Effect of Cavitation on Reacting Systems

When ultrasound is applied to a liquid reacting system, the reaction rates are often increased. The application of ultrasonics, therefore, provides additional modes of accelerating the reaction rates which are usually not considered by conventional mechanisms. In an attempt to study the effect of ultrasonics on chemical reactions, experimental work was undertaken in which the reaction rates of the hydrolysis of methyl acetate were measured under the presence of ultrasound. The temperature, the vapor pressure within the cavitating bubbles, the resonance characteristics, the volume of the reacting system, and the intensity and frequency of the ultrasound are all influencing parameters on the reaction rates.

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SCOPE

Much work has been done in the area of ultrasonics applied to chemical reactive systems ever since the first study in 1927. Increased yields are obtained in some systems, no effects occur in others, and some generate a whole new series of reaction products. In the present study, the shock wave pressures generated by the collapse of cavitation bubbles produced by ultrasonics are studied to interpret effects noted in experiments. The motion of the collapsing bubbles and their pressure distribution are obtained analytically and the hydrolysis of methyl acetate is investigated experimentally to ascertain the effects of ultrasonic intensity, frequency, temperature, vapor pressure, and reaction volume on the reaction rates.

CONCLUSIONS AND SIGNIFICANCE

The intensity of the sound waves controls the radii of the cavitating bubbles. Since the bubble radii control the shock wave pressures generated by the collapse of these bubbles, the cavitation activity is a strong function of the sound wave intensity. Increasing the intensity of the sound waves increases the shock wave pressures and cavitation activity as long as the collapse time of the cavitation bubbles is less than one-half the period of oscillation of the sound waves. If the collapse time of the cavitating bubbles is greater than one-half the period of oscillation of the sound waves, an increase in ultrasound intensity causes a decrease in the shock wave pressures and cavitation activity. The optimum cavitation intensity occurs when the collapse time of the cavitating bubbles is exactly one-half the period of oscillation of the sound waves.

The experimental reaction rates were found to be a strong function of ultrasound intensity. As the cavitation theory predicts, it was found that there was an optimum ultrasound intensity where the reaction rates were maximum for the hydrolysis of methyl acetate-water system. Below this optimum the reaction rates increased with an increase in sound wave intensity, and above this optimum a decrease in the reaction rates resulted with a further increase in sound wave intensity. No optimum ultrasound intensity was realized in the case of the hydrolysis of methyl acetate-water-acetone system; the reaction rates increased continually as the ultrasound intensity was increased, signifying that this reaction was carried out under conditions where the cavitation intensity was far from optimum.

When the reaction rates were measured as a function of volume, it was found that for the methyl acetate-water system there was a constant optimum power density (watts/kg-m^2) at each volume where the reaction rates were maximum. There was no optimum power density for the methyl acetate-water-acetone system.

A decrease in the reaction yields resulted by changing the frequency of the sound waves from 540 kHz to 780 kHz indicating that the resonance characteristics of the ultrasound were more favorable for the 540 kHz sound waves than they were for the 780 kHz waves.

The equilibrium constants for the methyl acetate-water system were unaffected by ultrasound while the ones for the methyl acetate-water-acetone system were increased.

The cavitation activity is a strong function of the vapor pressure of the cavitating medium. An increase in the vapor pressure of the medium causes a decrease in cavitation activity.

The classic theory of the growth and collapse of a cavity in a liquid was developed by Noltingk and Neppiras (1951), following the early work of Rayleigh. While their theory neglects the effects of viscosity, it does, nevertheless, lead to useful results. If a liquid is irradiated ultrasonically at low power levels, no observable effects, apart from slight heating due to absorption, occur. As the acoustic pressure amplitude is increased, however, small bubbles begin to appear at various nucleation sites. These pressure amplitude is increased, however, small bubbles begin to appear at various nucleation sites. These sites are comprised of microdust particles or dissolved gas bubbles in the liquid. Once these bubbles form, they grow during the

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rarefaction phase of the sound wave. During this growth phase, the liquid at the bubbles surface evaporates into the cavity until it reaches some maximum radius. The bubble then begins to collapse under the acoustic pressure of the compression phase of the sound wave. During this phase of the wave, the bubble contents are compressed to a minimum radius where the bubble finally collapses resulting into a violent shock wave which is transmitted through the liquid.

