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Effects of Ultrasonic Waves on Vapor-Liquid Equilibrium of an Azeotropic Mixture

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Abstract: Azeotropic and extractive distillation techniques used to separate azeotropic mixtures are among the most challenging separation processes in the chemical industry. In this work, an innovative distillation technique which employed ultrasonic waves was proposed to intensify the conventional multi-column azeotropic distillation method into a single-column alternative. The effects of ultrasonic intensity on the vapor-liquid equilibrium (VLE) of methyl-*tert*-butyl-ether (MTBE)-methanol was investigated at 50, 100, 200, and $250\,\mathrm{W/A \cdot cm^2}$ and at a fixed frequency of 40 kHz. Studies were also done to examine the effects of ultrasonic frequency on the VLE data at 25 and 68 kHz frequencies. It was found that ultrasonic waves at $50\,\mathrm{W/A \cdot cm^2}$ intensity and 25 kHz frequency gave the highest relative volatility (α) at 2.654 and completely eliminated the MTBE-methanol azeotrope, thereby allowing highly pure MTBE to be recovered in just a single distillation column. The results revealed that ultrasonic waves had the potential to favorably manipulate α, and hence, the VLE of an azeotropic mixture.

Keywords: Azeotropic mixture, methyl-*tert*-butyl-ether (MTBE)-methanol system, relative volatility, ultrasonic waves, vapor-liquid equilibrium

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INTRODUCTION

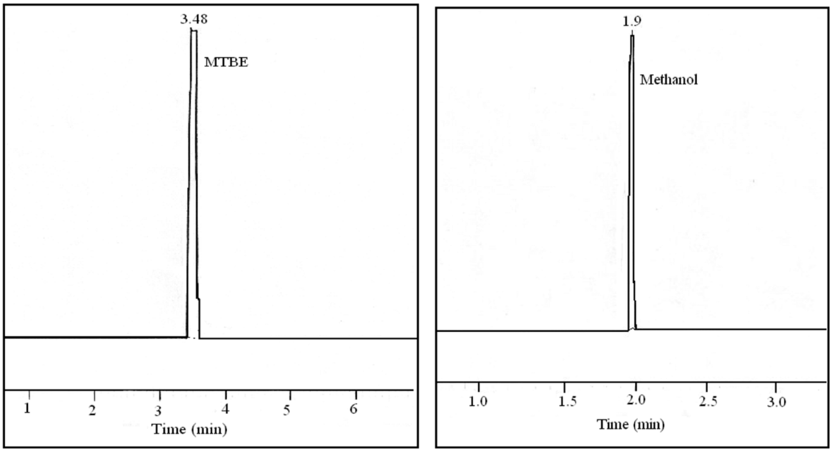
Methyl-*tert*-butyl-ether (MTBE) can be produced by reacting methanol with isobutylene over a strong acid and ion exchange resin as catalyst. Excess methanol is used in order to improve the reaction conversion. Unreacted methanol is then separated from the products via distillation. However, azeotrope formation limits the separation of methanol from MTBE by normal distillation (1,2). An azeotrope is the condition whereby a mixture exhibits the same composition in vapor and liquid phases which remains constant upon continuous heating. Separation of azeotopic mixtures by normal distillation is typically energy and capital-intensive. Currently, the azeotropic or extractive distillation technique is employed to separate either azeotropic or close boiling mixtures (3,4). These techniques require adding a third component called solvent or entrainer to overcome the azeotropic barrier, and additional columns to recover the solvent or entrainer. For all these reasons, industry is always eagerly looking for viable alternatives to obtain high purity MTBE.

The use of ultrasonic waves in various fields including separation processes is currently gaining popularity worldwide (5–10). For example, ultrasonic is used as a homogenizer to enable the determination of vapor-liquid-liquid equilibrium (VLLE) data in a system with limited miscibility (11,12). However, the use of ultrasonic waves in distillation, particularly to assist the separation of azeotropic and close-boiling mixtures has never been explored prior to this work. The objective of this study is to investigate the effect of ultrasonic waves on vapor-liquid equilibrium (VLE) data of MTBE-methanol azeotropic mixture using a developed VLE apparatus which was equipped with ultrasonic wave-generating equipment. The effects of different ultrasonic intensities as well as frequencies on VLE data were investigated. The results showed that ultrasonic waves could favorably change the VLE data and eliminate the azeotropic barrier during the separation of MTBE-methanol mixtures, thereby allowing a satisfactory MTBE recovery to be achieved in just a single distillation column.

