Potential Use of Ultrasound in Mixing

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Abstract

Ultrasound is a novel technology, which is attaining widespread use in various scientific and medical fields. In the medical domain, high frequency ultrasound is being used to replace x-rays in diagnosis. In the process industry, high intensity, low frequency ultrasound is being used to enhance various chemical and physical processes such as reaction initiation and mixing.

Mixing is a vital stage in most industrial processes, especially when fast reactions are involved to produce a final product. Recent advances in mixing technologies have revolved mostly around reducing diffusion distances to speed up mixing. In laminar- mixers, this is achieved through micro-channels. The diffusion distances are then limited by the current capabilities to construct micro channels and ensuring an even distribution of reactants across those channels. In turbulent mixing, this is achieved through eddy generation, where the eddy scales are as low as the Kolmogorov scales. Here, the diffusion distances are limited by the magnitude and randomness of turbulence and thus homogeneity of the turbulent field (and thus diffusion distances) is not guaranteed.

This paper talks about how ultrasound may be used in certain devices to make up for deficiencies in turbulent fields, as it has been found to be a source of turbulence by itself. When used locally in small areas, it was shown to be very effective in achieving physical mixing, especially when used in conjunction with micro channel devices.

Symbols

ε	Local energy dissipation rate (W/kg)
λ	Eddy length (cm)
U_λ	Eddy velocity (cm/s)
T_λ	Period of Eddy (s)
ν	Viscosity
λ_S	Smallest eddy size (m)
t_S	Time taken for smallest eddy to dissipate (s)

1. Introduction

Mixing operations are encountered in almost every productive industry. They are a central feature in many processes in industries, such as the pharmaceutical and specialty chemicals industries (Harnby, Edwards, & Nienow, 1992). Mixing is carried out in order to increase the homogeneity of a system. This may be in terms of temperature, viscosity and/or concentration gradients. Moreover it may be done in order to promote mass and heat transfer (Coulson & Richardson, 1990) and reactions.

When the rate of a chemical reaction is slower than the mixing rate, the outcome of the reaction (i.e. the product distribution) is determined by the reaction kinetics, the stoichiometric ratio of the reactants as well as the macroscopic/bulk flow pattern. The product distribution can not always be predicted from the chemical kinetics alone; when the half-life of a chemical reaction is of the order of or smaller than the corresponding mixing process, the outcome will also be seen to depend on the mixing intensity. Physical factors, influencing the reaction outcome, in addition to mixing, are solvent/reactant nature, feed pipe location, number and size and flow rate ratios and magnitudes. Non-uniform mixing and reactant segregation lowers reaction rates (Toor, 1975). Mixing is a key step in conducting reactions and incomplete mixing may lead to large recycled throughputs, increased capital costs, increased wastes and undesired side-product formation; all characteristics of an unsatisfactory process.

It is important to note that reactions whose rates are of the same order of or faster than mixing rates seldom occur throughout the whole reactor volume potentially available for reaction. The reactive mixture is inhomogeneous at the molecular scale and in this ‘partially segregated zone’ the reaction is localised (Danckwerts, 1957). The rate of consumption of the reactants is sufficiently high, that a steep concentration gradient is created. In order to calculate the overall reaction rate, the influence of mixing has to be considered concurrently with the reaction kinetics. Developing a reactor capable of achieving high mixing times will not only aid chemical processes, but will also have an impact on the study and characterisation of fast reactions and aid in identifying their kinetics.

In order to design such a reactor, a brief look back at the hierarchy of mixing and the factors influencing mixing (especially mixing mechanisms and ultrasound) is presented in this paper. The identification of key issues in this hierarchy should lead to a better understanding of the mixing process, and hence lead to a better design, capable of achieving faster mixing times.

2. Mixing Mechanisms

Mixing mechanisms may be broadly divided into two categories, laminar and turbulent. These are determined by the flow pattern of the reactor contents. The Reynolds number, Re, is usually used to characterise the flow pattern. In a pipe, laminar flow is characterised by $Re<2300$, whereas an $Re>3000$ corresponds to turbulent flow, with a transition region for $2300<Re<3000$ (Harnby, Edwards, & Nienow, 1992). It must be noted that the above values are upper estimates because other factors such as free-stream turbulence, surface conditions and disturbances may prompt transition at lower Re values.

