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EFFECTS OF ULTRASONIC WAVES ON ENHANCEMENT OF RELATIVE VOLATILITIES IN METHANOL-WATER MIXTURES

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Abstract. The application of ultrasonic wave in various fields including separation process has increased predominantly. This paper reports the practicability of using ultrasonic wave to enhance separation of binary mixtures by distillation. The binary mixture utilized was methanol-water. The effect of different ultrasonic intensity at 50, 100, 200 and 250 W/A.cm^2 with frequency of 40 kHz to vapor-liquid equilibrium (VLE) of methanol-water was investigated to obtain the most suitable operating intensity. Experimental studies were also carried out to investigate the frequency effect (25 and 68 kHz) to VLE data. It was found that the use of ultrasonic wave enhanced the separation process by increasing the relative volatility of components. The highest average relative volatility of methanol-water at 29.413 was obtained from experimental study using intensity 200 W/A.cm^2 and frequency of 25 kHz. The changes in relative volatility and VLE were caused by cavitational activities and vacuum effect that occur during transmission of ultrasonic wave in liquid medium. The results from this study proved the practical feasibility of using ultrasonic wave to enhance separation of binary mixtures in distillation column.

Keywords: Vapor-liquid equilibrium, methanol-water, ultrasonic waves, relative volatility

Abstrak. Penggunaan gelombang ultrabunyi dalam pelbagai bidang termasuk proses pemisahan telah meningkat sejak akhir-akhir ini. Kajian ini melaporkan keberkesanan penggunaan gelombang ultrabunyi dalam meningkatkan pemisahan campuran binari dalam turus penyulingan. Campuran binari yang digunakan adalah metanol-air. Kesan keamatan gelombang bunyi yang berbeza iaitu 50, 100, 200 and 250 W/A.cm^2 pada frekuensi 40 kHz terhadap keseimbangan wap-cecair (KWC) dikaji bagi mendapatkan nilai keamatan yang sesuai. Eksperimen juga dijalankan bagi mengkaji kesan frekuensi (25 and 68 kHz) terhadap data KWC. Didapati, penggunaan gelombang ultrabunyi berjaya meningkatkan proses pemisahan dengan meningkatkan nilai kemeruapan relatif. Purata kemeruapan relatif yang tertinggi bagi metanol-air iaitu 29.413 diperoleh daripada uji kaji yang menggunakan keamatan 200 W/A.cm^2 dan frekuensi 25 kHz. Proses peronggaan dan kesan vakum yang wujud semasa perambatan gelombang ultrabunyi dalam cecair membawa kepada perubahan nilai kemeruapan relatif dan data KWC.

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Keputusan yang diperoleh menunjukkan keberkesanan penggunaan gelombang ultrabunyi bagi meningkatkan pemisahan campuran binari dalam turus penyulingan.

Kata kunci: Keseimbangan wap-cecair, metanol-air, gelombang ultrabunyi, kemeruapan relatif

1.0 INTRODUCTION

Methanol can be produced from natural gases and coal. By a simple reaction between coal and steam, a gas mixture called syn-gas (synthesis gas) is formed. The components of this mixture are carbon monoxide and hydrogen, which through an additional chemical reaction with water as a side product before converted to methanol [1]. Separation of methanol-water in industry has been done using distillation technique. Although methanol-water mixtures do not form an azeotrope (normal binary), a number of distillation columns are required to obtain high purity methanol.

Ultrasonic wave is a sound wave having frequency higher than human audibility limits [2]. Sound wave with frequency above 20 kHz is usually considered as ultrasonic [3]. The use of ultrasonic wave has gain consumers interest in various fields, including separation process [4-6]. In distillation process, ultrasonic wave is believed to be capable of increasing separation of mixtures by altering the relative volatility of components in the mixtures. As an exploratory study, this research has primary aim to investigate the possibility of ultrasonic wave application in distillation to enhance separation of binary mixtures.