By application of an energy balance on the cavitating bubble, Noltingk and Neppiras express the equation of motion of the bubble as

$$2\pi\rho_0 R^3\left(\frac{dR}{dt}\right)^2 = \int_{R_0}^{R}\left\{4\pi R^2\left[P_u \sin wt - P_0 + \left(P_0 + \frac{2S}{R_0}\right)\frac{R_0^3}{R^3}\right] - 8\pi RS\right\} dR \quad (1)$$

Equation (1) can be integrated numerically to obtain the value of the maximum bubble radius R_{max} for a given set of parameters such as R_0, P_u, P_0, ρ_0, S, and w. The collapse velocity of a bubble containing both vapor and air is given by

$$\left(\frac{dR}{dt}\right)^2 = \frac{2P_0}{3\rho_0}\left\{\left(\frac{R_{max}}{R}\right)^3 - 1 - \frac{\delta}{\gamma - 1}\left[\left(\frac{R_{max}}{R}\right)^{3\gamma} - \left(\frac{R_{max}}{R}\right)^3\right]\right\} \quad (2)$$

with initial conditions

$$t = 0,\ R = R_{max},\ P = P_0 \quad (3)$$

The shock wave pressure generated by the bubble collapse is given by

$$P_r - P_0 = \frac{-R}{3r}\left[\frac{QZ^\gamma(3\gamma - 4)}{(1-\gamma)} + \frac{QZ}{(1-\gamma)} - (Z-4)P_0\right] - \frac{R^4}{3r^4}\left[P_0(Z-1) - \frac{Q(Z - Z^\gamma)}{(1-\gamma)}\right] \quad (4)$$

The pressure of the gas within the bubble is given as

$$P_g = Q(R_{max}/R)^{3\gamma} \quad (5)$$

which is the same as P_r at $r = R_{min}$ as calculated from Equation (4).

By the use of Equation (2) and Equation (4), therefore, the shock wave pressure can be evaluated as a function of time and radial distance from the collapsing bubble, hence, obtaining an indication as to how this pressure varies with the several variables involved.

EXPERIMENTAL APPARATUS AND PROCEDURE

In order to gain further insight as to the nature of ultrasonic reactions, the effects of ultrasonics on the hydrolysis of methyl acetate in different solvents were investigated. Ultrasonic waves were generated and passed through a batch ultrasonic reactor containing the reacting mixture, and the rates of these reactions were measured as a function of several experimental variables such as frequency, ultrasonic wave intensity, volume of reaction mixture, and temperature.

The experimental apparatus consisted of a Hewlett Packard Model 606B signal generator, an Eico radio transmitter, a crystal ultrasonic reactor, a Hewlett Packard Model 727A voltmeter, a Blue M Model Magni Whirl water bath, and a Fisher Automatic titrimeter. The signal generator generated a low power signal at a very wide range of frequencies (50 kHz-65 MHz). The frequencies of interest in this work were 540 kHz and 780 kHz, and thus two different crystals were employed. The output of the signal generator was

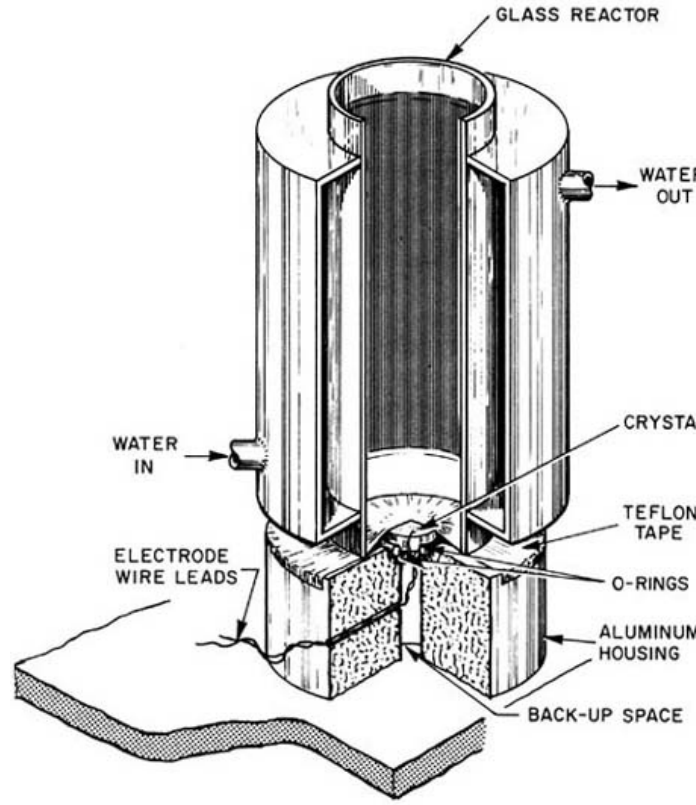

Fig. 1. Experimental equipment.

fed into the transmitter for purposes of power amplification. The power obtained from the transmitter was finally fed into the crystal element of the ultrasonic reactor while being monitored with a voltmeter. The crystal element of the ultrasonic reactor was a 0.0381 m in diameter ceramic lead-titanate-zirconate disk with a specified thickness-mode resonant frequency. The ceramic disk was fitted with electrode leads and then placed in an aluminum housing (Figure 1). Rubber O-rings protected the crystal from coming in contact with the aluminum housing as well as holding the crystal firmly in place. The top face of the crystal was covered with a 2.54×10^{-5} m thick Teflon tape with an adhesive backing in order to avoid contact between the crystal and corrosive acids of the reaction mixtures. A glass reactor was fitted on top of the crystal with the walls of the glass reactor resting on a Teflon O-ring which was placed on top of the aluminum housing. Plate clamps held the glass reactor firmly in place. The glass reactor was 0.048 m in O.D. with an 0.088 m O.D. cooling jacket and was 0.229 m in length.