MATERIALS AND METHOD

Materials

MTBE and methanol used in this study were supplied by Fisher Scientific, UK and R&M Chemicals, UK respectively. MTBE was 99.7% pure and methanol 99.8% pure. Both substances needed no further purification since no significant impurities were detected by gas chromatography (See Fig. 1).



(a) (b)

Figure 1. Chromatogram of (a) MTBE (b) Methanol.

Method

The VLE measurements were performed using an ultrasonic distillation system shown in Fig. 2. The apparatus consists of a distillation flask, a condenser, a water bath, an ultrasonic generating equipment, and thermocouples. The apparatus has a 250 cm^3 capacity and can be operated between low to moderate pressure range. The distillation flask was immersed in a heating bath equipped with a 40 kHz ultrasonic transducer. The ultrasonic transducer, supplied by Crest Ultrasonic (M) Sdn Bhd, was connected to a 500 Watt ultrasonic generator. Vapor and liquid temperatures were measured using thermocouples TC-08 with precision of 0.01°C and linked using Pico data logger to a computer. MTBE-methanol mixtures at different compositions were fed into the distillation flask and were left to boil either in the presence or absence of ultrasonic wave until equilibrium between the vapor and liquid phases were reached. This happened when the vapor temperature remained constant for a period between 10 to 20 minutes. When equilibrium was reached, liquid samples from the distillation flask and condensed vapor were taken and their compositions were measured using gas chromatography. Distillation was initially done at atmospheric pressure to obtain MTBE-methanol VLE data in the absence of ultrasonic waves. Then, distillation was repeated using ultrasonic waves at intensities of 50, 100, 200, and 250 $W/A \cdot cm^2$ and frequency of 40 kHz to determine the most suitable operating intensity. After that, the same procedure was repeated at

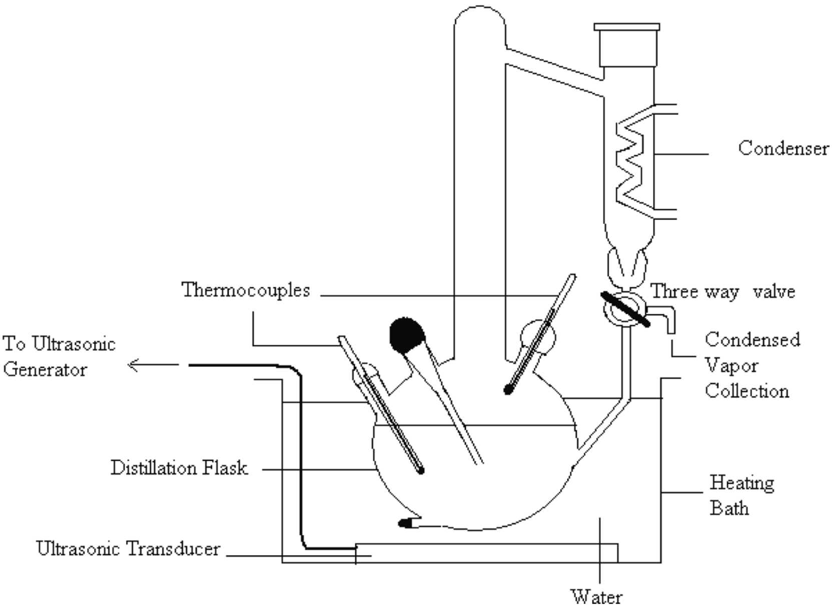


Figure 2. Schematic diagram of Ultrasonic-Distillation System.

25 kHz and 68 kHz frequency. The analysis using gas chromatography was run under specific conditions as stated in Table 1.

RESULTS AND DISCUSSION

VLE Study without Sonication

VLE data of MTBE-methanol was measured at atmospheric pressure. In order to verify the reliability of the developed system, the data measured

Table 1. Analysis specification using gas chromatography

Samples analyzed	GC conditions
Methyl *tert* butyl ether-Methanol	Column – SPB-1, 30 m × 0.53 mm ID, 5.0 μm film Oven Temperature – 40°C (5 min) to 100°C at 5°C/min Carrier Gas – Nitrogen 90 psi Detection – Flame Ionize Detection, 220°C Injection Volume – 0.2 μL, split injection at 220°C