Since the successful application of distillation is greatly dependent upon an understanding of equilibrium existed between vapor and liquid phases of the mixtures, the study on ultrasonic effect to VLE was firstly done using typical binary mixture found in literature. The binary mixture was methanol-water [7-8]. The effects produced by different ultrasonic intensities and different ultrasonic frequencies to VLE data were investigated. The results show that ultrasonic wave can favorably change the relative volatility of methanol-water mixtures, thereby allowing an easier separation compared to an ordinary distillation process.

2.0 ULTRASONIC CAVITATION THEORY

Cavitation normally takes place in liquid medium once the media is subjected to rapid, alternating high pressure, ultrasonic excitation or pulsed heating lasers [9]. Voids containing small micro bubbles are created when the differences between amplitude pressure of ultrasonic waves and the hydrostatic pressure in the liquid are large enough to exceed the local tensile strength of the liquid medium. These bubbles expand during negative part of pressure cycle (rarefaction cycle), reach the maximum radius and then collapse at the onset of positive pressure cycle (compression cycle) [10]. This process repeats continuously according to pressure oscillation of ultrasonic waves. Depending on some circumstances, the bubbles will be filled either by gases or by vapor of the liquid itself [11]. The vacuum environments/spots which created inside the liquid medium during negative pressure cycle or expansion cycle of ultrasonic wave, also helps towards inducing the boiling process as well as drawn the fluids into cavitation micro bubbles[12-13]. Due to this situation, at high temperature (near boiling point), the vapors of volatile component enter the cavitation bubbles and released during the bubbles collapse.

3.0 EXPERIMENTAL METHOD

3.1 Materials

Methanol used in this study was supplied by R&M Chemical Industries (M) Sdn Bhd. The purity of the chemical was 99.8%. It was used without further purification since no significant impurities was detected by the gas chromatography. Water used in this study was distilled water. The refractive indices and boiling points of each material used were measured, and the results with those reported in the literature are listed in Table 1.

Table 1 Physical properties of materials

Material	Refractive indices, η_D		Boiling point, T_b (K)	
	Experimental	Literature [8]	Experimental	Literature [8]
Methanol	1.3280	1.3290	337.97	337.80
Water	1.3330	1.33301	373.15	373.13

3.2 Apparatus and Procedure

The experimental studies were performed using an Ultrasonic-Distillation System. The apparatus consists of a distillation flask, a condenser, a water bath, ultrasonic generating equipments, 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 water bath equipped with 40 kHz ultrasonic transducer and heater. The ultrasonic transducer, supplied by Crest Ultrasonic (M) Sdn Bhd, was connected to 500 Watt ultrasonic generator. The liquid and vapor temperatures were measured using thermocouples, TC-08 with precision of 0.01^{o}C and linked using Pico data logger to a computer. Methanol-water mixtures at different compositions were prepared and fed into the distillation flask. The mixtures were let to be boiled with the absence or the presence of ultrasonic wave until reached an equilibrium. The vapor and liquid phases reach equilibrium once the vapor temperature remained constant for a period of 10-20 minutes. When equilibrium was reached, liquid samples from the distillation flask and condensed vapor were taken and their compositions were measured using a refractometer at ambient condition. Distillation was initially done at atmospheric pressure to obtain methanol-water 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.cm^2 and frequency of 40 kHz to determine the most suitable operating intensity. After that, the same procedure was repeated at 25 kHz and 68 kHz frequency.

3.3 Analysis Procedure

In order to analyze the mixture of methanol-water, a calibration curve of the refractive index versus mole fraction of the methanol is required. Samples in Table 2 were prepared and measured using a refractometer at ambient condition. The composition of distillate and bottom products was determined by interpolation from the plotted graph (Refer to Figure 1).

