CHEMICAL ENGINEERING TRANSACTIONS

VOL. 56, 2017

A publication of AIDIC
The Italian Association of Chemical Engineering
Online at www.aidic.it/cet

Guest Editors: Jiří Jaromír Klemeš, Peng Yen Liew, Wai Shin Ho, Jeng Shiun Lim

ISBN 978-88-95608-47-1; **ISSN** 2283-9216

DOI: 10.3303/CET1756233

Flammability Assessments of Sonication Process in Organic Mixture

Nur Amira Hasnul Hadi[a], Arshad Ahmad*[,b], Tuan Amran Tuan Abdullah[b], Adnan Ripin[b]

[a]Faculty of Chemical & Energy Engineering, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
[b]Centre of Hydrogen Energy, Institute of Future Energy, Universiti Teknologi Malaysia, 81310 Johor Bahru, Malaysia
arshad@cheme.utm.my

The prospect of sonication phenomenon in facilitating separation of azeotropic mixtures calls for more detailed study towards developing an intensified distillation system. One important element that require in depth consideration is safety since ultrasound is a potential ignition source with a low threshold value of 1 mW/mm^2. In this study, the aim is to investigate the potential of fire hazards that may be introduced by sonication when used in the environment of flammable organic liquid. Simulation study in MATLAB programming environment is carried out based on a mathematical model developed using first principle. Simulations of bubble conditions covering its whole life cycle regimes are carried out and validated with experimental works. Evaluation is made for an extreme condition where the ultrasonic waves are focused directed towards a stainless steel target material immersed in ethanol-water mixture. As sonication occurs, bubbles form slowly by rectified diffusion process with radius of 6 μm, and move toward the metal target. The experimental results revealed that cavitation bubbles filled with explosive vapor are not ignited. This is consistent with the simulation study where the maximum energy released during the bubble collapse is found to be small, which is 0.19267 pJ compared to minimum ignition energy of the liquid at 0.23 mJ. This concludes that the focused ultrasound wave in organic liquid does not trigger ignition, thus suggesting the ultrasonic distillation system is potentially.

1. Introduction

In recent years, separation of liquid mixtures has become one of the most important tasks in process industry. From all separation technique available, distillation has been the most common method used. Because distillation offers many processing advantages and mostly used, it still remain as the preferred process. For mixtures that have azeotrope, separation process must have a specially chosen chemical to eliminate the azeotropes points, namely entrainer (Ripin et al., 2009). Since azeotropic mixture could not be separated using conventional distillation, it requires a new method for the separation.

Over the last few years, a large number of scientists has been working on chemical intensification process and has developed an interest in ultrasonic distillation (Stankiewicz and Moulijin, 2002). The uniqueness of ultrasound is that it is only operated in the presence of liquid to transmit its energy to enhance the physical and chemical change of a liquid medium. Acoustic cavitation is the major phenomena that arise from the propagation of ultrasonic waves in liquid (Ashokkumar, 2011). Power of ultrasound enhances the chemical and mechanical effect by the generation and destruction of cavitation bubbles occur during the process (Contamine et al., 1994).

Growth and collapse of bubble in sonication has yield the energy transfer from ultrasonic transducer to the vapour inside the bubble (Gong and Hart, 1998). During this time, extremely high pressure in orders of hundreds of atmosphere and high temperature up to 5,000 K are generated inside the bubble. Since ultrasound are considered to be an ignition source by International Standard, this separation method has reported no explosion neither fire accident in conjunction to ultrasound. However, incendivity of acoustic cavitation on vapour liquid equilibrium in ultrasonic distillation is not yet to be to be study. This present work is undertaken to determine whether will sonication during ultrasonic distillation triggered ignition.