In a typical experimental run, 10^{-4} m^3 of 1.18 N HCl were placed in the glass reactor. The ultrasonic field was then applied to the reaction vessel and time was allowed for the reactor to reach the desired reaction temperature. The temperature was controlled to ± 0.5°K by water being circulated from the water bath through the cooling jacket of the reactor. Concentration changes resulting from the heating of the reactants were accounted for in the calculations. After a constant temperature was obtained, 5×10^{-6} m^3 of methyl acetate were added to the reactor and allowed to react for a specified length of time. At the end of this reaction time a 2×10^{-6} m^3 sample was withdrawn from the reactor and diluted in 10^{-4} m^3 of pure distilled water. The mixture was then titrated with NaOH with the aid of the automatic titrimeter. This titration procedure provided a direct method for determining the amount of acetic acid formed in the hydrolysis reaction and thus determining the extent of the reaction. The above procedure was repeated until enough points were obtained to determine the concentration versus time profiles. Discontinuous sampling was chosen in order that the height of the reacting mixture above the transducer was the same in all the runs (Fogler, 1968). In the reactions where the volume of the reacting mixture was varied, the amount of methyl acetate added was also varied in order to keep the initial concentrations of the HCl and methyl acetate constant. More details of the experiment and analyses are given by Couppis (1972).

RESULTS AND DISCUSSION

Absence of Ultrasonics

Several systems were first studied without ultrasonics and, therefore, in the absence of cavitation in order to establish a base from which to compare the ultrasonic experiments.

For the acid catalyzed hydrolysis of methyl acetate-water, a pseudo first order reaction system results for large concentrations of the solvent and for short times. The rate constants for this system were within 5% of the data obtained by both Griffith and Lewis (1916) and Chen and Kalback (1967).

The rate constants k were also found to be proportional to the hydrogen ion concentration by varying $[H^+]$. The activation energy, E_a, for the hydrolysis reaction was calculated to be 77.6 MJ/kg-mole. This value agrees well with the data of Chen and Kalback and the activation energies for chemical reactions in solution reported by Frost and Pearson (1953).

For the hydrolysis of methyl acetate-water-acetone, the reaction proceeds the same way as the one with pure water as the solvent. The main difference in this reaction is that now the initial concentration of water is reduced by displacing it with acetone. The average pseudo first order reaction rate constants are summarized in Table 1.

By comparsion, the pseudo first order rate constants of the methyl acetate-water-acetone system are smaller than the ones for the methyl acetate-water system. Similar results were reported by Burrows (1919). The activation energy E_a was found to be 56.1 MJ/kg-mole for the acetone system. This value is smaller than the one found for the methyl acetate-water system which is 77.6 MJ/kg-mole.

Table 1. Rate Constants for Hydrolysis without Ultrasonics

	Methyl acetate-water-acetone system	Methyl acetate-water system
M_i	0.60 kg-moles/m^3	0.60 kg-moles/m^3
W_i	17.78 kg-moles/m^3	50.60 kg-moles/m^3
$[H^+]$	1.123 kg-moles/m^3	1.123 kg-moles/m^3
Acetone$_i$	8.07 kg-moles/m^3	
	$k(s^{-1}) \times 10^5$	$k(s^{-1}) \times 10^5$
298 T(°K)	7.65	12.35
303 T(°K)	11.6	20.8
308 T(°K)	16.7	34.9

Ultrasonics (Methyl Acetate-Water System)

The previous chemical reaction systems were then treated with ultrasonics to establish this effect and thus the effect of cavitation. The acid catalyzed hydrolysis of methyl acetate subjected to ultrasonics was found to obey the same linear rate laws as the reaction without ultrasonics. The rate constants, however, were increased and varied with the intensity of the sound waves (Table 2).

The rate constants and hence the yields are a strong function of the voltage applied to the ultrasonic reactor. There also appears to be an optimum power at which a maximum rate constant is obtained as also seen by Fogler