A mixing time may then be defined as the time measured from the instant of addition of a certain material to the vessel, until the time when the contents of the vessel have reached a desired degree of homogeneity, at which the system is said to be mixed

(Baldyga, Bourne, & Hearn, 1997). The overall mixing time will be determined by the slowest of the stages by which it occurs. The first step in mixing enhancement would thus have to be identifying that stage, and subsequently taking measures to improve it.

Ultimately, the role of mixing would be to promote molecular diffusion of reactants which is the final step preceding molecular reaction. The two mixing mechanisms induce this promotion in different ways (Figure 1). In laminar mixing, the reactant streams are well defined and ordered and diffusion distances are reduced by pumping the reactants through micro-channels, leading to faster diffusion times. In turbulent mixing, turbulent fields exist in a reactor leading to the formation and dissipation of eddies. Eddies can be described as small whirlpools. That is, instead of flowing in distinct flow lines, the liquid rotates. These eddies are unstable and continue to breakdown into successively smaller eddies, until they reach a size having insufficient energy to break down further. This is the Kolmogorov eddy size.

Generated eddies may contain any combination of reactants. Within these eddies, diffusion occurs (via the same mechanism as laminar mixing). Turbulent flow also results in regions of high shear. Mixing is highest in the high shear regions due to the presence of vortices and associated Reynolds stresses; it is here that a large portion of energy is dissipated. Turbulent flow may be considered as a spectrum of velocity fluctuations and eddies of different sizes superimposed on an overall time-averaged mean flow.

It must be noted that eddy collisions lead to eddy dissipation, and thus different diffusion distances (depending on the size of the eddies). The higher the turbulence intensity the smaller are the eddies generated, and thus the faster is the ultimate diffusion step (provided the eddy contains both A and B).