Please cite this article as: Hadi N.A.H., Ahmad A., Abdullah T.A.T., Ripin A., 2017, Flammability assessments of sonication process in organic mixture, Chemical Engineering Transactions, 56, 1393-1398 DOI:10.3303/CET1756233

2. Research Framework

2.1 Mathematical Modelling

For development of mathematical model in ultrasonic distillation, behaviour of collapsing bubbles during sonication with assumptions is made on the physical characteristic of bubble. Cavitation bubble formed during sonication is assumed to be spherically symmetric and composed of gas and liquid vapour. Surrounding liquid is assumed incompressible, with constant and dynamic viscosity. Non-equilibrium condition occurs during the growth of bubble at a very short time (microsecond). Bubble during this time is not stable because of the material gets into the bubble during expansion is larger compare to during compression (Mahdi et al., 2015). This model started with bubble expansion, sonication effect, maximum size and the bubble energy during collapsing.

2.1.1 Bubble Expansion

Consider an initial bubble containing a very tiny mass m_g of non-condensable gas and liquid vapour at ambient temperature T, the pressure of bubble according to ideal gas law as shown in Eq(1) (Meidani et al., 2004):

$$P_g = \frac{M_g \mathrm{RT}}{M_g\left(\frac{4}{3}\right)\pi {R_O}^3} \tag{1}$$

Where, M_g is the molecular weight of air, R is the universal gas constant. There are two pressure inside the bubble which are P_g, pressure of non-condensable gas and vapour partial pressure denoted as P_v. Sum of two partial pressure is equal to total pressure of inside the bubble ($P_T = P_v + P_g$).Laplace pressure phenomenon occurs at the bubble interface where the liquid pressure is lower than pressure inside the bubble as in Eq(2) (Franc, 2006):

$$P_g + P_v = P_o + \frac{2\sigma}{\mathrm{R}} \tag{2}$$

Substitute Eq(1) into (Eq)2, giving the liquid ambient pressure P_o as in Eq(3):

$$P_o = P_v + \frac{M_g \mathrm{RT}}{M_g\left(\frac{4}{3}\right)\pi {R_O}^3} - \frac{2\sigma}{R_O} \tag{3}$$

and R_o is the initial bubble radius as shown in Eq(4):

$$R_o = \frac{1}{2\pi \mathrm{f}}\left(\frac{3P_o}{P_i}\right)^2 \tag{4}$$

2.1.2 Sonication Effect

Due to the ultrasonic wave, liquid medium is exposed to sonication generated from ultrasonic wave transducer with pressure amplitude P_A and frequency *f*. Therefore, the pressure P_∞ inside liquid at any time t is given as in Eq(5) (Moholkar et al., 1999):

$$P_\infty(t) = P_o - P_A \sin(2\pi f t) \tag{5}$$

and P_A is the pressure amplitude of sound field given by Servant et al. (2000) as in Eq(6):

$$P_A = \sqrt{2IpC} \tag{6}$$

where, I represent intensity of ultrasound and C is the velocity of sound through liquid.

$$R\frac{\mathrm{d}^2\mathrm{R}}{\mathrm{dt}^2} + \frac{3}{2}\left(\frac{\mathrm{dR}}{\mathrm{dT}}\right)^2 = \frac{1}{p}\left[P_i - P_\infty - \frac{2\sigma}{\mathrm{R}} - \frac{4\mu}{R}\left(\frac{dR}{dT}\right)\right] \tag{7}$$

Eq(7) is the Rayleigh-Plesset equation that study about bubble dynamic in which collapse of an empty spherical bubble from initial radius, R_o to new radius R at time *t* was considered and P_i is the pressure in the bubble.