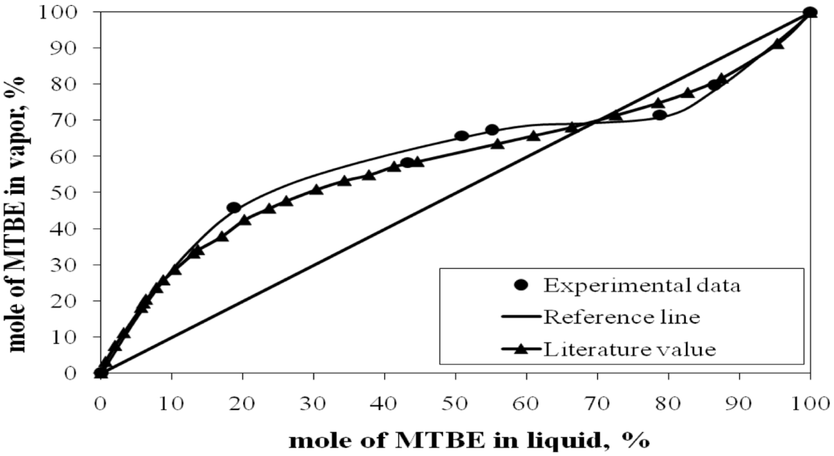


Figure 3. xy-diagram for MTBE–methanol system at atmospheric pressure: (◆) Experimental data, (■) Literature value[2].

by the system was compared to the VLE data obtained from literature. Figure 3 and Table 2 show that the VLE data obtained from this work are within 5.2% average deviations from those reported in the literature. This confirms that the developed apparatus is reliable for obtaining VLE data and for studying the effects of ultrasonic waves on MTBE-methanol

Table 2. Vapor and liquid compositions of MTBE-methanol

	Mole MTBE in vapor, %		
Mole MTBE in liquid, %	Experimental data	Literature value (2)	% Deviation
10	30.0	28.0	7.1
20	46.0	42.0	9.5
30	55.5	51.0	8.8
40	60.0	56.5	6.2
50	65.0	61.0	6.6
60	68.0	66.5	2.3
70	70.0	70.0	0.0
80	72.0	76.0	5.3
90	84.0	85.0	1.2
Average Deviation			5.2

Table 3. Antoine constants for MTBE and methanol

Component	A	B	C
Methanol (13)	8.08097	1582.271	239.726
MTBE (14)	7.12997	1265.40	242.517

VLE. The relative volatility of MTBE-methanol was calculated using equation (1):

$$\alpha_{12} = \frac{y_1/x_1}{y_2/x_2} = \frac{\lambda_1 P_1^{sat}}{\lambda_2 P_2^{sat}} \tag{1}$$

P_i^{sat} was calculated using Antoine equation (See equation 2) with P_i^{sat} in mmHg, T in °C and Antoine constant shown in Table 3 (13,14). The liquid activity coefficient, γi was calculated using equation (3):

$$\log P_i^{sat} = A - \frac{B}{T + C} \tag{2}$$

$$\gamma_i = \frac{y_i \cdot P}{x_i \cdot P_i^{sat}} \tag{3}$$

VLE Study at Different Ultrasonic Intensities

Effects of Ultrasonic Intensity on VLE

The VLE data for MTBE-methanol mixture at different ultrasonic intensities are shown in Fig. 4. The figure shows that increased ultrasonic intensity tends to shift the azeotropic point on the MTBE-methanol *xy*-diagram. For experimental study without sonication, MTBE-methanol mixture forms an azeotrope at 70 mol% MTBE. At an ultrasonic intensity 50 $\mathrm{W/A \cdot cm^2}$, the azeotrope shifts to 86 mol% MTBE, which is a marked increase from the unsonicated data. However, the azeotrope composition later decreased with increased ultrasonic intensity. Figure 4 shows that the azeotropic point decreases to 78, 69, and 68 mol% of MTBE at ultrasonic intensity at 100, 200, and 250 $\mathrm{W/A \cdot cm^2}$, respectively. This situation indicates that separation of MTBE-methanol is easier at lower ultrasonic intensities. The azeotrope compositions corresponding to the different ultrasonic intensities for MTBE-methanol system are illustrated in Fig. 5.