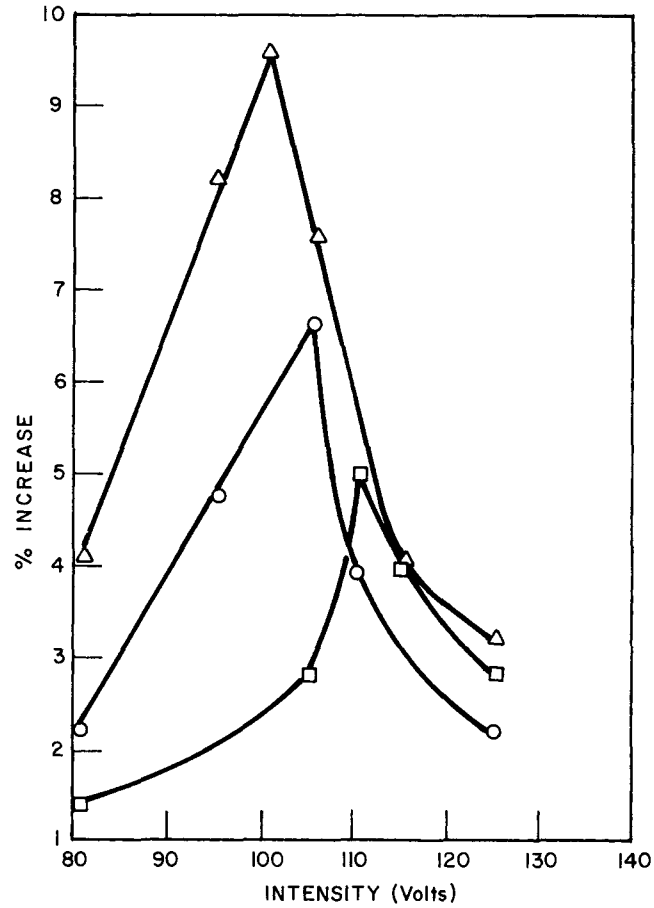

Fig. 2. Effect of ultrasound intensity and temperature on reaction yields for the methyl acetate-water system: □—293°K; ○—298°K; △—303°K; time = 2400 sec; frequency = 540 kHz; and reaction volume = 1.05 × 10^{-4} m^3.

Table 2. Rate Constants for the Hydrolysis of Methyl Acetate-Water System with Ultrasonics

	293°K	298°K	303°K
M_i	0.60 kg-mole/m^3	0.60 kg-mole/m^3	0.60 kg-mole/m^3
W_i	50.6 kg-mole/m^3	50.6 kg-mole/m^3	50.6 kg-mole/m^3
$[H^+]$	1.123 kg-mole/m^3	1.123 kg-mole/m^3	1.123 kg-mole/m^3
T	293°K	293°K	303°K
Frequency	540 kHz	540 kHz	540 kHz
Reaction volume	1.05 × 10^{-4} m^3	1.05 × 10^{-4} m^3	1.05 × 10^{-4} m^3
Volts	k' (s^{-1}) × 10^5	k' (s^{-1}) × 10^5	k' (s^{-1}) × 10^5
0	7.4	12.3	20.8
80	7.9	13.3	22.5
100			24.8
105	8.67	15.1	24.0
110	9.48	14.0	
115			22.0
125	8.58	13.3	22.2

and Barnes (1968). For example, at 293°K a maximum rate constant is obtained at 110 volts while at 298°K the optimum power is at 105 volts and at 303°K the optimum power is at 100 volts. Below this optimum power an increase in the voltage applied to the ultrasonic reactor would increase the reaction rate constants, and above this optimum power an increase in the voltage would cause a reduction in the rate constants (Figure 2).

As already stated, the voltage supplied to the ultrasonic reactor controls the intensity of the sound waves generated at the crystal element of the reactor, and this in turn controls the radii of the cavitating bubbles formed by the ultrasonic waves in passing through the reacting mixture. The intensity of a cavitation event depends on the maximum radii R_{max} of the cavitating bubbles. As can be seen from Equations (2) and (4), the greater R_{max} is the greater the shock wave pressures will be that are generated by the collapse of these cavitating bubbles. This will be true as long as the bubbles have time to collapse completely. The complete collapse will happen as long as one-half the period of oscillation of the sound wave $1/2T'$ is equal to or is greater than the collapse time of the cavitating bubbles. The maximum pressure will thus occur when the collapse time is equal to $1/2T'$. If a cavitation activity can be defined as the product of the intensity of a cavitation event and the number of such events, then the cavitation activity can be thought as the variable affecting the reaction rate constants and reaction yields. Thus, it can be said that the cavitation activity and reaction rate constants will increase with an increase in the sound wave intensity as long as the resulting R_{max} is less than optimum while the reaction rates and cavitation activity will decrease with an increase in sound wave intensity if the resulting R_{max} is greater than optimum.

Since the rate constants for a given voltage or sound wave intensity are obtained as a function of temperature, the activation energy can be calculated. From Figure 2, the activation energy is seen to be constant for powers less than about 110 volts. The activation energy at 105 volts is 73.6 MJ/kg-mole and at 80 volts it is 75.5 MJ/kg-mole while at 0 volts it is 77.6 MJ/kg-mole. This shows that the application of ultrasonics changes the frequency factor k_0. A possible explanation for the increase in the frequency factors could be that the generation of tremendous local pressure and temperature gradients increases the vibrating motion of the reacting molecules. Similar results were also reported by Chen and Kalback (1967).

