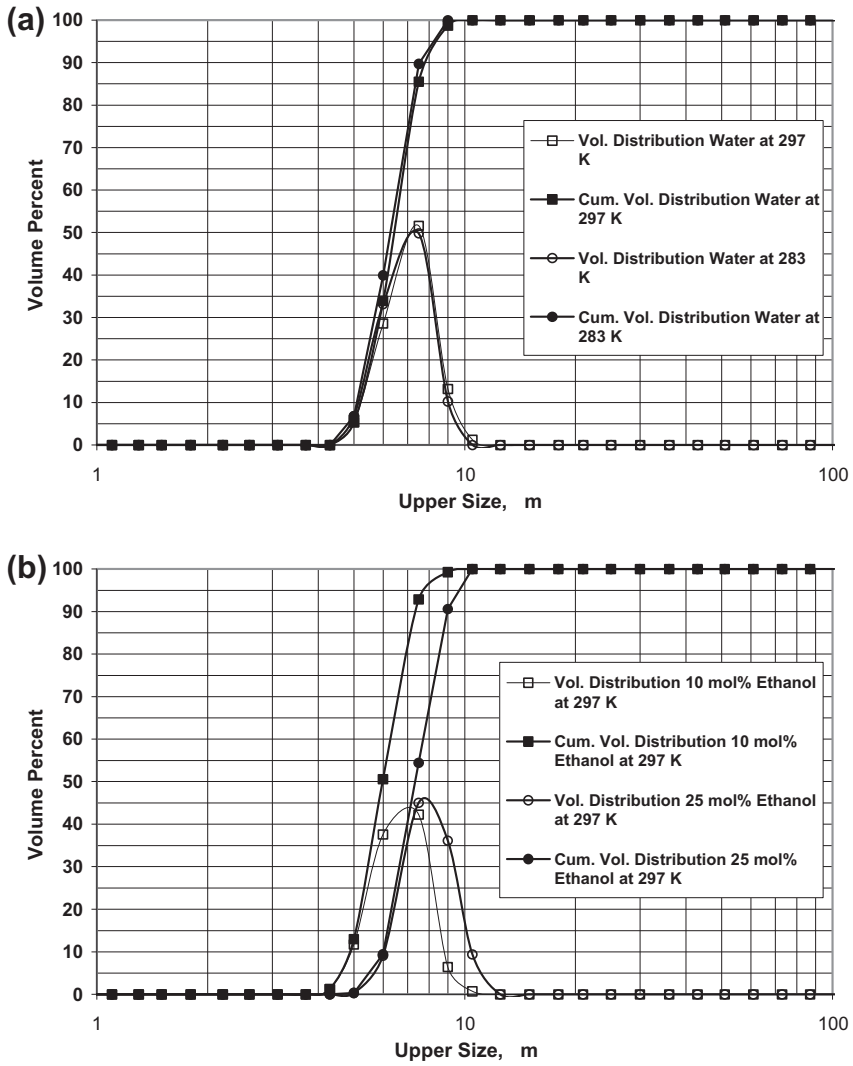

Fig. 3. (a) Droplet size measurements during ultrasonic atomization at 2.47 MHz for (a) water at 283 K and 297 K. (b) 10 mol% ethanol and 25 mol% ethanol at 297 K.

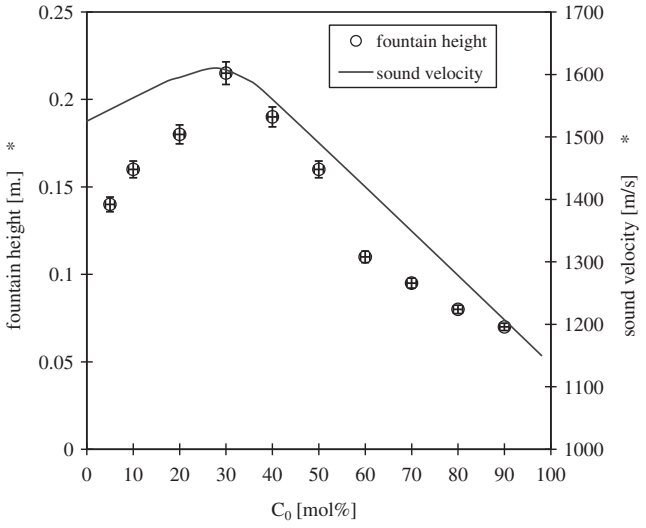

Fig. 4. Measured ultrasonic jet height and velocity of sound (Blitz, 1967) in ethanol–water mixtures.