Table 2 Refractive indices with different compositions of methanol-water

Samples		Mole fraction of methanol, %	Refractive indices, η_D (27°C)
Methanol (mL)	Water (mL)		
0	10	0	1.3330
1.0	9.0	5	1.3340
2.0	8.0	10	1.3356
3.0	7.0	16	1.3376
4.0	6.0	23	1.3389
5.0	5.0	31	1.3401
6.0	4.0	40	1.3410
7.0	3.0	51	1.3395
8.0	2.0	64	1.3372
9.0	1.0	80	1.3333
9.5	0.5	89	1.3312
10	0	100	1.3280

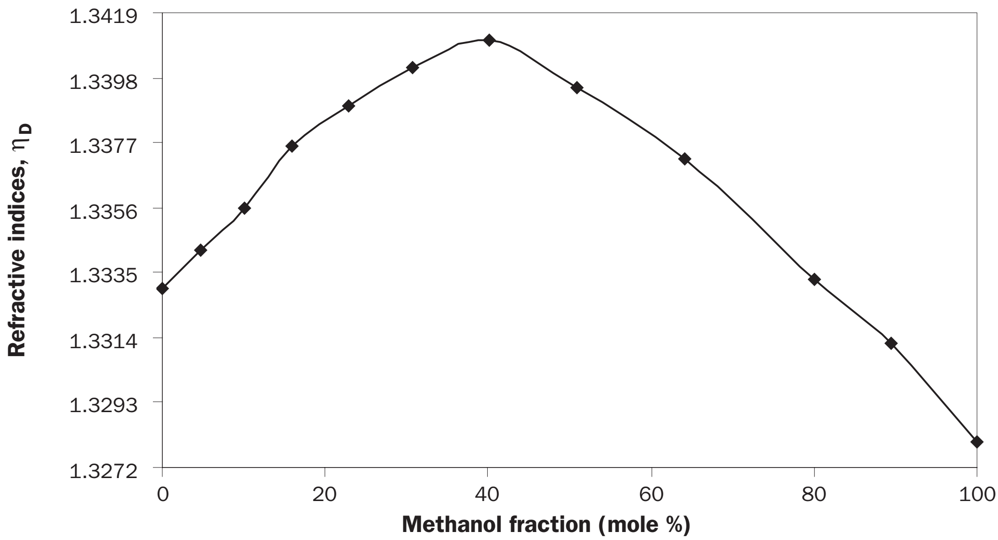

Figure 1 Refractive index of methanol-water mixtures against mole fraction of methanol

4.0 RESULTS AND DISCUSSION

4.1 Experimental Study without Sonication

VLE data for methanol-water was measured at atmospheric pressure without the presence of ultrasonic wave. Figure 2 illustrates the VLE data of methanol-water in comparison with Khalfaoui *et al.* [7], where the vapor phase composition was plotted against the liquid phase composition. This was done to verify the reliability of developed method and VLE apparatus that was used to obtain VLE data. As illustrated in the figure, the VLE data obtained concurred with those found in the literature [7]. The average deviations of experimental data with the literature values are less than 10% and thus lay within an acceptable limit (Refer Table 3). This proves the practical feasibility of using the developed method and VLE apparatus to obtain VLE data.