The optimum powers shifts with temperature (Figure 2); at 293°K the optimum voltage is 110 volts, at 298°K the optimum goes to 105 volts, and at 303°K it is 100 volts. Thus, the optimum power decreases as temperature increases. This fact can be explained theoretically by realizing that the temperature controls the vapor pressure parameter δ which in turn controls the collapse time and R_{max} of the cavitating bubbles. Increasing temperature increases the parameter δ and also R_{max}. The collapse time of the bubbles, therefore, increases as temperature increases at a fixed power. Since it was seen that the optimum rates are obtained when the cavitating bubbles have a collapse time equal to $1/2T'$, the power supplied to the ultrasonic reactor would have to be decreased when the temperature is increased in order to compensate for the expansion of the bubbles and thus keep the collapse times constant at an optimum value. By solving Equation (2) numerically the maximum radii R_{max} can be found which give a collapse time of $1/2T'$ or 0.926×10^{-6} s at the various temperatures and 540 kHz. The R_{max} that gives a collapse time of 0.926×10^{-6} s at 293°K is 1.01×10^{-5} m, at 298°K it is 1×10^{-5} m and at 303°K it is 0.99×10^{-5} m. This indicates that since an increase in δ results in an increase in the collapse times, the R_{max} has to be decreased by decreasing the power in order to keep the collapse time at its optimum value of $1/2T'$. A summary of experimental and theoretical results is shown in Table 3. The theoretical voltages are obtained since the optimum R_{max} is known for each temperature as calculated from Equation (2). R_{max} is directly proportional to the voltage supplied to the ultrasonic reactor.

As seen in Figure 2 the percent increase in the methyl acetate converted over the nonultrasonic applications increases with temperature. The maximum increase at 293°K is at 110 volts and it is 5.00% at 298°K and 105 volts it is 6.65%, and at 303°K and 100 volts it is 9.60%.

The reaction rate constants were also measured as a function of reaction volumes in order to ascertain to what extent the volume influences a chemical reaction when ultrasonics are present (Figure 3). The most obvious conclusion is that there is an optimum volume for each power where the reaction rate is maximum. The optimum power density for all volumes is constant at 17×10^4 watts/(kg) (m^2) and 298°K.

The height of the reacting mixture above the crystal element of the reactor affects the standing wave pattern in the fluid. The sound wave will be reflected totally 180° out of phase at the liquid-air interface because of the great

Table 3. Theoretical and Experimental Values of Optimum Power at 540 kHz

T(°K)	$R_{max}{}^m$	Theoretical voltage	Experimental voltage
293	1.01×10^{-5}	110.8	110
298	1.00×10^{-5}	base	105
303	0.99×10^{-5}	99.8	100

Table 4. Rate Constants for the Hydrolysis of Methyl Acetate-Water-Acetone System with Ultrasonics

	298°K	303°K	308°K
M_i	0.60 kg-mole/m^3	0.60 kg-mole/m^3	0.60 kg-mole/m^3
W_i	17.78 kg-mole/m^3	17.78 kg-mole/m^3	17.78 kg-mole/m^3
$[H^+]$	1.123 kg-mole/m^3	1.123 kg-mole/m^3	1.123 kg-mole/m^3
Acetone$_i$	8.07 kg-mole/m^3	8.07 kg-mole/m^3	8.07 kg-mole/m^3
T	298°K	303°K	308°K
Frequency	540 kHz	540 kHz	540 kHz
Reaction volume	1.05×10^{-4} m^3	1.05×10^{-4} m^3	1.05×10^{-4} m^3
Volts	k' (s^{-1}) $\times 10^5$	k' (s^{-1}) $\times 10^5$	k' (s^{-1}) $\times 10^5$
0	7.66	11.6	166
105	7.77	11.6	170
120	8.32	13.2	193
130	10.5	14.6	218

difference in the acoustic impedance of the liquid and air. At the liquid-solid interface at the bottom of the reactor, part of the wave will be reflected back into the medium in phase and part will be transmitted through the crystal and out of the reactor because now the acoustic impedances of the liquid and solid crystal are closer in magnitude than the ones of the liquid and air. If the height of the liquid above the transducer is an integral multiple of one-half the wave length, resonance occurs and the cavitation activity is maximum under these conditions. Resonance affects the maximum radii R_{max} to which the cavitating bubbles can grow, thus affecting the intensity of cavitation. The maximum increase in the conversion of methyl acetate occurs at a volume of 1.575×10^{-4} m^3 and at 120 volts (Figure 3).