3.3. Condensate concentration

Experiments conducted with ethanol–water feed concentrations at conditions reported by Sato et al. did not produce pure ethanol at 10 °C. Fig. 5 shows the separation characteristics of ethanol–water mixtures at 10 and 24 °C. Fig. 5 indicates a lower ethanol condensate concentration at feed temperatures of 24 °C as compared with 10 °C and approaches the vapor–liquid equilibrium curve at 101.3 kPa. Mist formation, observed at higher feed temperature, combined with lower product (ethanol) concentration that approaches the VLE curve indicates that vaporization occurs as the temperature of the feed liquid is increased. The separation characteristics were quite unaffected by a change in condenser height as shown in Fig. 5.

3.4. Temperature distribution in sonicated liquid

Sato et al. assumed that the separation was isothermal in nature. The sonicated liquid temperature was measured at various locations along the surface of the liquid, radial to the oscillating jet formed, using a K-type thermo couple as shown in Fig. 6. At both 24 and 10 °C, temperature at the base of the ultrasonic jet was higher than the feed temperature by approximately 14 °C.

Table 1
Droplet mist statistics from ultrasonic atomization experiments at 2.47 MHz using laser diffraction.

Atomized solution	Temperature (°C)	Dv0.10 (μm)	Dv0.50 (μm)	Dv0.90 (μm)	Span	
De-ionized Water	10	5.2	6.5	8	0.439	Dv0.10 = 4z.8 μm Dv0.50 = 6.0 μm Dv0.90 = 7.4 μm Span = 0.431
De-ionized Water	10	5.1	6.3	7.5	0.387	
Ethanol (10 mol%)	24	4.8	6	7.4	0.431	Dv0.10 = 6.0 μm Dv0.50 = 7.4 μm Dv0.90 = 9.0 μm Span = 0.403
Ethanol (25 mol%)	24	6	7.4	9	0.403	

Dv0.10 – linear mean diameter.
Dv0.50 – volume median diameter.
Dv0.90 – droplet diameter such that 90% of the total liquid volume is in drops of smaller diameter (μm).

$$Span = \frac{Dv0.90 - Dv0.10}{Dv0.50}$$

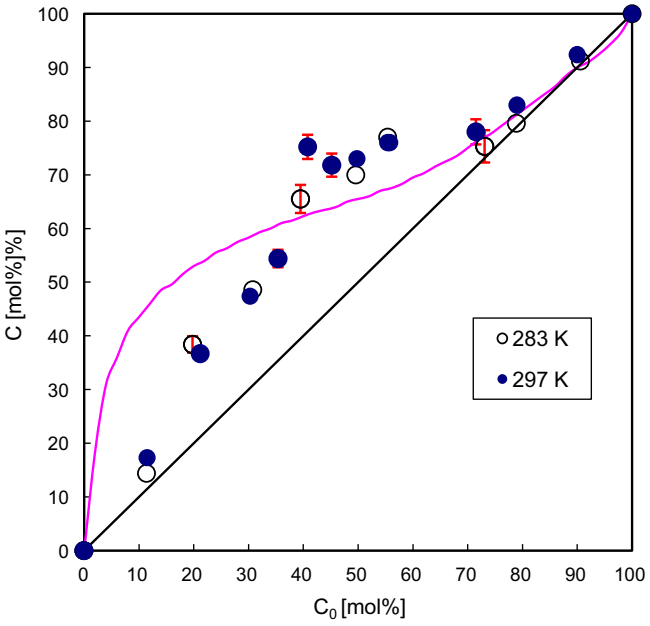

Fig. 5. Ultrasonic enrichment characteristics of ethanol–water solution at T = 283 K and T = 297 K, frequency = 2.4 MHz, air flow rate = 2.9 cm^3/s, height of gas outlet = 0.9 m. Vapor–liquid equilibrium curve at 100 kPa is shown as solid curve.

The temperature of the surrounding feed liquid decreases rapidly and approaches the feed temperature. Viscosity of the feed mixture decreases and vapor pressure of the feed increases with an increase in temperature, thereby increasing the vaporization rate of ethanol. As a result, we can hypothesize that ethanol concentration in the condensate approaches the vapor–liquid equilibrium curve when separation experiments are conducted at 297 K as shown in Fig. 6.