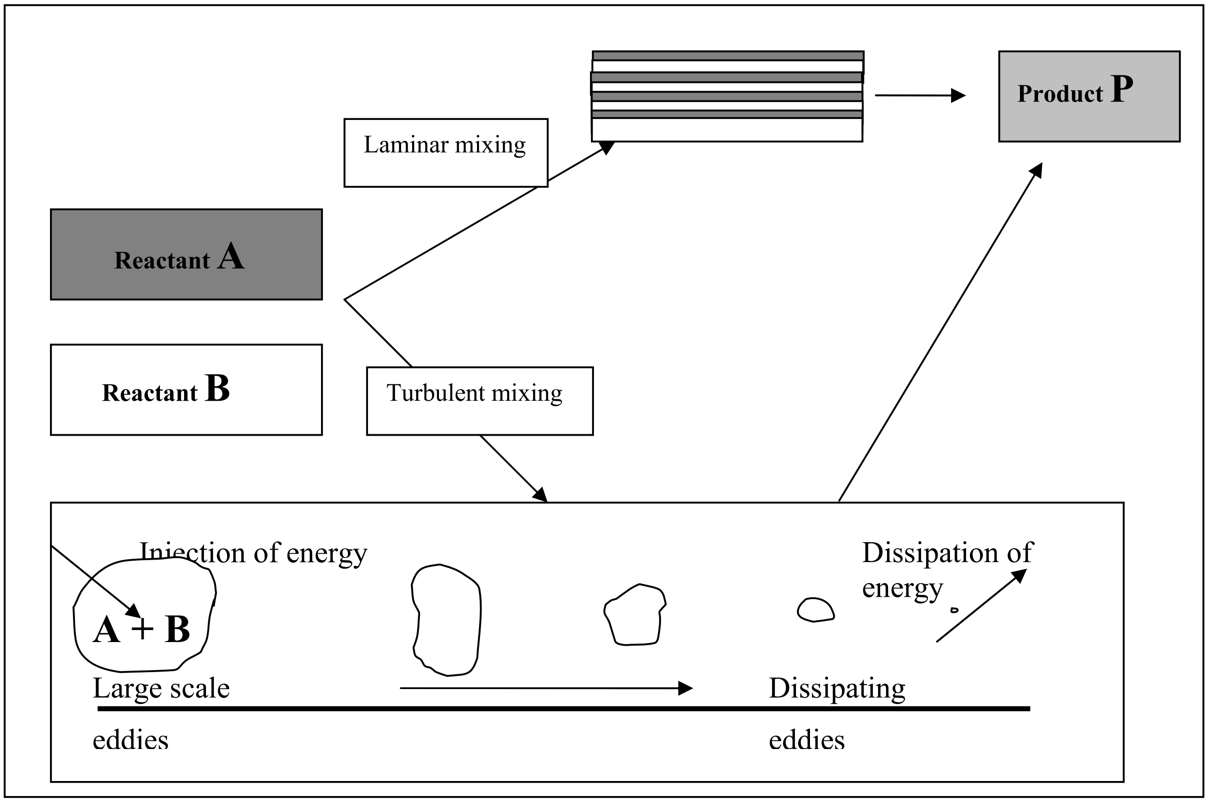

Figure 1. Mixing mechanisms.

3. Ultrasound

Not so long ago, ultrasound was a new-born technology, and on its own, it would be very expensive to implement compared to analogous methods in chemical processing. However, it is the reduction in downstream and upstream process times and costs, which could make ultrasound technology a favoured method in many industries. It has been shown to successfully increase the conversion, improve the yields, change the reaction pathway and/or initiate a reaction in biological, chemical or electrochemical systems. This non-classical method of rate enhancement is a field of science called sonochemistry (Kirk & Othmer, 1969; Mason & Lorimer, 1988; Thompson & Doraiswamy, 1999).

Ultrasound is envisaged to have a potential impact on turbulent energy dissipation rates, and hence on turbulent mixing timescales. In order to understand how ultrasound may influence mixing, a brief look at its origins and possible mechanism of enhancement is given.

Sixty years ago, sonochemistry was first used in laboratories to initiate unruly reactions. Since then, despite the lack of complete understanding of its inherent science: acoustic cavitation, sonochemistry has found considerable interest and use in the chemical engineering industries (Mason & Lorimer, 2002). It uses sound frequencies ranging from 20 kHz to 500 kHz. Low intensity, high frequency ultrasound does not alter the material through which it travels, and it is this property that allowed it to be used in diagnostic medicine. On the other hand, high intensity, low frequency ultrasound does, and is used for chemical processing applications.

The influence of ultrasound is not solely limited to agitation effects, but in fact ultrasound exhibited its own peculiarities as well. This was demonstrated by (Ando et al., 1984)), who described “sonochemical switching” in a paper considered the first to present evidence on the nature of sonochemistry. Using a suspension of benzyl bromide and alumina-supported potassium cyanide in toluene, ultrasound was hypothesized to cause a structural change of the catalytic sites on the solid support. In brief, their results showed that the use of ultrasound yielded one product, while the non-irradiated reaction yielded two. Luche (1993) and Luche *et al.* (1990) conducted a comprehensive literature survey and came up with an empirical systemization of sonochemistry. They examined the types of reactions ultrasound might affect, and concluded three rules which govern these effects. This classification was based on the source of effect of sonochemistry. It recognizes that ultrasound may act in a mechanical sense, a chemical sense or both.

In the scope of this work, sonochemistry will be used in enhancing mixing (physical phenomenon), while recognising the potential effect it may have on the kinetics (chemical phenomenon) of a reaction. Currently, the effects of ultrasound are not accurately predictable, and the principal reason for its enhancing properties is attributed to cavitation; the phenomenon associated with bubble production, expansion and collapse within a sonicated liquid.

3.1. Cavitation

While cavitation is the most known phenomena related to the passage of ultrasound through a liquid medium, it is the least understood (Mason & Lorimer, 2002). Cavitation in a liquid occurs due to the stresses induced in the liquid by the passing of a sound wave through the liquid. Sound waves consist of compression and decompression /

rarefaction cycles. If the pressure during the decompression cycle is low enough, the liquid can be torn apart to leave small bubbles.