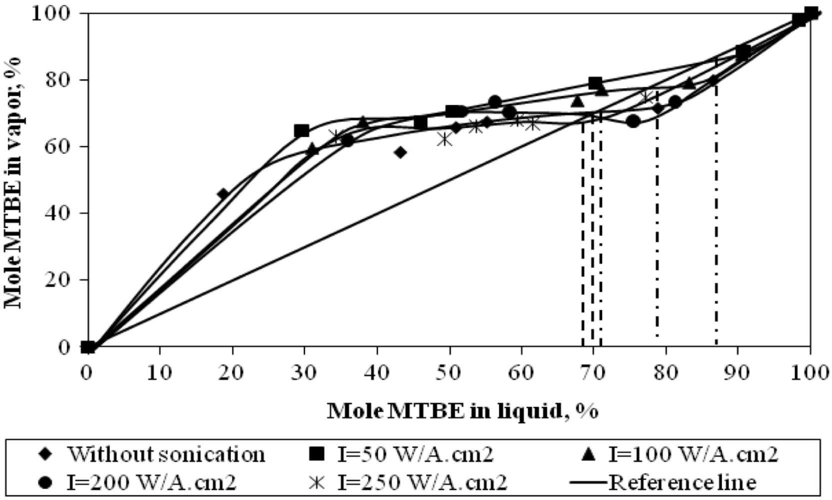


Figure 4. xy-diagram of MTBE-methanol system at different ultrasonic intensities (at 40 kHz frequency).

Effects of Ultrasonic Intensity on Relative Volatility, α

Relative volatility, α, is a measure of the relative ease of separating components by distillation (12). Separation of two components by distillation

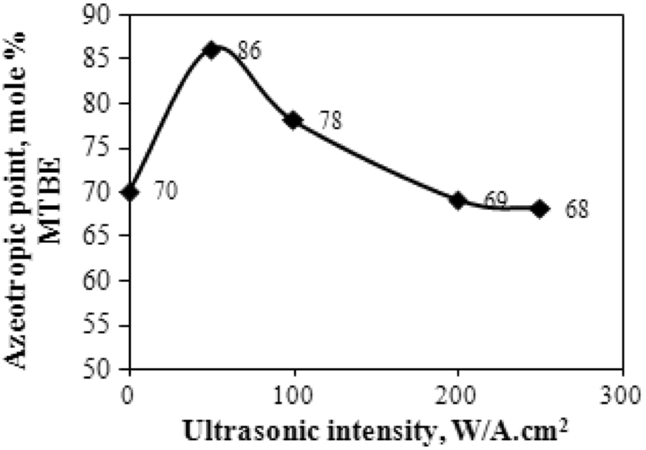


Figure 5. Azeotropic points for MTBE-methanol mixture as a function of ultrasonic intensity at 40 kHz frequency.

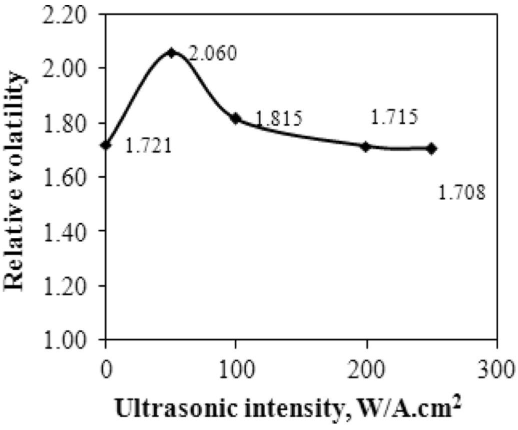


Figure 6. Relative volatility of MTBE-methanol versus ultrasonic intensity at 40 kHz frequency.

is impossible when the relative volatility is equal to 1.0 (15,16). Note that α is directly related to the changes in azeotrope compositions (x and y) through equation (1). Thus, the plot of relative volatility for MTBE-methanol mixture (α_{12}) at different ultrasonic intensities and at a frequency of 40 kHz (Fig. 6) follows the same trend as the plot in Fig. 5 which shows the change in azeotropic points at different ultrasonic intensities. As in the case of Figs. 5 and 6 exhibits a maximum at ultrasonic intensity of 50 $W/A \cdot cm^2$.

The changes in relative volatility and VLE data of MTBE-methanol mixture were caused by cavitational activities that occurred during transmission of ultrasonic waves in liquid medium. Cavitation normally takes place in liquid medium once the media is subjected to rapid, alternating high pressure. Voids containing small microbubbles are created when the differences between amplitude pressure of ultrasonic waves and the hydrostatic pressure in the liquid is large enough to exceed the local tensile strength of the liquid medium. These bubbles expand during the negative part of pressure cycle (rarefaction cycle), reach the maximum radius, and then collapse at the onset of a positive pressure cycle (compression cycle) (17). During negative pressure cycle or expansion cycle of ultrasonic waves, a vacuum environment is created inside the liquid medium. This phenomenon helps to draw the fluids into the cavitation microbubbles (18,19).