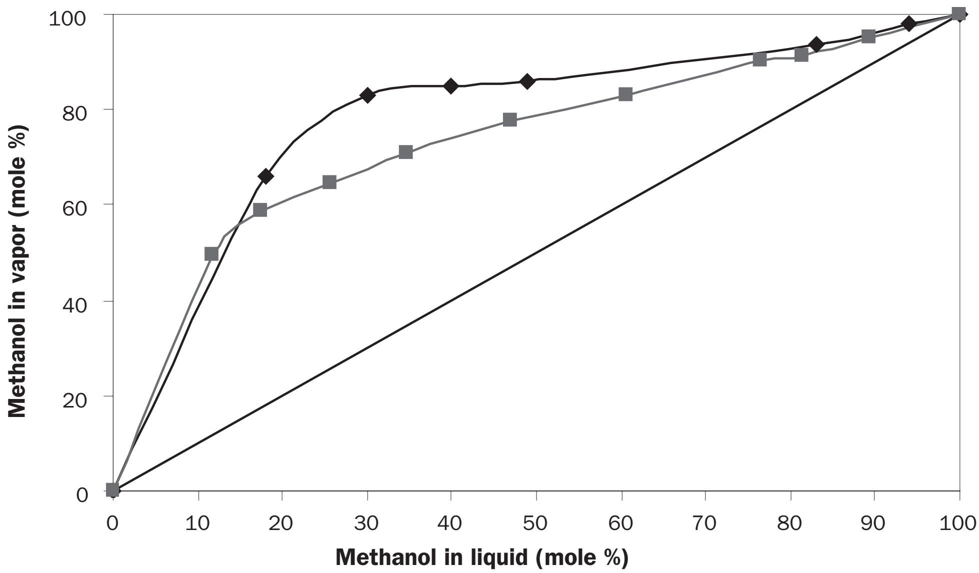

Figure 2 *xy*-diagram of methanol-water system at atmospheric pressure: (◆) Experimental data, (■) Literature value [7]

Table 3 Vapor and liquid composition of methanol-water

x_1,%	y_1,%		% deviation
	Experimental data	**Literature value, [7]**	
10	38	43	-11.6
20	70	61	14.8
30	83	68	22.1
40	85	74	14.9
50	86	79	8.9
60	88	83	6.0
70	90.5	87	4.0
80	93	91	2.2
90	96	95	1.1
		Average deviation	**6.9**

4.2 Experimental Study with Sonication

4.2.1 Effect of Ultrasonic Intensity on VLE

Figure 3 shows the equilibrium curve of methanol-water system with different ultrasonic intensities in comparison to the unsonicated data. As can be seen in this figure, the equilibrium curves of methanol-water were shifted upward and become further from the reference line when the ultrasonic intensity increased up to 200 W/A.cm^2. Geankoplis [14] stated that the further the equilibrium curve lies from the 45^o line, the easier the separation of components. However, the VLE curve was shifted downward and become closer to the reference line when intensity of 250 W/A.cm^2 was applied to the system. The changes on VLE data with ultrasonic application were related to the changes of mixtures' relative volatility (Refer Figure 4). The relative volatility of methanol-water was calculated using the following equation:

$$\alpha_{12} = \frac{(y_1 / x_1)}{(y_2 / x_2)} \tag{1}$$

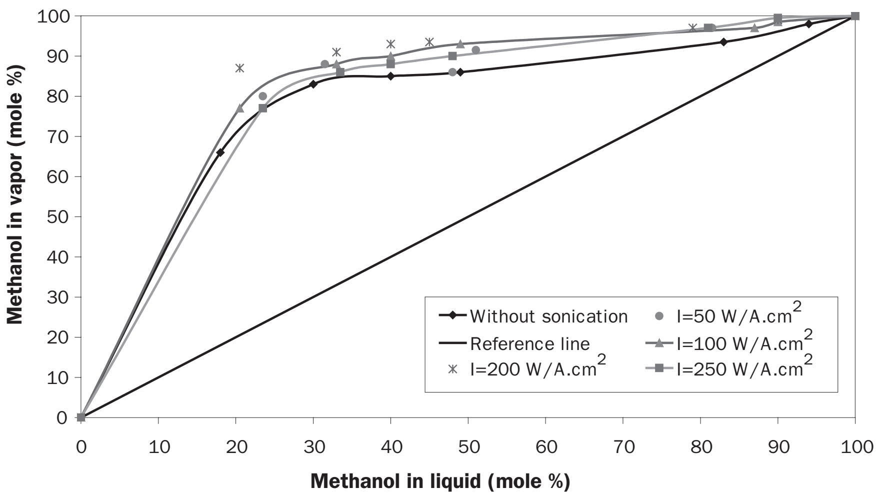

Figure 3 Equilibrium curve of methanol-water system with different ultrasonic intensity at frequency of 40 kHz