2.1.3 Maximum Size of Bubble

During the rarefaction phase, radius of bubble that was initially at R_o will expand to maximum radius, R_{max}. The maximum radius is from Rayleigh-Plesset equation, which given by Mason and Philip (2002) as in Eq(8):

$$R_{max} = \frac{2}{3\pi f}(P_A - P_o)\left(\frac{2}{pP_A}\right)^{1/2}\left(1 + \frac{2(P_A - P_o)}{3P_o}\right)^{1/3} \tag{8}$$

2.1.4 Energy of Bubble During Collapse

Collapse and growth of bubble during sonication cause the transfer and focus energy from ultrasonic transducer to vapour inside the bubble. Extremely high pressure and temperature are produce when the bubbles are collapse and highly reactive free radicals are form. Maximum radius from the bubble will decrease as the pressure increase. Energy collapse due to this will be measured and used to compare with minimum ignition energy of liquid. The total energy E of cavity is given as the potential energy at time of maximum radius R_{max}:

$$E = \frac{4\pi}{3} P_\infty R_{max}^3 \quad (9)$$

The energy dissipated during one cycle of bubble oscillation is given by the potential energy difference. The energy of cavities before and after collapse can be plotted versus maximum radius, R_{max}. The shock wave energy E_s radiated during collapse is;

$$E_s = \frac{4\pi R_m^2}{pc} \int P^2 \, dt \quad (10)$$

where, c velocity of sound and R_m is the distance of collapsing bubble center to the point where pressure amplitude P is measured.

2.2 Experimental Work

In order to assess the safety issue of ultrasonic distillation in term of ignition source of ultrasound in liquid, a worst case situation has to be developed which provoke ignition. The experimental work consists of 40 kHz frequency transducer, type K thermocouples, pressure detector and 316 stainless steel. All of these equipment are immersed inside a large water ethanol bath that contain 15 mol% of water and 85 mol% of ethanol mixture with continuous supply of air from compressor. 316 stainless steel had a cylindrical shape with a radius of 30 mm and a thickness of 10mm. A thermocouple was inserted into a bore hole to measure the core temperature under insonification by the transducer. The stainless was fixed underwater at a distance greater than the focal length of transducer. To measure distance needed, a near field length zone equation is used, given as in Eq(11):

$$N = \frac{D^2}{V}$$

Where, N is the distance from transducer to target material, D is transducer diameter (obtain from transducer specification) and V is the shear sound speed in water. Figure 1 illustrates the worst case situation for ignition of ultrasound coupled to liquids with respect to explosive atmosphere at liquid surface

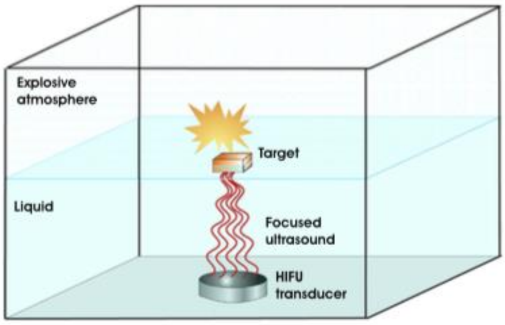
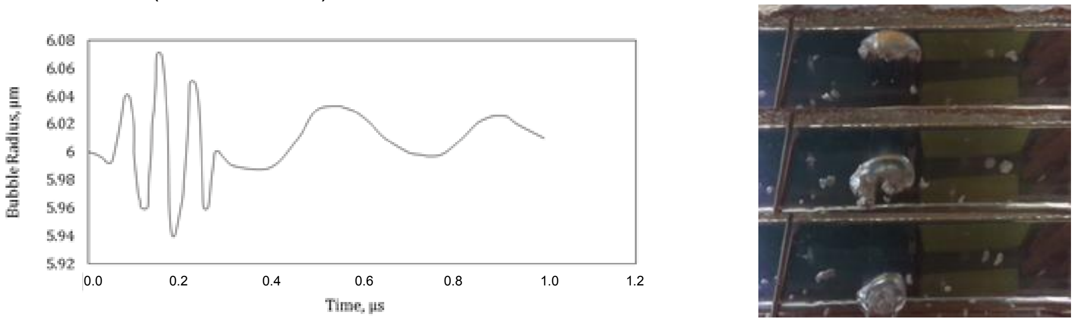


Figure 1: Worst case situation for ignition of ultrasound coupled to liquids with respect to explosive atmosphere at liquid surface