Contents of the bubbles greatly depend on the nature of the sonicated medium. According to Mason (19), when a more volatile component is present in the liquid medium, vapor of the volatile component will enter the cavitation bubbles during its formation (19). Since MTBE is more volatile than methanol, more MTBE vapor will be trapped inside the bubbles. Wu and Ondruschka (20) reported that, besides volatility, the mass transfer of a component from bulk liquid into cavitation microbubbles are affected by its polarity. Less polar components tend to dominate the mass transfer process. In the case of MTBE-methanol mixture, in addition to the volatility, the nonpolarity of MTBE causes it to dominate the mass transfer process from the liquid mixtures into cavitation microbubbles. During the collapse of the bubbles, the trapped MTBE were released and this enriched its concentration in the vapor phase. As a result of pressure reduction, cavitational activities that occurred near the boiling point also helped boil the liquid mixtures (19).

In comparison to the unsonicated data, the relative volatility of MTBE-methanol increased with the application of ultrasonic waves. Figure 5 shows that the application of ultrasonic intensity up to $50\,\mathrm{W/A\cdot cm^2}$ increased the relative volatility of MTBE-methanol mixtures. The highest α_{12} value of 2.061 with 20% increment was obtained at $50\,\mathrm{W/A\cdot cm^2}$. According to Mason, an increase in ultrasonic intensity will contribute to an increase in the cavitation effect (19). Larger ultrasonic intensity indicates greater ultrasonic energy entering the liquid system, thereby producing more cavitation microbubbles and creating larger vacuum effects inside the liquid medium. This consequently enhances vaporization of liquid mixtures and increases the relative volatility of MTBE-methanol mixture.

Figure 5 also shows that the increase in ultrasonic intensity beyond $50\,\mathrm{W/A\cdot cm^2}$ decreases the relative volatility of MTBE-methanol. This situation is caused by the formation of a large amount of cavitation micro bubbles at intensity above $50\,\mathrm{W/A\cdot cm^2}$. When a large amount of cavitation bubbles are present inside the liquid medium, the tendency of the bubbles to collide becomes higher. Upon collision, bigger microbubbles are created at an intensity higher than $50\,\mathrm{W/A\cdot cm^2}$. Since the time available for the bubbles to collapse is insufficient, the bubbles will form a bubble "cushion" at the radiating face of the ultrasonic transducer, thereby reducing the effects of coupling sound energy to the liquid system (19). Such phenomenon tends to reduce the amount of ultrasonic energy being transmitted to the liquid medium and produces less cavitational and vacuum effects. This ultimately results in reduced vaporization of the volatile component in the liquid mixture. This phenomenon explains why further increase in ultrasonic intensity beyond $50\,\mathrm{W/A\cdot cm^2}$ decreases the relative volatility and lowers the azeotropic composition of MTBE-methanol mixture.

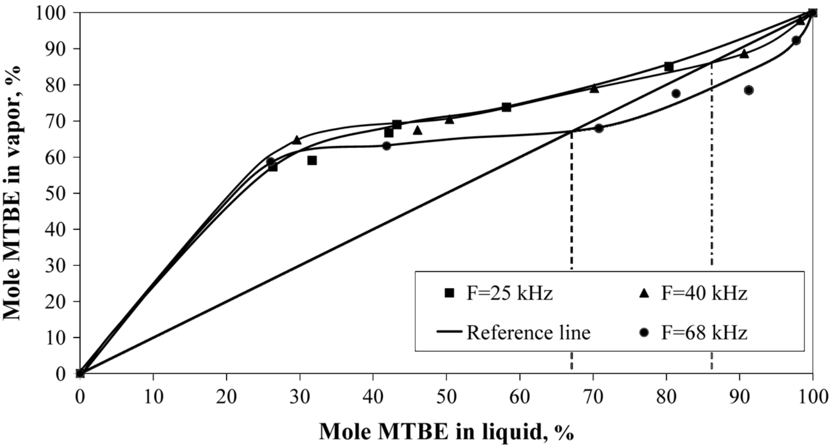


Figure 7. *xy*-diagram for MTBE-methanol system at different ultrasonic frequencies at $50\,W/A \cdot cm^2$ intensity.