The changes of relative volatility and VLE data of methanol-water were caused by the cavitational activities and vacuum effects, which occur during transmission of ultrasonic wave in the liquid medium. Detailed mechanism of cavitation activities has been mentioned previously in Section 2.0. Vacuum conditions, which were created at low-pressure phase of ultrasonic cycle, aid the vaporization of volatile component in the liquid medium and draw it into the cavitation micro bubbles [12-13]. According to Mason [13], the presence of volatile components in liquid mixtures would cause the cavitation micro bubbles to be filled with the vapor of the volatile component. Since methanol is more volatile than water, more vapor of methanol was vaporized and trapped inside the micro bubbles. The trapped vapor was released during the bubble collapses and increase its concentration in vapor phases. Due to this situation, more methanol was vaporized during ultrasonic-distillation process compared to ordinary distillation procedure.

As shown in Figure 4, the application of ultrasonic wave up to 200 W/A.cm^2 increased the average relative volatility of methanol-water, $\bar{\alpha}_{12}$. The highest $\bar{\alpha}_{12}$ value at 17.264 was obtained at intensity 200 W/A.cm^2. This finding aligned with the statement given by Mason [13] who stated that an increase in ultrasonic intensity would contribute to an increase in cavitation and vacuum effect. This is because, as ultrasonic intensity increased, greater ultrasonic energy enters the liquid medium and produce more cavitation micro bubbles and creates larger vacuum effects inside the liquid medium. This helps in increasing the amount of methanol that is trapped inside the cavitation micro bubbles and thus released during their collapse. This phenomenon has consequently increased the relative volatility of methanol-water mixtures. However, Mason [13] also stated that ultrasonic intensity could not be increased indefinitely.

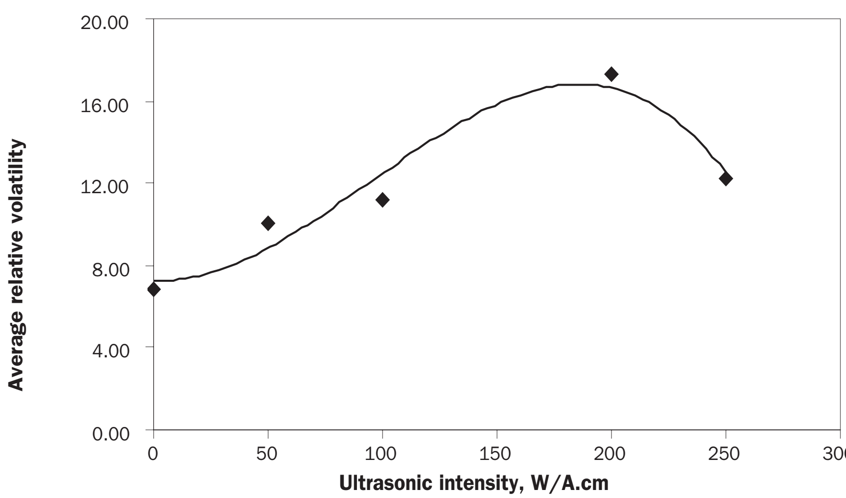

Figure 4 Average relative volatility of methanol-water as a function of ultrasonic intensity at frequency of 40 kHz

Figure 4 also shows that the average relative volatility of methanol-water decreased with the application of ultrasonic wave above 200 W/A.cm^2. The $\bar{\alpha}_{12}$ value obtained with sonication at 250 W/A.cm^2 was 12.256. This is because, as ultrasonic intensity increased beyond 200 W/A.cm^2, too many cavitation micro bubbles were formed and perturbed the normal cavitation processes. These bubbles collide with each other and produce bigger bubbles. Some of the bubbles do not collapse and form a bubble cushion at the radiating face of ultrasonic transducers that reduce the effect of coupling sound energy into the liquid system [15]. Hence, less cavitational and vacuum effects are produced. This consequently reduced vaporization of volatile components in the liquid medium and decreased the average relative volatility of methanol-water with the application of ultrasonic intensity beyond 200 W/A.cm^2. Therefore, the best operating intensity at frequency of 40 kHz was 200 W/A.cm^2.