3. Results and Discussion

3.1 Mechanism of Bubble Collapse

From Rayleigh-Plesset Eq(7), a function by using MATLAB was implemented (MATLAB, 2012). The equation parameters have been set to model an air filled bubble surround by water at ambient temperature and pressure. When passing an ultrasound through a liquid medium, mechanical vibration occurred. Ultrasound generates acoustic streaming within the liquid and hence produce an ultrasonic field called acoustic cavitation. From the Figure 2 (a) and (b), the bubble formed slowly by process called rectified diffusion until it reaches a critical size knows as resonance size. Bubbles become unstable and collapse within a single acoustic cycle or over a small number of cycle when it reached this size. A gas bubbles in liquids under the influence of sound field can meet another bubbles in solution. They combine to form a larger bubbles and grow with time over several acoustic cycle. Bubbles at this condition too bubble can become unstable and collapse, often violently same as before (Wu et al., 2013).



(a) (b)

Figure 2: (a) Simulated radial response of a 6 µm radius RP air micro bubble in water with frequency 40 kHz, (b) Bubble formation during sonication with frequency 40 kHz

For free bubble (using Rayleigh-Plesset equation), the resonant frequency for bubble with radius 6 µm in fluid density about 1,000 kg/m^3 and pressure 101.3 kPa was simulated in Figure 3. Relationship that relate resonance size of bubble with the frequency given in Eq(12):

$$\omega_0 = \frac{1}{R0}\sqrt{\frac{3\gamma P0}{\rho}} \qquad (12)$$

where γ is the specific heat ratio of the gas inside the bubble, ρ is the liquid density, P_0 is initial pressure, R_0 initial bubble radius and ω_0 is angular frequency. From the above equation, it is found out that the resonance frequency is inversely proportional to the radius of bubble. As shown in Figure 3, increasing bubble radius decrease the resonance frequency.

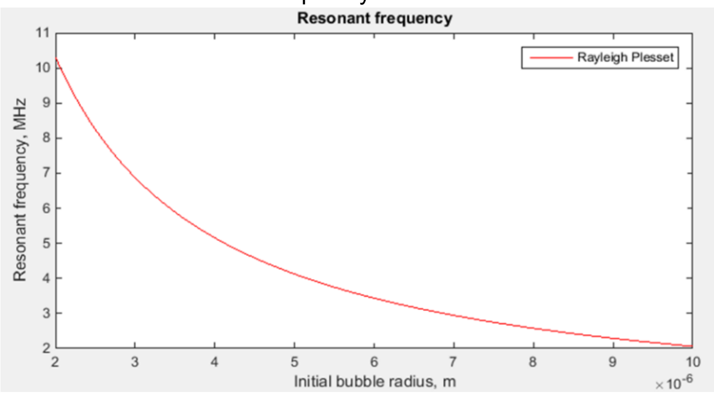


Figure 3: Resonance frequency for Rayleigh-Plesset equation

At 40 kHz ultrasound frequency, the bubble generated in the sound field are relatively large (Leong et al., 2009). During sonication, the bubbles was compressed and the gas inside the bubble was heated. Since surrounding liquid is colder, heat can easily escape by diffusion from the bubble towards the liquid causing centre of the bubble is hotter than the surface (Figure 4) (Chen, 1967). Bubbles collapse has induce a higher temperature which can be more valuable for sonochemical purposes (Suslick and Price, 1999).
Potential energy inside the bubble when the radius of bubbles are at maximum is 0.19267 pJ. Collapsing of cavitation bubble filled with explosive vapour could not cause an explosion because energy release when the bubble collapse is so small compared to minimum ignition energy of liquid which is 0.2 mJ.

