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Mathematical modeling of a single stage ultrasonically assisted distillation process

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ABSTRACT

The ability of sonication phenomena in facilitating separation of azeotropic mixtures presents a promising approach for the development of more intensified and efficient distillation systems than conventional ones. To expedite the much-needed development, a mathematical model of the system based on conservation principles, vapor–liquid equilibrium and sonochemistry was developed in this study. The model that was founded on a single stage vapor–liquid equilibrium system and enhanced with ultrasonic waves was coded using MATLAB simulator and validated with experimental data for ethanol–ethyl acetate mixture. The effects of both ultrasonic frequency and intensity on the relative volatility and azeotropic point were examined, and the optimal conditions were obtained using genetic algorithm. The experimental data validated the model with a reasonable accuracy. The results of this study revealed that the azeotropic point of the mixture can be totally eliminated with the right combination of sonication parameters and this can be utilized in facilitating design efforts towards establishing a workable ultrasonically intensified distillation system.

1. Introduction

In process industries, distillation is still one of the preferred processes despite its difficulties in separating mixtures with very close boiling points and those that form azeotrope. To overcome this limitation, variety of frontier technologies have been explored [1]. For example, dividing-wall column has been introduced to separate more components in a single distillation unit, thereby offering energy savings along with substantial capital and space reduction [2,3]. Furthermore, it is also possible to implement this separation technique with azeotropic distillation [4], or extractive distillation [5], so that it can be integrated into single column configuration. However, this process is marred by high pressure drop and temperature difference caused by the increase in the boiling point [6].

Another new approach is to intensify the process by adding ultrasonic equipment to the distillation system. Using cavitation as a source of energy input for chemical processes to generate rapidly formed and disappearing hot-spots under nearly ambient conditions offer potential improvements to conventional distillation. The whole process of generation, growth and collapse of cavities occurs rapidly, of the order of few microseconds, and this phenomenon alters physical properties of the mixtures and enhances the mass [7] and heat [8] transfer, thus offering further exploitation to intensify vapor–liquid separation.

As a foundation for the development of ultrasonic distillation process, studies on vapor–liquid equilibrium (VLE) under ultrasonically intensified environment have been carried out. These include experimental works on the VLE of methanol–water [9], MTBE-methanol [10] and cyclohexane-benzene [11]. In all cases, positive changes on the VLE characteristics were observed and sonication effects have been proven to alter the relative volatility of azeotropic mixtures, thus enabling higher purity separation in a single distillation column.

To facilitate further development, a mathematical model describing the process is needed so that comprehensive design study of the ultrasonic distillation system can be carried out. In this paper, this issue is addressed. A mathematical model that represents a single stage vapor–liquid equilibrium system with intensification using ultrasonic waves is derived and validated.

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This is followed by a simulation study to investigate the process characteristics and determination of optimal operating condition for separation this system.

2. Mechanism of ultrasonic separation

2.1. Mechanisms of bubble collapse

Acoustic cavitation is a phenomenon by which ultrasonic waves induce bubbles formation, growth and collapse [12]. The collapse normally takes place when the bubble reaches critical size referred to as the resonance size. Depending on the operating condition, the growth-collapse process may end up in two possible scenarios. Firstly, if they are smaller than the resonance size, bubbles tend to migrate from the minimum pressure, also known as pressure node to the maximum pressure referred to as antinode. This is driven by primary Bjerknes forces, and will lead to a condition whereby bubbles are collapsing inside the liquid and generating high temperature [13]. This causes the formation of radicals and highly reactive intermediates within the bubbles during the collapse. For this reason, they are called "active" cavitation bubbles. This condition facilitates various chemical pathways, thus enhancing sonochemical reactions [14]. Recently, numerous papers have reported enhancement effect of ultrasound on biodiesel synthesis with basic strength of catalyst [15–17]. They established the mechanism of this enhancement by discrimination of the physical and chemical effects of cavitation bubbles in the system on transesterification of oil with alcohol using a catalyst.

Secondly, if they are larger than the resonance size, they will be forced to the node to become "inactive". These bubbles eventually float out of the liquid due to buoyancy forces and collapse at the liquid surface [18]. Similar observation is reported in a study involving ethanol/water mixture, where the bubble travel through the liquid mixture and collapse in the fountain jet formed at the liquid surface releasing the alcohol vapor in the bubble [19]. These phenomena have significant impact on mechanical and physical processes such as cleaning and vapor–liquid separation processes. However, certain combination of operating conditions may also create exceptions. For example, a study by Matula [20] revealed that at 20 kHz and 1.8 bar, the bubble is repelled from the antinode even if the size is smaller than the resonance size.