4.2.2 Effect of Ultrasonic Frequency on VLE

Ultrasonic frequency is another important parameter that defines sound field and significantly influences the cavitation formation. Therefore, upon examining the effect of ultrasonic wave to VLE data, the selection of operated ultrasonic frequency is very crucial. In this section, the influence of different ultrasonic frequencies to VLE data at constant intensity (200 W/A.cm^2) is discussed. Figure 5 illustrates the VLE data of methanol-water with different ultrasonic frequency. The equilibrium curves were shifted downward and closer to the reference line with the increased of applied frequency. The changes in average relative volatility of binary mixture with the presence of ultrasonic wave caused the shifting of VLE curves. Figure 6 illustrates the relation of average relative volatility of methanol-water, $\bar{\alpha}_{12}$ with different ultrasonic frequency.

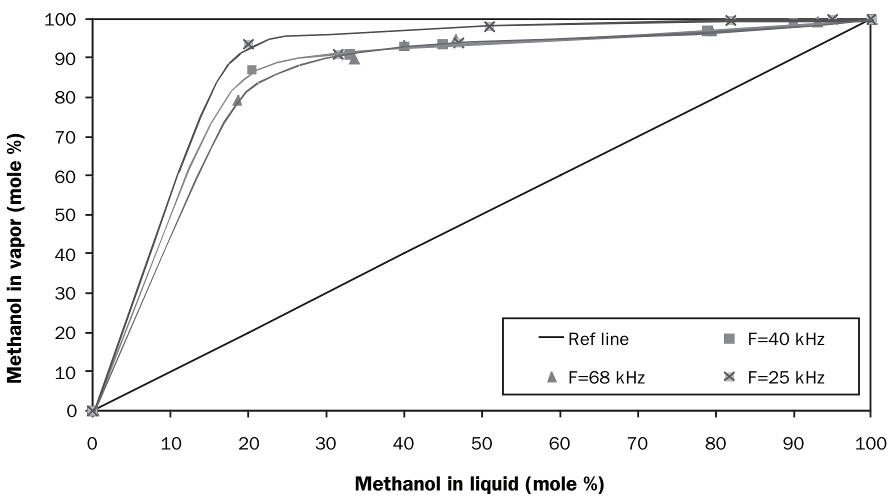

Figure 5 Equilibrium curve of methanol-water system with different ultrasonic frequency at intensity 200 W/A.cm^2

The results obtained demonstrate that an increase of ultrasonic frequency at constant intensity decrease the average relative volatility of the mixture. The highest $\bar{\alpha}_{12}$ at 29.413 for methanol-water was obtained at frequency of 25 kHz while the lowest value was obtained at frequency of 68 kHz. According to Van Winkle, the largest relative volatility indicates the easiest separation process [16]. As a result, the separation of binary mixture by distillation becomes easier with the application of ultrasonic wave at the frequency of 25 kHz. As discussed before, cavitation phenomenon is responsible for the changes in relative volatility and VLE data of methanol-water mixtures.

During cavitation processes, the liquid molecules are wrench apart and create voids that contain small gas bubbles and vacuum spots [10]. At constant ultrasonic power the cavitation formation is greatly dependent on the ultrasonic frequency. According to Mason [15], more power is required at higher frequency to produce the same cavitation and vacuum effects in a liquid medium. At higher frequency, the rarefaction cycle is shortened. This result in production of smaller cavitation micro bubbles and generation of smaller vacuum environment inside the liquid medium, which in turn, reduced the vaporizations of volatile component in liquid mixtures. This phenomenon explains why the increase of ultrasonic frequency decreases the relative volatility of binary mixtures.