These cavitation bubbles (similar to those seen arising from the action of a boat propeller on water) are at the heart of sonochemistry systems. These bubbles are subjected to the stresses induced by the sound waves. This causes the bubbles to grow during a decompression phase, and contract or even implode during a compression phase. The bubbles may be filled with vapour and gas, and can produce radicals during implosions. It is these implosions which are the high-energy part of sonochemistry. Each one of these imploding bubbles can be seen as a micro-reactor, with effective temperatures reaching an estimated 5000°C and pressures of several hundreds of atmospheres (Figure 2) (Mason, 1997; Thompson & Doraiswamy, 1999).

It is thought that these extreme conditions are responsible for the manipulation of reactions kinetics. Furthermore, at the instant of the bubbles' collapse, powerful hydraulic shocks occur. It is thought that these shocks are responsible for the rupturing of neighbouring solids (which maybe the vessel walls or reacting solids) and lead to the generation of shear forces and eddies (Mason & Lorimer, 2002) which in turn may lead to an increase in turbulent energy dissipation. The number of these shocks is related to the frequency of the wave.

It must be noted that some bubbles, depending on their size and applied ultrasonic conditions, may not collapse and instead undergo growth and shrinkage at a frequency equal to that of the transmitted wave. Since the conditions of the transmitted wave directly influences the state of the cavitation bubbles, which lead to the enhancement effects of ultrasound, the discussion on ultrasound should begin with some information about the transmitted ultrasonic waves and the factors influencing their motion.

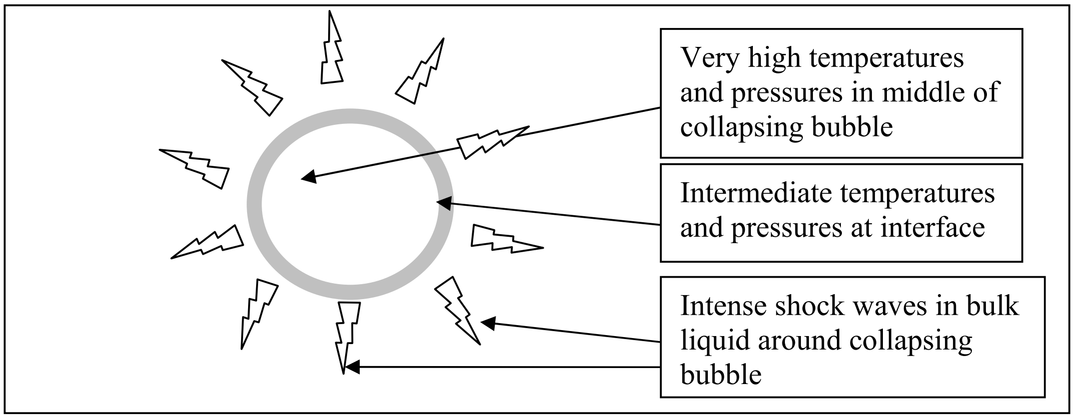

Figure 2. Collapsing bubble in liquid solution

Cavitation is classified mainly as two types, Transient and Stable. The type of cavitation that occurs depends mainly on the energy input. At the higher intensities (10W/cm^2), transient cavitation predominates, while at the lower energy inputs (1-3W/cm^2), stable cavitation does. The two types of cavitation result in bubbles that exhibit very different behaviours.

Transient cavitation bubbles exist for a maximum of a few acoustic cycles, and will expand to a radius at least double their initial size, before collapsing, after which they either disintegrate into smaller bubbles, or dissolve into the bulk of the solution, under the action of the large forces due to surface tension. The lifetime of such bubbles is too small, that is normally assumed no mass transfer takes place across their boundaries. Their collapse results in extreme temperatures and pressures close to the collapsing surfaces. (Mason & Lorimer, 2002)

Stable cavitation bubbles oscillate, usually non-linearly, about an equilibrium size for many acoustic cycles. These bubbles exist for time scales sufficiently long enough for mass (gas) and thermal diffusion to take place, as a result of which vapour evaporation and condensation will still take place. The size oscillation of stable bubbles results in a slightly milder temperature rise. (Mason & Lorimer, 2002)

Some of the factors that influence cavitation are as follows (Pandit & Moholkar, 1996),

*<u>Presence and nature of dissolved gases</u>***:** they act as nucleation sites for cavitation. Soluble gases decrease cavitational effects and vice-versa.