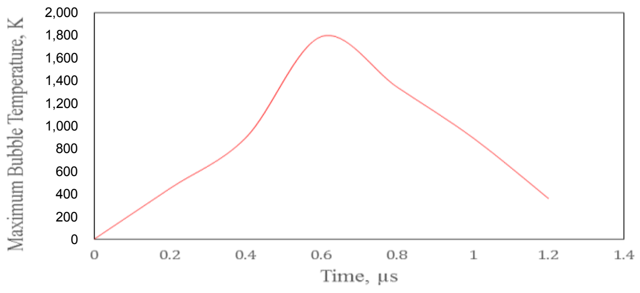


Figure 4: Maximum Bubble Temperature against time

3.2 Experimental

In pre-test, PEEK material was chosen as a target material, mainly because it satisfied all the requirement for ignition mechanism at liquid surface. Graph obtained in Figure 5 (a) almost similarly the same as the data journal provided. This shows that the system work well for transforming acoustic energy into heat and is ready for real experiment using 316 stainless steel.

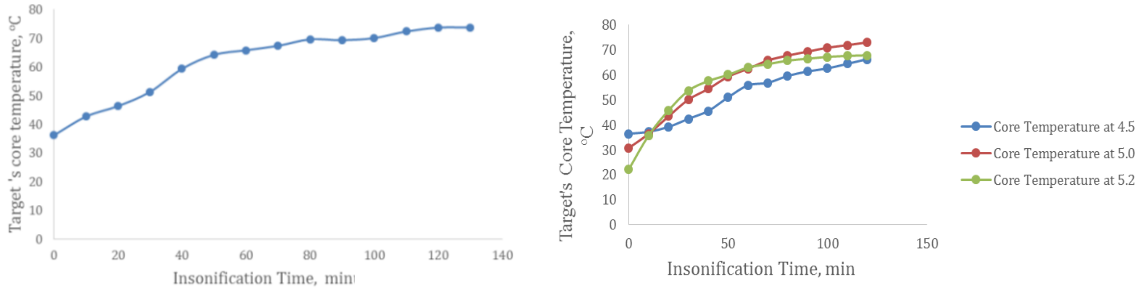


Figure 5: (a) PEEK target's material core temperature at 40 kHz, (b) Temperature development core of stainless steel at certain acoustic power

Figure 5 (b) shows the temperature developments at the center hole over time at different acoustic power for ignition tests. At early stage of the acoustic power, a jump in the target core temperature can be seen. Even though there are jump in temperature, sign of eruption of stainless steel metal still could not be observed. The ignition test on stainless steel generally shows that it is not possible to ignite by ultrasonically heating up a target at the liquid surface. For ignition to occur, many requirements have to be fulfilled at the same time (Simon and Meyer, 2015). First, a high-intensity focused ultrasound field is required. Focus ultrasound was used to create a hot spot on an insonified target material which fixed at the liquid surface. Second, a specific target material property is needed. Acoustic impedance of stainless steel is 4.516 MNsm^{-3} is far from the acoustic impedance mixture. High value of acoustic impedance is inappropriate because the reflection will be high at the phase interface between liquid and target material. It needs to be close to the one of the liquid used so major part of ultrasound is transmitted into it.

In addition, target material used has absorptivity as low as 0.5 which failed to transform acoustic energy into heat follow by eruption. In order to absorb an ultrasonic wave, it requires a high absorptivity and a size of at least one wavelength in the direction of propagation. Stainless steel can endure up to 1,198 K temperature which makes it impossible to ignite during the experiment. Finally, high thermal conductivity of the target material increases the cooling by the surrounding liquid. These material properties are in accordance with those found by Tingaud et al. (2013). The fact that no ignition on stainless steel could be observed is possible if all of the properties are followed.

4. Conclusion

Mathematical model describing bubble condition starting from expansion of bubble before sonication effect up to the energy of bubble release during collapse has been established. It is assumed that these bubble is spherically symmetric and composed of gas and liquid vapour, with surrounding liquid is assume to be incompressible and constant dynamic viscosity. Process characteristic and operating condition during cavitation of bubble is done by simulation study (MATLAB) has showed the bubble formed and expand through a few acoustic cycle to a radius of 6 μm before collapsing violently on compression. Energy release during collapsing of bubble is way too small compare to the minimum ignition energy of liquid making ignition mechanism fail to occur which is 0.19267 pJ compared to minimum ignition energy of the liquid at 0.23 mJ. It is shown that focused ultrasound coupled into liquid failed to trigger any ignition during sonication process. It turned out that many conditions have to be met at the same time on the characteristic target material being used for ignition to occur. Ultrasonic distillation system is considered safe to be done experimentally in this case.