3.5. Condensate collection

To reduce the effect of convective forces, air was introduced as a carrier gas at a low flow rate (~0.3 cm^3/s) through the air inlet shown in Fig. 1 and to focus this study on the separation mechanism. However, it was also important to identify the role of convective forces in this process due to their direct influence on product yield. Effect of gas flow rate on product rate of mist is shown in Fig. 7. As shown in Fig. 7(a) and (b), higher gas flow rate increases the volume of condensate collected without affecting condensate

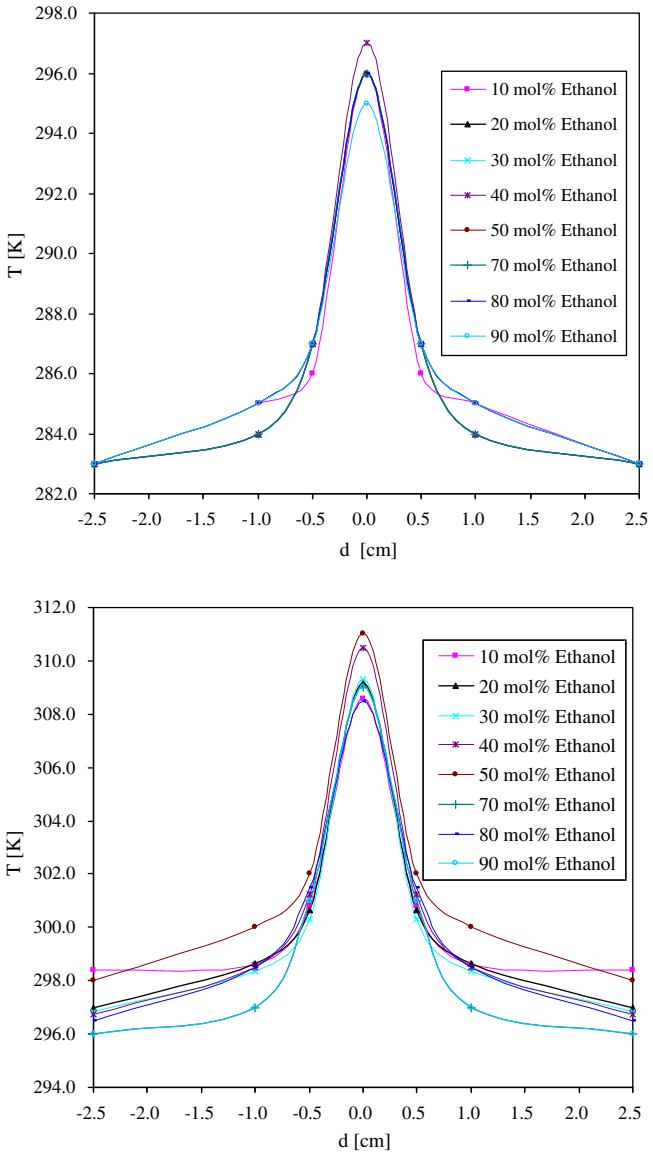

Fig. 6. Temperature distribution in the sonicated ethanol–water mixture at feed temperature of 297 and 283 K, respectively.

concentration. Condensate was also collected at three different heights of 0.3, 0.6 and 0.9 m above the transducer. Also, the prod-