<u>Ambient temperature:</u> increased temperatures results in a decrease in the sonochemical effect because high temperatures lead to bubbles which contain largely vapour, which reduces the ultrasonic energy produced upon cavitation.

<u>Ambient pressure:</u> increased pressure results in an increase in the sonochemical effect because of the higher intensity required to cause cavitation.

<u>Choice of solvent:</u> Cavities are more readily formed when using high vapour pressure, low viscosity, and low surface tension solvents.

<u>Ultrasonic frequency:</u> low frequency (intense temperature and pressure required) ultrasound produces more violent cavitation, leading to higher localised temperatures and pressures. High frequency may also increase the number of free radicals (highly reactive species) in a system, despite making cavitation less violent because of allowing more cavitational events to occur.

4. Enhancement Mechanism

The published literature on ultrasound and its enhancement effects on processing (particularly mixing) never failed to deliver on the promise of improving mixing times. However, all the literature surveyed presented at best guesses and/or experimentally correlated parameters as an explanation to the observed results. In other words “yes we know it works, yes we can show you it does, but we don’t know how”

This paper offers a new explanation to the observed effects. It links the improvement observed in our experiments directly to an enhancement in turbulence, which is thought to directly influence mixing.

Turbulent mixing is characterized by a fluctuating velocity at each point in the flow field. Kinetic energy is associated with such fluctuations and is maintained by a power input to the system and is dissipated to internal energy, through the action of viscosity. The rate of dissipation per unit mass of fluid, denoted by ε (W/ kg), plays a central role in the classical theory of turbulence. ε is related to a variety of factors influencing processing. These include reaction rate enhancements (Davies, 1987).

The process of turbulent mixing is very complex. It may be simplified, however, by identifying three stages by which it occurs, namely macromixing, mesomixing and micromixing (Bourne, Kut, & Lenzner, 1992; Bourne, Moergeli, & Rys, 1978). Macromixing may be identified with the mean velocity convection. Mesomixing reflects the coarse-scale turbulent exchange between the fresh feed and its surroundings; a fast chemical reaction is usually localised near the feed point, forming a plume of fresh feed. This plume is of a coarse scale relative to the micromixing scale but is of a fine scale relative to the scale of the system. Micromixing is the last stage of turbulent mixing; occurring at the length scales of the Kolmogorov eddies, and immediately preceding diffusion.

The various equations relating ε to mixing times show an inverse relationship between the two. Hence, the higher ε, the lower should be the mixing times, provided the reactants are in efficient contact with each other.

It is thought that the intense collapse pressure generated when transient cavitastion bubbles collapse may result in the release of intense shock waves, which in turn may dissipate in the medium and influence the microscopic processes, such as diffusion and micromixing.

The following equation to estimate the energy dissipation due to large scale waves (i.e. eddies) (Doulah 1979),

$$\varepsilon \approx \frac{U_\lambda^3}{\lambda} \qquad \textbf{Eq. 1}$$

U_λ can be estimated using T_λ, the period of the eddy (Doulah 1979),

$$T_\lambda = \frac{\lambda}{U_\lambda} \qquad \textbf{Eq. 2}$$

Commonly, the duration of shock waves in cavitation fields was found to be in the order of 10^{-7}s (Doulah 1979). As an example, the velocity of a 0.1 cm eddy (equivalent to the radius of a bubble) would be 10^6cm/s. Then, using Eq. 1, ε is estimated to be around 1 x 10^{19} cm^2/s^3. It must be noted that Eq. 1 only applies when the Schmidt number is greater than one, so that the length of the eddies lies between the Batchelor and Kolmogorov Length scales.

The generation of eddies due to the collapse of the bubbles seems the most viable explanation to the observed increase in turbulent energy dissipation within the flowing liquid by changing the friction factor, in the same way as turbulent eddies. Collapse of the bubbles is hypothesized to result in the generation of turbulent eddies which may also cause a break-up and further dissipation of the larger eddies already present in the liquid (in the case of turbulent flows) and it remains to be found which of the two effects contributes more. The interaction between the eddies generated by flow and those generated by ultrasound is possible because the length scales of the flow generated eddies and their time scales are comparable to those generated by ultrasound.