Other researchers [21,22] also proposed an alternative mechanism based on capillary wave. In this hypothesis, a liquid is parametrically excited by ultrasound waves such that capillary waves are formed on the surface. As the amplitude of these waves increase, the capillary become instable and small liquid droplets pinch off from the crests (peaks) of the capillary wave causing atomization. Oscillation and collapses of the cavitation bubbles enhance the capillary wave perturbations and thus facilitate the pinch-off of droplets mist formation [23]. However, the visible mist was produce by mixture droplets which is depend on the physical properties of a mixture and operation conditions. If the boiling points of the components of a mixture are close, the percentages of these components in the droplet mist are also close; and vice versa [21,22]. Therefore, in the present system this theory is futile to break the azeotrope.

2.2. Factor influencing the mechanisms of bubble collapse

Many literatures have examined the effect of physical properties of mixtures and operating conditions on the activity of acoustic cavitation bubbles [24–30]. In summary, there are three important conditions that may cause cavitation bubbles to lose their activities. The first condition is concerned about the influence of ultrasonic frequency on the cavitation bubbles. At lower frequencies, since the cycle of expansion and compression is slower, larger bubbles are produced. Moreover, when the population of bubbles is high, which typically happen at high sonication intensity, some of the bubbles coalesce to form larger bubbles [24]. As a consequence, the bubbles have larger surface area of contact with the surrounding liquid, thus allowing more light molecules to diffuse into the bubble, thus increasing its vapor pressure, which in turn further increase the bubble size. When the bubble is larger than the resonance size, it will be pushed toward the nodes by primary Bjerknes forces and becoming inactive [26,27].

The second condition is related to the operating temperature. An increase in the bulk liquid temperature leads to a reduction in bubbles' activities due to two reasons [25–27]. Firstly, dissolved gases in the liquid evaporate to the surface at high temperature, thus reducing the bubble population. Secondly, as temperature of the bulk liquid increases, the liquid vapor pressure inside a cavitation bubble is increased, leading to an increase of the bubble size. When the size exceeds the resonance size and become "inactive" as mentioned previously.

The third condition is related to decomposition of components in the presence of hydrocarbons [28,29]. When molar heat of hydrocarbons is much larger than that of gases inside the bubble, the temperature generated during the bubble collapse decreases monotonously to an extent that it is unable to dissociate hydrocarbons inside the bubble, thus making it inactive. This is contrary to the observation by Yasui et al. [30,31] when the liquid environments were aqueous. In their work involving aqueous methanol environment, they reported that as the bubbles collapsed methanol molecules were dissociated inside a bubble. Similarly, when pure water is used, water vapor dissociated inside the heated bubble and chemical species such as OH radical and H atom are created inside the bubble during the violent collapse of bubbles [31].

Based on the above arguments, "inactive" conditions are established when the operating conditions are at low frequency, high temperature, and hydrocarbons. It is also important to note that the ultrasonic wave generates micro-point vacuum condition within the liquid during bubbles formation. In this condition, azeotrope of the vapor components inside the bubbles is altered, resulting in changes in vapor liquid equilibrium. This is confirmed by a various studies that proved the breaking of azeotrope under vacuum pressure condition [32,33]. To understanding the mechanism of the enhancement separation of the system in this process, these bubbles eventually float out of the liquid due to buoyancy forces and collapse at the liquid surface in the fountain jet releasing the vapor in the bubble to the vapor phase. Thus, the mole fractions of the vapor inside the bubbles are considering equal to those in the vapor phase. These are the scenarios considered in this study.

3. Mathematical modeling

The mathematical model developed here is focusing on the use of ultrasound in facilitating a distillation process. To simplify model development efforts, a number of assumptions on the physical characteristics of the bubble are made. The cavitation bubble is assumed to be spherically symmetric and is initially composed of mixture of gas (air) and liquid vapor. The surrounding liquid is assumed incompressible, with constant and uniform dynamic viscosity, and is at steady-state condition. The non-equilibrium condition is during the growth of a bubble which is very short time (microsecond). During this time, the bubble is unstable due to the amount of material that gets into the bubble (during expansion) is larger than what comes out of the bubble (during compression). Therefore the final number of molecules inside the bubble will be calculated at equilibrium condition. The validity of the model