In order to study the effect of frequency on reaction rates, data was taken at two different frequencies; 540 kHz and 780 kHz. As shown in Figure 4 when the voltage is varied from 90 volts to 125 volts at 1.05×10^{-4} m^3 reaction volume and 303°K, no change occurs in the percent increase in the conversion of methyl acetate at 780 kHz; the percent increase stayed constant at 3.35. No maximum in the percent increase occurs at 780 kHz similar to the 540 kHz case. The maximum percent increase at 540 kHz at 1.05×10^{-4} m^3 and 303°K is 9.6% while the percent increase at 780 kHz stayed constant at 3.35%. This shows that the reaction rate constants decrease with an increase in frequency which agrees with the theoretical predictions. Increasing the frequency decreases the period of oscillation of the sound waves which inhibits the growth of the cavitating bubbles to their maximum radius R_{max}, which decreases the cavitation intensity. In addition, since no maximum is seen in the percent increase, the resonance characteristics must have been inhibited at a volume of 1.05×10^{-4} m^3. This fact was verified visually while the reaction was taking place. The cavitation intensity at 780 kHz was easily seen to be much less than the intensity at 540 kHz. The hissing noise that is characteristic of cavitation was not as pronounced at 780 kHz as it was at 540 kHz. When the reaction volumes were increased, the cavitation activity was seen to increase very drastically from what it was at 1.05×10^{-4} m^3 of reaction volume. When the reaction volume was increased to 1.84×10^{-4} m^3 and 303°K, there was a maximum percent increase at a power density of 14.9×10^4 watts/(kg)(m^2) and at 2.10×10^{-4} m^3 and 303°K the optimum power density was 14.7×10^4 watts/(kg)(m^2). The optimum power density at 540 kHz and 303°K as seen from Figure 2 was 12.8×10^4 watts/(kg)(m^2) which is smaller than at 780 kHz. This finding could be explained if the resonance characteristics at 780 kHz were inhibited, thus hindering the growth of the cavitating bubbles. Hence, in order to compensate for this inhibiting action, the power density had to be increased in order to allow the bubbles to grow to a larger R_{max} where the cavitation activity would be more intense.

In general, the resonance characteristics at higher frequencies are much more sensitive to the experimental variables. Small changes in such variables as reaction volumes and temperatures might cause considerable changes in the resonance characteristics because of smaller wave lengths and smaller periods of oscillation.

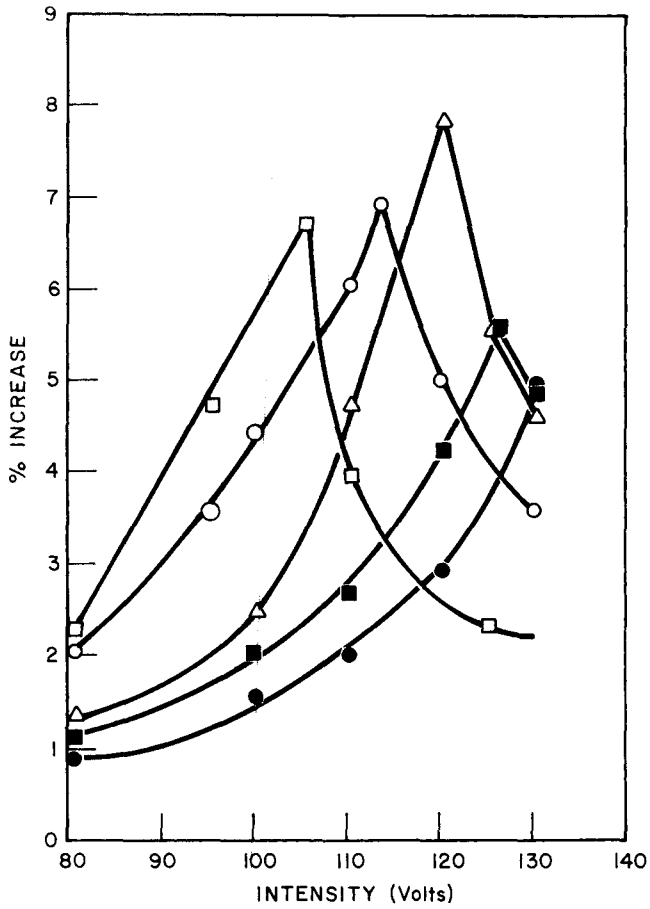

Fig. 3. Effect of ultrasound intensity and volume on reaction yields for the methyl acetate-water system at 298°K: □—1.05×10^{-4} m^3; ○—1.31×10^{-4} m^3; △—1.58×10^{-4} m^3; ■—1.84×10^{-4} m^3; ●—2.10×10^{-4} m^3; time = 2400 sec.; and frequency = 540 kHz.