The length scales of the eddies generated by flow, for the different flow rates, range in size from the diameter of the inlets down to the Kolmogorov length scale (if not smaller). The smallest eddy size, λ_s and the time taken for them to dissipate, t_λ, may be given by (Baldyga & Bourne, 1999),

$$\lambda_s = \left(\frac{\nu^3}{\varepsilon}\right)^{1/4}$$ **Eq. 3**

$$t_s = \left(\frac{\nu}{\varepsilon}\right)^{1/2}$$ **Eq. 4**

If the turbulent energy dissipation rate, ε, is taken to be 50% of the global energy dissipation rate (it may range from 30-90%, (Baldyga & Bourne, 1999)), then the smallest eddy length scales and the time taken for them to dissipate are calculated using Eq. 3 and Eq. 4 respectively, and the values for the different FR-values, are shown in Table 1.

Table 1. Kolmogorov length and time to dissipate of smallest eddies generated by different FR-values.

FR	Kolmogorov scale (m)	Time (s)
50	1.62×10^{-5}	0.000261
60	1.47×10^{-5}	0.000215
70	1.33×10^{-5}	0.000177
90	1.11×10^{-5}	0.000122

The length scales fall within the range of the expected eddies generated by ultrasound (size of the typical nuclei in water), and the eddies' lifetime are long enough for the ultrasonically generated eddies (lifetime estimated at one-fifth of the cycle time, 0.00001s) to have the possibility of interacting with them.

Furthermore, if the size of the eddy is taken to be equal to the mean size of the available nuclei (1×10^{-5}), and the typical collapse times of the bubbles are taken to be one fifth of the cycle period (1×10^{-5}s), then the velocity of the eddy, U_λ, found by dividing the length by the collapse time, will be 1m/s. Since the length of the eddies generated by bubble collapse was of the same order as the bubble sizes, the following equation may be used to estimate the energy dissipation due to the eddies (Doulah 1979),

$$\varepsilon \approx \frac{U_\lambda^3}{\lambda}$$ **Eq. 5**

What Doulah failed to take into account was the number of bubbles, their initial size and their spread over the reaction volume. Thus knowledge of the size distribution of the nuclei present in the reactant(s) combined with the Rayleigh-Plesset Equation for predicting the change in bubble size in the presence of a varying pressure field (i.e. ultrasonic field), would then allow a more accurate visualization of the turbulent field generated by ultrasound. Bearing in mind the total number of bubbles, and assuming an average size for them allows for the calculation of the total ε. Subsequently, allowing for the spread of this energy dissipation from the overall volume of the bubbles to the whole of the reactor volume would give an idea of the overall energy dissipation rate across which the reaction may take place.

5. Experiment

The aim of the following experiment was to show the enhancement effect of ultrasound on mixing. A simple t-piece (Figure 3) was used as the mixer of a neutralization reaction carried out continuously using 1.0M HCl with a few drops of phenolphthalein indicator, and 1.1M NaOH.

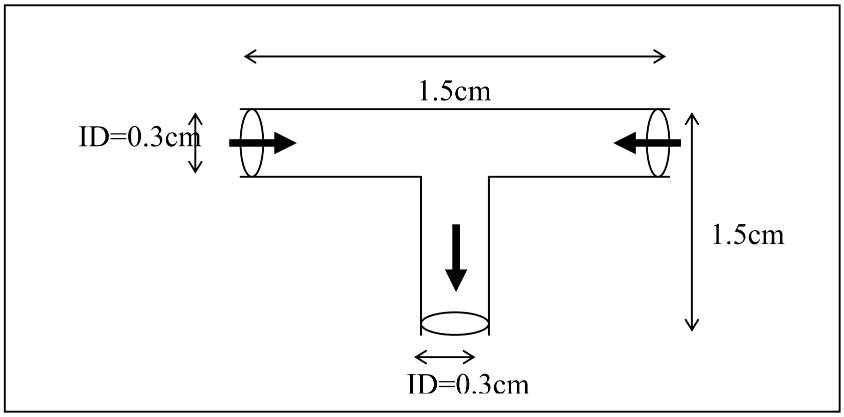

Figure 3. T-mixer used, and schematic of its dimensions

5.1. Setup

The equipment was set up to allow a smooth fluid flow through the mixers, while allowing the ultrasonic waves in from one end, and out through the other end, in which the temperature probe was inserted, as shown in Figure 4.