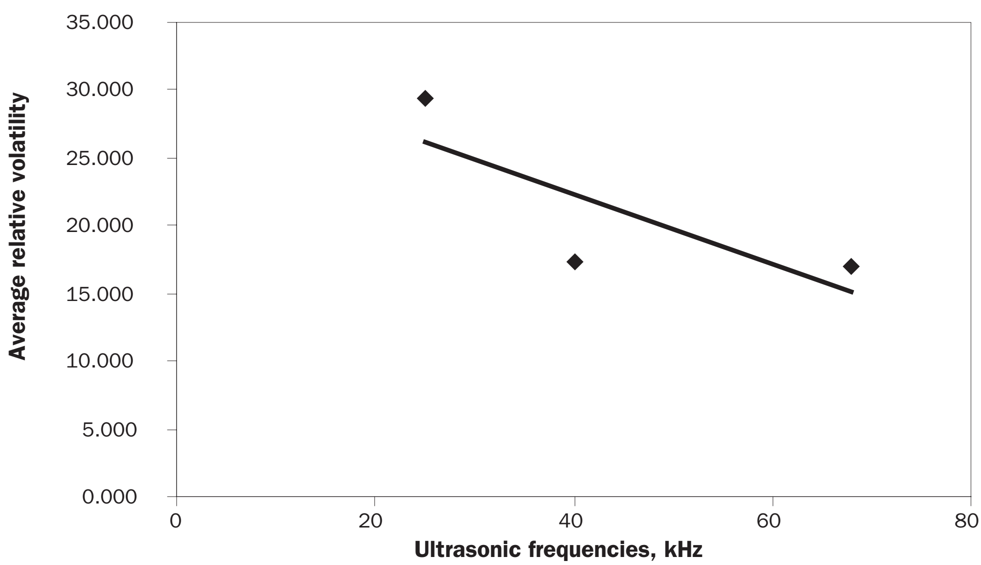

Figure 6 Relative volatility of methanol-water system with different ultrasonic frequency at intensity 200 W/A.cm^2

4.3 Changes in Chemical Properties

The literature review shows that the sonolyis of chemical compound that originated from acoustic cavitation would cause chemical decomposition and change the chemical properties [17-20]. In this research, sonication of liquid mixtures was done at high operating temperature, which is at the mixture's boiling point. Therefore, the chemical changes with respect to ultrasonic wave application at high temperature were negligible [13, 17]. According to Mason [13], it is not very sensible to attempt sonochemical reaction in a liquid medium near its boiling point since the sonication of liquid mixtures at their boiling point will cause boiling. This is because, the vacuum effects that occurred at low-pressure phase of ultrasonic cycle, induce boiling in liquid medium and drawn it into cavitation micro bubbles. Due to this situation, the cavitation processes and vacuuming effects, which occur during propagation of ultrasonic waves in distillation flask, are technically responsible on the changes of average relative volatility and VLE data instead of the changes on the chemical properties.

5.0 CONCLUSION

Ultrasonic waves has the potential to manipulate the relative volatility (α), and hence, the VLE of a binary mixture. Results from experiments conducted at different ultrasonic intensities and at frequency of 40 kHz show that 200 W/cm^2 was the best sonication intensity for methanol-water mixture within the range of investigated intensities. Further increase in ultrasonic intensity beyond 200 W/A.cm^2 decreased the $\bar{\alpha}_{12}$ methanol-water mixture. Results obtained from experimental study at different ultrasonic frequencies and constant intensity of 200 W/A.cm^2 show that the $\bar{\alpha}_{12}$ decreased with the increase in ultrasonic frequency. The highest $\bar{\alpha}_{12}$ obtained at frequency of 25 kHz and intensity of 200 W/A.cm^2 was 29.413. Results from this study prove that ultrasonic waves can be employed to improve the relative volatility of components in binary mixture and hence increase the separation of methanol-water in distillation column.

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List of Symbols and Greek Letters

T	temperature (°C)
x_i	liquid phase mole fraction
y_i	vapor phase mole fraction
α_{ij}	relative volatility of component *i* and *j*
$\bar{\alpha}_{12}$	average relative volatility of component 1 and 2
η_D	refractive indices
T_b	boiling point (K)

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