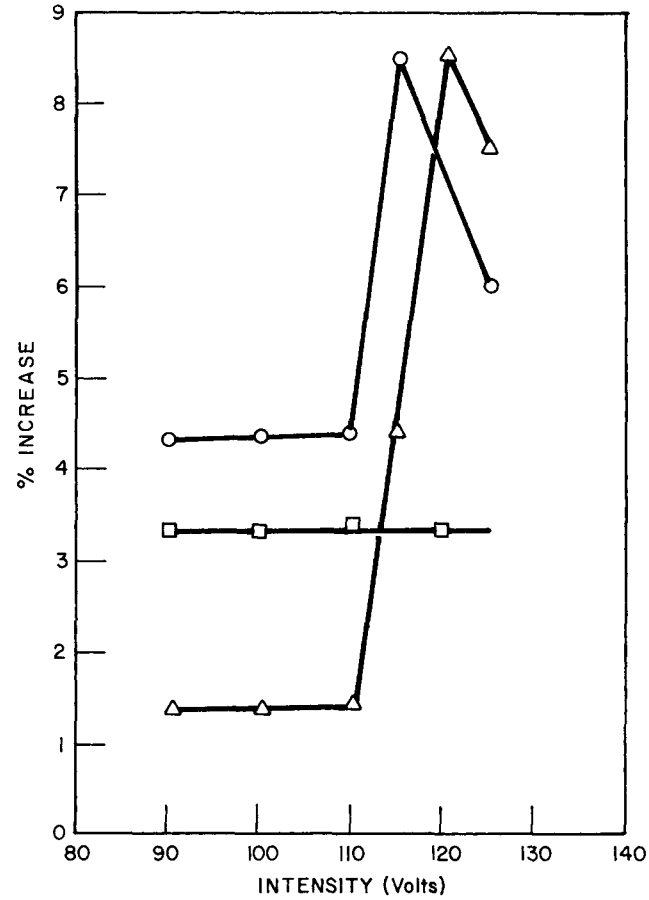

Fig. 4. Effect of ultrasonic intensity, volume, and frequency on reaction yields for the methyl acetate-water system at 303°K: □—1.05×10^{-4} m^3; ○—1.84×10^{-4} m^3; △—2.10×10^{-4} m^3; time = 2400 sec., and frequency = 780 kHz.

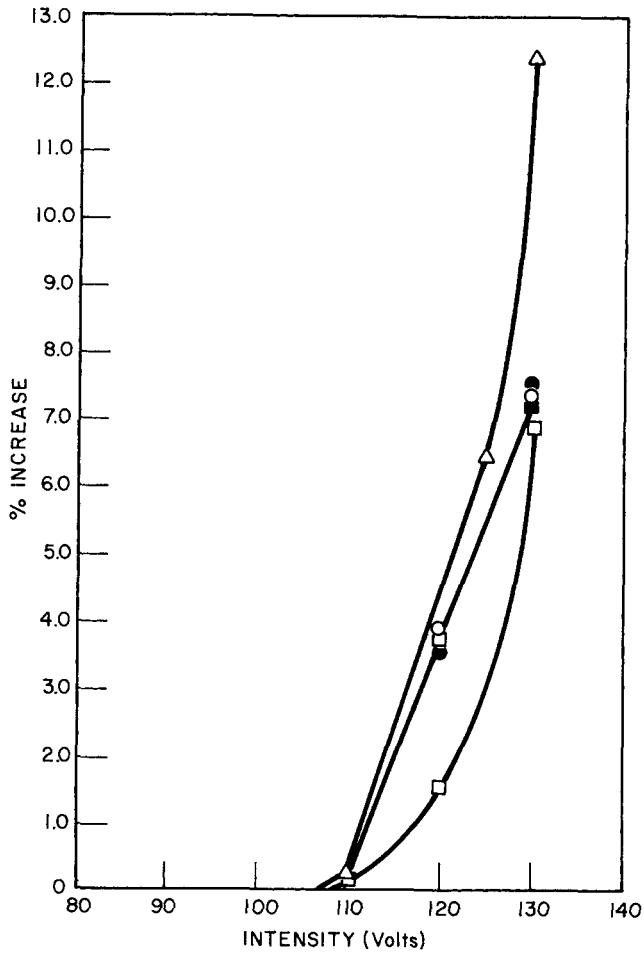

Fig. 5. Effect of ultrasound intensity, temperature, and volume on reaction yields for the methyl acetate-water-acetone system: □—298°K, 1.05 × 10^{-4} m^3; ○—303°K, 1.05 × 10^{-4} m^3; △—308°K, 1.05 × 10^{-4} m^3; ■—303°K, 1.58 × 10^{-4} m^3; ●—303°K, 2.10 × 10^{-4} m^3; time = 2400 sec., and frequency = 540 kHz.

Ultrasonics (Methyl Acetate Water-Acetone System)

The hydrolysis of methyl acetate in a water-acetone mixture as the solvent subjected to ultrasonics follows the pseudo first order reaction law. The experimental data for this system (Figure 5) shows that the reaction rate constants increase with increasing power or voltage applied to the reactor. No optimum power is obtained where a maximum rate results as in the case of the methyl acetate-water system. This indicates that the maximum radii R_{max} of the cavitating bubbles are well below their optimum value or the collapse time of the bubbles is less than $1/2T'$ or 0.926 × 10^{-6} sec as in the case of a 540 kHz frequency sound wave. Since an optimum rate does not occur and the bubble radii were not measured experimentally, it is not possible to know exactly what the value of R_{max} is. It can be said though that the bubble radii are such that their collapse time is less than one half the period of oscillation of the sound waves.