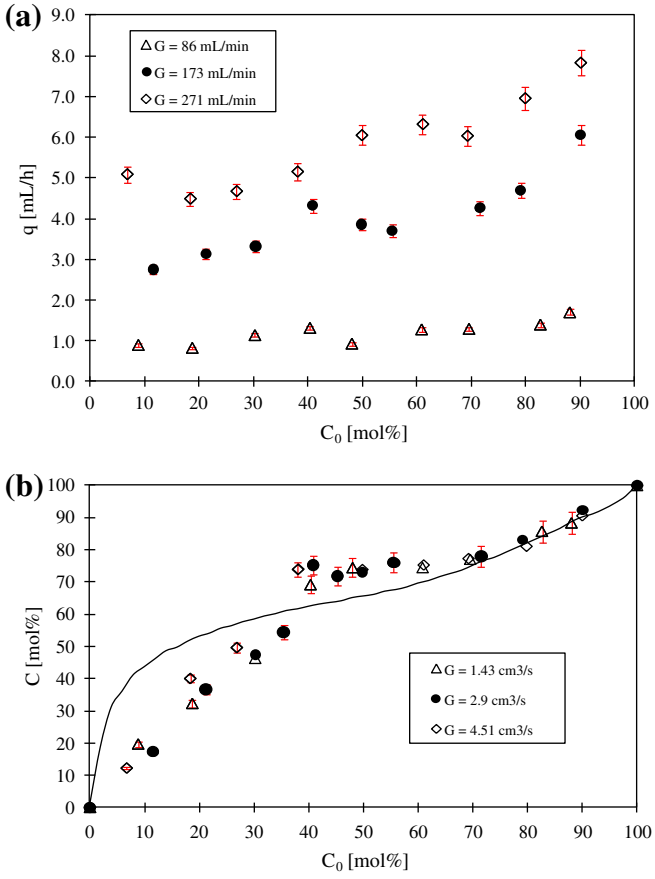

Fig. 7. Effect of gas flow rate, *G*, on ethanol-rich mist collection using ultrasonic separation at 2.4 MHz, liquid temperature = 297 K and height of collection outlet = 0.9 m.

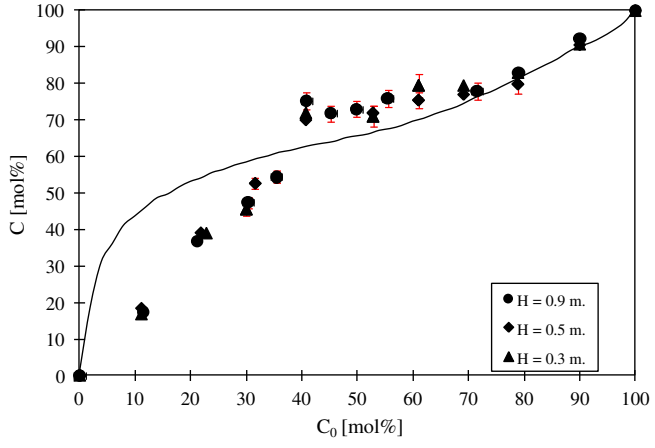

Fig. 8. Ultrasonic enrichment behavior of ethanol–water solution at different condensate collection heights, frequency = 2.4 MHz, air flow rate = 2.9 cm^3/s and feed liquid temperature = 297 K. Vapor–liquid equilibrium curve at 100 kPa is shown as solid curve.

uct concentration was quite unaffected by changes in collection height as shown in Fig. 8. However, the product (condensate) collection rate increased at lower collection heights as shown in Fig. 9.

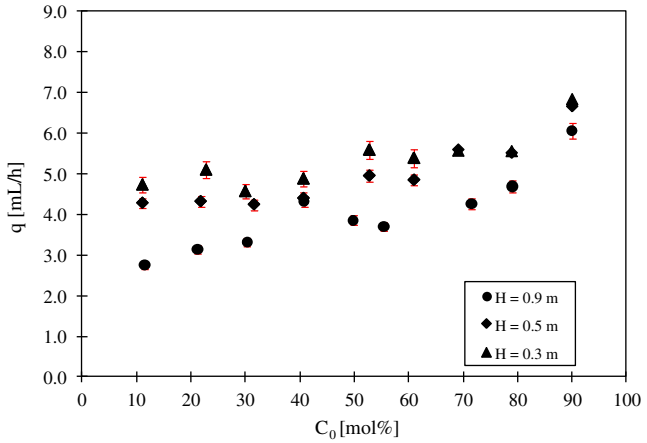

Fig. 9. Decrease in ethanol condensate collection rate with increasing collection height, frequency = 2.4 MHz, air flow rate = 2.9 cm^3/s and feed liquid temperature = 297 K.

4. Conclusion

A detailed study of ethanol enrichment in a continuous separation process was discussed. Well-controlled ultrasound experiments on different concentrations of ethanol–water mixtures conducted with direct measurement of collected condensate indicate that the concentration of ethanol is higher in the condensate than the feed, well above the vapor liquid equilibrium curve between 40 and 70 mol%. An increase in temperature form 10 to 24 °C increases the mist generation rate significantly while the concentration of the collected condensate is not affected significantly. The increase in mist generation rate at a higher temperature (higher vapor pressure) indicates that cavitation may play an important role in the process. The complexity of high frequency ultrasonic atomization in liquids and the need for a more comprehensive multiphase physico-chemical model for high frequency ultrasonic atomization has been identified since the present capillary instability model and cavitation model are limited and cannot be applied to predict the droplet size generated during high frequency ultrasonic atomization. The critical role of surface characteristics of the ultrasonic jet formed in the separation process have been elucidated and a physico-chemical mechanism based on the conjunction theory has been supported by the experiments in this work. Potential applications of this research include removal of surfactants from solutions, aero sol–gel synthesis of nanocomposites [11], concentration of Japanese rice wine (sake) [7] and wastewater purification.

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