Acknowledgments

This work was supported by Universiti Teknologi Malaysia, UTM RUG Q.J130000.2509.07H12 and Q.J130000.2509.13H95.

References

Ashokkumar M., 2011, The characterization of acoustic cavitation bubbles – An overview, Ultrasonic Sonochemistry 18, 864-872.

Chen J.W., Kalback W.M., 1967, Effect of ultrasound on chemical reaction rate, Industrial & Engineering Chemistry Fundamentals 6, 175-178.

Contamine F., Faid F., Wilhelm A.M., Berlan J., Delmas H., 1994, Chemical Reaction under ultrasound: discrimination of chemical and physical effects, Chemical Engineering Science 49, 5865-5873.

Franc J.P., 2006, Physics and control of cavitation, design and analysis of high speed pumps, Educational Notes RTO-EN-AVT-143, 2-1 – 2-36.

Gong C., Hart D.P., 1998, Ultrasound induced cavitation and sonochemical yields, Journal of the Acoustical Society of America 104, 2675, DOI:10.1121/1.423851

Leong T.S., Wooster T.J., Kentish S.E., Ashokkumar M., 2009, Minimising oil droplet size using ultrasonic emulsification, Journal of Ultrasonic Sonochemistry 16, 727-731.

MATLAB and Statistics Toolbox Release 2012b, The MathWorks Inc., Natick, Massachusetts, United States.

Mahdi T., Ahmad A., Ripin A., Tuan Abdullah T.A., Nasef M.M., Ali M.W., 2015, Mathematical modelling of a single stage ultrasonically assisted distillation process, Ultrasonic Sonochemistry 24, 184-192.

Mason T.J., Phillip J., 2002, Applied Sonochemistry, Wiley-VCH, Weinheim, Germany.

Moholkar V., Senthil Kumar P., Pandit A., 1999, Hydrodynamic cavitation for sonochemical effects, Journal of Ultrasonic Sonochemistry 6, 53-55.

Meidani N.A., Hasan M., 2004, Mathematical and physical modelling of bubble growth due to ultrasound, Application Mathematic Model 28, 333-351.

Ripin A., Abdul Mudalip S.K., Sukaimi Z., Yunus R.M., Manan Z.A., 2009, Effect of ultrasonic waves on vapour liquid equilibirum of an azeotropic mixtures, Separation Science and Technology 44 (11), 2707-2719.

Servant G., Caltagirone J.P., Gerard A., Laborde J.L., Hita A., 2000, Numerical simulation of cavitation bubble dynamics induced by ultrasound wave in a high frequency reactor, Journal of Ultrasonic Sonochemistry 7, 217-227.

Simon L.H., Meyer L., 2015, Ultrasonic triggered ignition at liquid surfaces, Ultrasonic Sonochemistry 22, 235-42.

Stankiewicz A.I., Moulijn J.A., 2002, Process intensification, Industrial & Engineering Chemistry Research 41 (8), 1920-1924.

Suslick K.S., Price G.J., 1999, Application of ultrasound to material chemistry, Annual Review of Material Science 29, 295-326.

Tingaud F., Ferrouillat, Colasson S., Bontemps A., Bulliard-Sauret O., 2013, Experimental characterisation of the thermal behaviour of different materials submitted to ultrasound in an ultrasonic fountain, Ultrasonic Sonochemistry 20, 1046-1053.

Wu T.Y., Guo N., Teh C.Y., Hay J.X.W., 2013, Theory and fundamental of ultrasound, Advances in Ultrasonic Technology for Environmental Remediation, SpringerBrief in Molecular Science, 5-12, Springer Netherlands, Dordrecht, Netherlands.