The activation energy for this system at 120 volts is 57.5 MJ/kg-mole and at 130 volts it is 56.6 MJ/kg-mole while at 0 volts it is 56.2 MJ/kg-mole. The activation energy remains constant as was the case for the methyl acetate-water system. Hence, the effect of ultrasonics is to change the frequency factor k_0 in the Arrhenius rate expression. Below a voltage of 110 volts no change appears in the rate constants which indicates that there is a low power threshold under which ultrasonics do not affect the reaction rates of this system.

The percentage increase in the methyl acetate conversion is not as high for the methyl acetate-water-acetone system as it is for the methyl acetate-water system. To obtain comparable yields in the acetone system as in the water system, higher sound wave intensities have to be used. The decrease in reaction yields can be explained in view of the analytical predictions that the cavitation activity decreases with an increase in the vapor pressure parameter δ (Khoroshev, 1964). The vapor pressure of the water-acetone mixture is higher than that of pure water; therefore, greater changes in the reaction rates can be expected in the methyl acetate-water system than in the methyl acetate-water-acetone system. This prediction can be seen more clearly by calculating the shock wave pressures obtained from the water-acetone mixture which are very much lower than those obtained from the water system.

The reaction volume was not an important variable in this system. No noticeable change in the reaction rates was realized by varying the reaction volumes. This trend indicates that the bubble radii are far from their optimum value. A close examination of Figure 3 shows that even in the methyl acetate-water system, the volume becomes less important as the power is lowered far from the optimum value. All of the curves in Figure 3 seem to approach the same value as the power is decreased from the optimum point. The same results were obtained by Weissler et al. (1950) in their oxidation of a potassium iodide solution.

The use of ultrasonic irradiation at 780 kHz on the methyl acetate-water-acetone system clearly shows that the percentage increase in the conversion of methyl acetate is not a function of wave intensity or reaction volume. The percent conversion is constant at 3.25% at 303°K which is lower than the conversions obtained at 540 kHz and 303°K. This fact once again is to be expected because the cavitation intensity decreases with increasing frequency as analytically predicted. The fact that the percent increase in conversion is constant for all wave intensities and all reaction volumes shows that the resonance characteristics are again inhibited at this new frequency and, therefore, the reaction is taking place far from the optimum operating conditions.

NOTATION

P = pressure of liquid at any time, t
P_g = pressure of gas inside a collapsing bubble
P_0 = ambient pressure
P_r = instantaneous pressure at r
P_u = ultrasonic pressure of the sound wave
Q = pressure of gas inside the bubble at $t = 0$
r = radial distance from the center of the cavitating bubble
R = bubble radius at any time, t
R_0 = bubble radius at $t = 0$
R_{max} = maximum radius of the cavitating bubble
R_{min} = minimum radius of the cavitating bubble
S = surface tension of the liquid
t = time
w = angular frequency
z = $(R_{max}/R)^3$

Greek Letters

γ = specific heat ratio
ρ_0 = average density of the liquid
δ = Q/P_0

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Synthesis Strategies for Multicomponent Separation Systems with Energy Integration

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The problem of synthesizing an optimal multicomponent separation system which is energy integrated is solved by a combined decomposition and dynamic programming technique.

Dynamic programming is an optimization technique which allows the solution by decomposition of a multistage or serial optimization problem. Whenever the special serial structure is absent, again decomposition can be tried, but in this case it is by no means obvious how to decompose effectively the given problem into subproblems. In this paper the nonserial problem of synthesizing an energy integrated separation system is solved by decomposing the original problem so that a serial structure results.

SCOPE

In the synthesis of chemical processing systems two key subproblems are:

1. The selection of the basis and sequence of separation, and
2. The determination of a heat exchanger network for energy recovery.

The quality of solution of these subproblems can have a large effect on the overall efficiency of a chemical processing system. The separation problem is important in that a major part of the capital investment and utilities for a process are determined by the separator types and sequences. The recovery of energy in heat exchanger networks is also an important feature as energy integration reduces consumption of increasingly expensive energy resources.

Each of the subproblems has been solved separately. The separation problem has been solved by three basic techniques. Heuristic methods in which rules of thumb are used to limit the search to solutions which appear to be best have been developed by several workers including Thompson and King (1972). An embedding approach in which all possible separation sequences are embedded in a structure on which parameter optimization is performed has been advanced by Ichikawa and Fan (1973). In this method all possible separators considered for a given problem are interconnected and optimization is performed over stream split parameters.

A final approach is a dynamic programming method developed by Hendry and Hughes (1972). In their method, Hendry and Hughes systematically generate the separation subproblems which can occur in all possible separation sequences. They then use the principle of optimality to select the optimal separation sequence.

The heat exchanger network synthesis problem has been studied by modern methods since Hwa (1965) developed a separable programming method to determine the optimal network. Kesler and Parker (1969) developed a linear programming model and Masso and Rudd

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