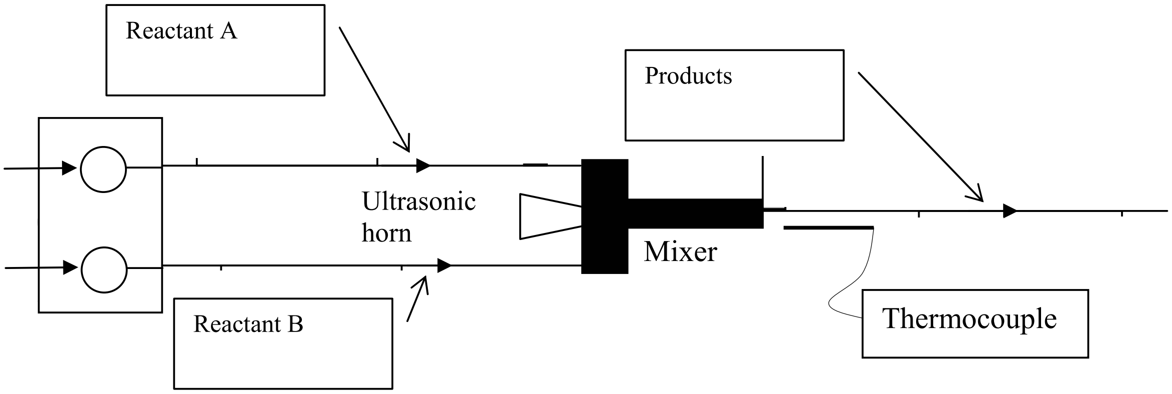

Figure 4. Schematic of Experimental set-up in acid-base neutralization experiment

5.2. Results and Discussion

The results are best shown as observed in the lab and can be seen in Figure 5. It was seen that sonication of the reaction medium resulted in a shortening of the reaction length and hence reaction time. The enhancement effects of ultrasound were visually demonstrated. The appearance of the pink/purple colour was closer to the outflow of the pipe. At the higher ultrasonic intensity, the colour was deeper and darker, indicating a more complete reaction resulting from further enhancement of the mixing rate.