VLE Study at Different Ultrasonic Frequencies

Effects of Ultrasonic Frequency on VLE

This section discusses the results obtained from VLE studies at different ultrasonic frequencies. Figure 7 shows the equilibrium data for MTBE-methanol at frequencies of 25, 40, and 68 kHz at $50\,W/A \cdot cm^2$. The trend observed shows that the equilibrium curves and azeotropic points are shifted downwards with the increase in ultrasonic frequency. At a frequency of 25 kHz, the equilibrium curve does not show an intercept at the reference line. This situation means that no azeotrope exists when the binary mixture was sonicated at 25 kHz ultrasonic frequency and intensity of $50\,W/A \cdot cm^2$. The azeotropic points of MTBE-methanol at different ultrasonic frequencies are shown in Table 4.

Table 4. Azeotropic points of MTBE-methanol at different ultrasonic frequencies and $50\,W/A \cdot cm^2$ intensity

Ultrasonic frequency, kHz	Azeotropic point, mole % of MTBE
25	none
40	86
68	67

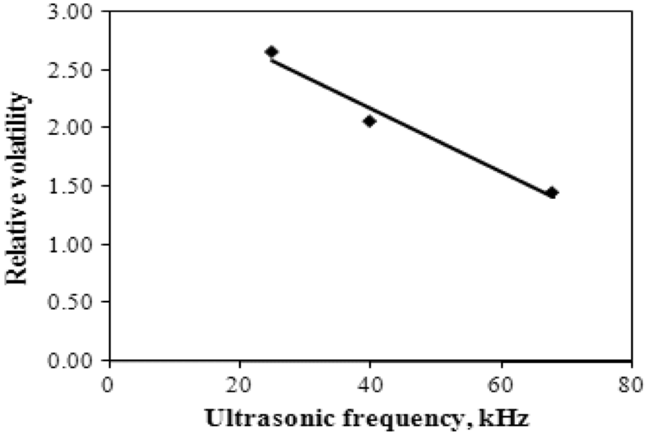


Figure 8. Relative volatility of MTBE-methanol at different ultrasonic frequencies and $50\,\mathrm{W/A\cdot cm^2}$ intensity.

Effect of Ultrasonic Frequency on Relative Volatility

Ultrasonic frequency is another key parameter that can influence the VLE data and relative volatility. Figure 8 shows that the relative volatility of MTBE-methanol decreases with an increase in ultrasonic frequency. Frequency of 25 kHz gives the highest α_{12} value at 2.654, representing a 44.66% increment from the unsonicated conditions. As discussed before, the presence of ultrasonic waves changes the VLE data and the relative volatility through the cavitation phenomenon which involves the formation of microbubbles and generation of a vacuum environment in liquid medium during rarefaction cycle of ultrasonic waves. At higher frequencies, the rarefaction cycle is shortened, leading to the formation of smaller cavitation microbubbles and the generation of smaller vacuum effects within the liquid medium, and ultimately reduced vaporization of the more volatile component in the liquid mixture. This phenomenon explains the decrease in relative volatility, α_{12} at higher ultrasonic frequencies.

CONCLUSIONS

This work successfully proved that ultrasonic waves at different intensities and frequencies had potential to favorably manipulate the relative volatility (α), and hence, the VLE of an azeotropic mixture. Results from experiments conducted on MTBE-methanol mixture at various ultrasonic intensities and frequencies showed that:

- $50\,\mathrm{W/cm^2}$ was the best sonication intensity at frequency of 40 kHz. Further increase in ultrasonic intensity beyond $50\,\mathrm{W/A \cdot cm^2}$ decreased the relative volatility and azeotropic composition of MTBE-methanol mixture.
- As the ultrasonic frequencies were varied, the azeotropic composition decreased with increased ultrasonic frequency.
- The highest relative volatility was obtained at frequency of 25 kHz and intensity of $50\,\mathrm{W/A \cdot cm^2}$ where the azeotropic point was totally eliminated.

This study proved that ultrasonic waves can be employed to remove the barrier for separation of azeotropic mixtures and ultimately intensify the conventional multi-column azeotropic distillation scheme into a single-column alternative.

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NOMENCLATURE

Symbols

A, B, C	Antoine constant in Table 3
P	pressure
P_i^{sat}	pure component vapor pressure
T	temperature (°C)
x_i	liquid phase mole fraction
y_i	vapor phase mole fraction

Greek Letters

α_{ij}	relative volatility of component i and j
γ_i	liquid activity coefficient

Subscripts

i, j, 1, 2	component identification

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