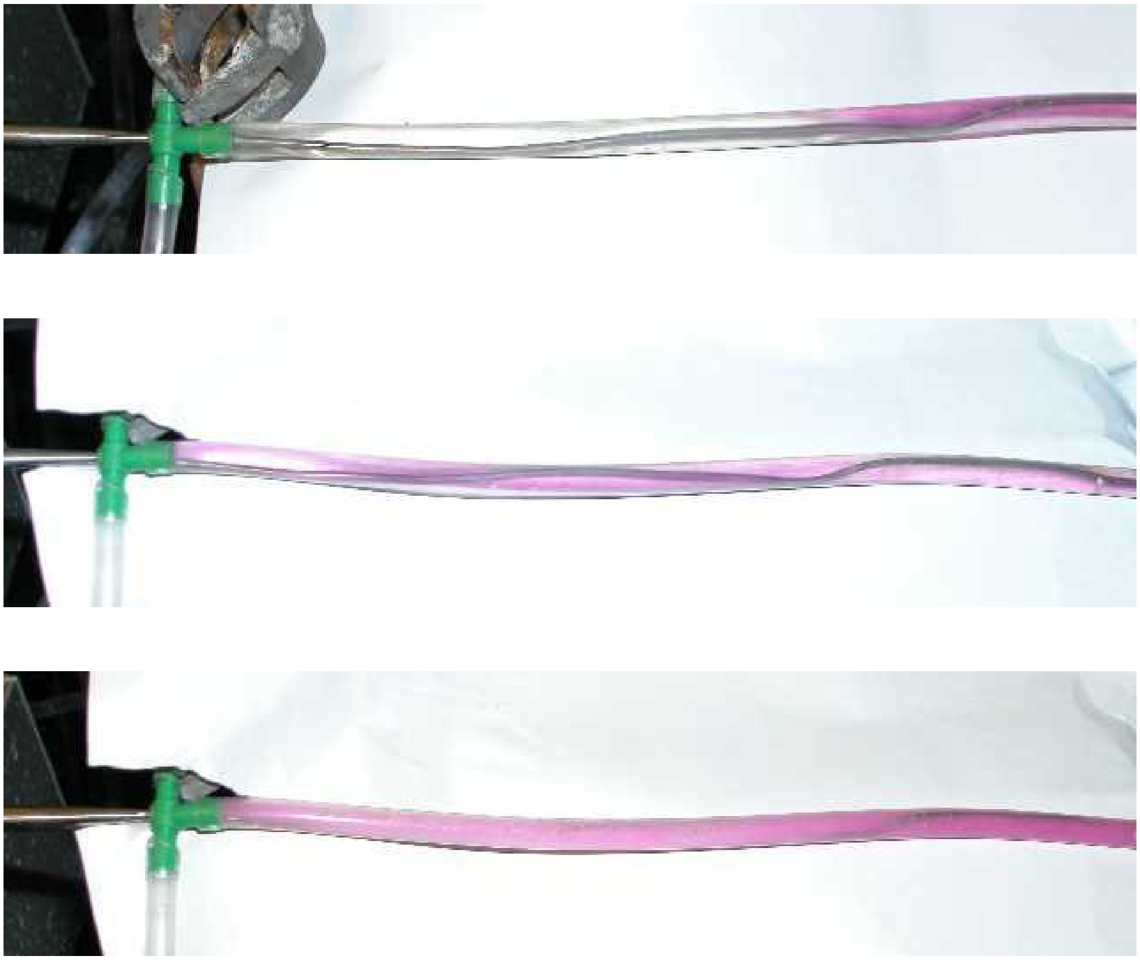

Figure 5. Pictures of phenolphthalein end point indication for 3 different ultrasonic intensities. From top to bottom: end point indicated in the absence of ultrasound, at electric ultrasonic intensity of 55W, at electric ultrasonic intensity of 82.5W.

As the reaction was extremely fast, (reaction constants in the order of 10^8 $mol^{-1}s^{-1}$, with reaction times less than 10^{-6}s), the process was limited by the mixing characteristics of the system. Even if ultrasound resulted in a chemical enhancement of the reaction kinetics, the latter would still be much faster than the mixing rate. Thus the observed effects of ultrasound were on the mixing stage of the process. Increasing the ultrasonic intensity resulted in an increase in the mixing rate.

Increasing the flow rate showed similar results, with the faster flow rates generating a higher turbulent energy dissipation rate. However, using the t-piece mixer, even at the highest flow rates available (2l/min), the reaction could not be complete within the residence time of the t-piece. Here ultrasound was shown to make up for the inadequacy of the mixer by allowing this to happen.

Using other mixers (not presented here), which were similar in pipe size and volume to the t-piece, the above reaction was shown to be complete within the residence time without the use of ultrasound. When the size of such devices was increased, ultrasound was again needed to allow completion of the reaction within the residence time.

This was attributed to the different turbulent energy dissipation rates possible with such devices.

4. Conclusions and Recommendations

The effects of ultrasound were shown both qualitatively. For a given flow rate, the average reaction length (seen by observing at what point the solution turns pink) was reduced upon sonication. The reduction was also dependant on ultrasonic intensity; as a higher intensity was used, more reduction was observed. Furthermore, similar enhancement effects were observed using increased flow rates, however these were not as good as the ones observed using ultrasound, for the t-piece mixer. Other devices with better turbulence generation, operating at adequate flow rates, did not require ultrasonic enhancement.

These observations lead to the belief that ultrasound may indeed induce turbulence, and thus promote mixing via increased turbulent energy dissipation, in the same way as increased flow rates does.

Further experiments to justify these claims will be needed. One idea would be to measure the pressure drop associated with sonicating a volume across a device. If ultrasound does indeed increase turbulence energy dissipation, then it is likely to influence the apparent viscosity of the sonicated liquid, and if the overall flow rate remains the same, this change could be measured as a change in pressure drop.

5. References

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