ABSTRACT

MIXING PERFORMANCE OF A NOVEL, CONTINUOUS CONFINED IMPINGING JETS MIXER USING COMPETITIVE REACTIONS

by
Han Zheng

In this work, a novel continuous flow apparatus featuring the impingement of fluid jet streams in the presence of ultrasonic energy provided by an ultrasonic probe was tested using competitive reactions in order to determine its mixing effectiveness. The ultrasonic energy enhances micromixing of the fluid jet streams, which results in an overall mixing effectiveness improvements in different physical and chemical processes.

In the competitive reactions system used here (third Bourne reaction), one stream containing sodium hydroxide was continuously fed to the first impinging jet, while an aqueous solution of hydrochloric acid and ethyl chloroacetate was fed to the second jet. The concentration of ethanol in the final solution was experimentally determined by gas chromatography (GC) to determine the mixing efficiency: higher ethanol concentrations implied poorer mixing. In all experiments, the volumetric flow rate of sodium hydroxide solution was always kept the same, while the flow rate of the other solution was changed. The sonication power was also varied.

It was experimentally found here that improved mixing was achieved by increasing volumetric flow rate with or without sonication. If sonication was applied, mixing also improved significantly and it was further improved when a higher sonication power was applied. This trend was especially evident at lower flow rates. At high flow rate, sonication played a smaller role. A quantitative comparison of the results based on the use of the Damköhler number is provided.

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APPROVAL PAGE

MIXING PERFORMANCE OF A NOVEL, CONTINUOUS CONFINED IMPINGING JETS MIXER USING COMPETITIVE REACTIONS

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To my Parents and my Family, who offered me unconditional love and support in
all the way since the beginning of my life

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TABLE OF CONTENTS

TABLE OF CONTENTS
(Continued)

LIST OF TABLES

LIST OF FIGURES

LIST OF SYMBOLS

C_i Solution concentration of reactant i, mol/L

D   Diameter of sonication unit hole, m

d   Diameter of outlet hole, m

Da   Damköhler number, ratio of reaction time to mixing time

H   Height of chamber, m

h   Height of jets fixed on the chamber wall, m

I   Inter-diameter of jet, m

k_i Chemical kinetic rate constant of reaction i, $m^3/(mol \cdot s)$

L   Length of chamber, m

$\dot{m}$ Mass flow rate, g/min

N   1. Mole of reactant, mol
                         2. nth-order reaction

$\dot{n}$ Molar flow rate, mol/min

$\dot{Q}$ Volumetric flow rate, m^3/min

T   Temperature, K

u_i Average velocity of liquid stream i, m/s

W   Width of chamber, m

X_Q Ethanol yield (Conversion of slow reaction)

Greek letters

Δ   Dimensionless number, D/I

ν_i Momentum diffusivity of liquid stream i, m^2/s

τ_M Mixing time, s

τ_R Reaction time, s

CHAPTER 1

INTRODUCTION

Mixing of reacting or non-reacting homogeneous liquids is a very common operation in the chemical and pharmaceutical industries. Depending on the type of application, different mixing devices can be used. For example, blending of homogeneous, low-viscosity non-reacting liquids can be easily accomplished in stirred tanks. However, the product composition of fast simultaneous homogeneous reactions occurring when two liquids, each one containing one of the reactants, are mixed together is highly dependent on how fast the reactant are brought in contact with each other. In such a case, small continuous reactors are more appropriate to achieve the desired conversion and minimize undesired by-product formation.

1.1 Stirred Tank

The stirred tank is a type of mixer widely used in the chemical and pharmaceutical industries. A stirred tank consists of a large, possibly jacketed and baffled, vessel to hold liquids, an impeller to agitate the liquid content, and a motor to provide mechanical energy to the impeller. There are many commercially available stirred tanks with different sizes and impeller types for engineers to choose. Sometimes engineers also design non-conventional stirred tanks to meet different process requirements. Different types of impellers can be used to generate axial flow or radial flow in the tank. In addition to mixing, chemical reactions are routinely

conducted in stirred tanks. Because of their importance in chemical industry, stirred

tanks have been extensively studied in the past.

1.2   Impinging Jets Mixers

Impinging Jets Mixers are relatively novel devices, compared to stirred tanks.

Common types of this type of mixers include Submerged Impinging Jets (SIJ) mixers

and Confined Impinging Jets (CIJ) mixers.   A submerged impinging jets mixer

includes two jets with very small inner diameters (0.5 mm~2 mm) that are typically

mounted in the stirred tank and are submerged below the liquid surface. (Figure 1.1)

During operation, two liquid streams are fed to the jets and made to collide with each

other. Furthermore, the tank is provided with an impeller provide macroscopic

recirculation of the liquid in the tank.
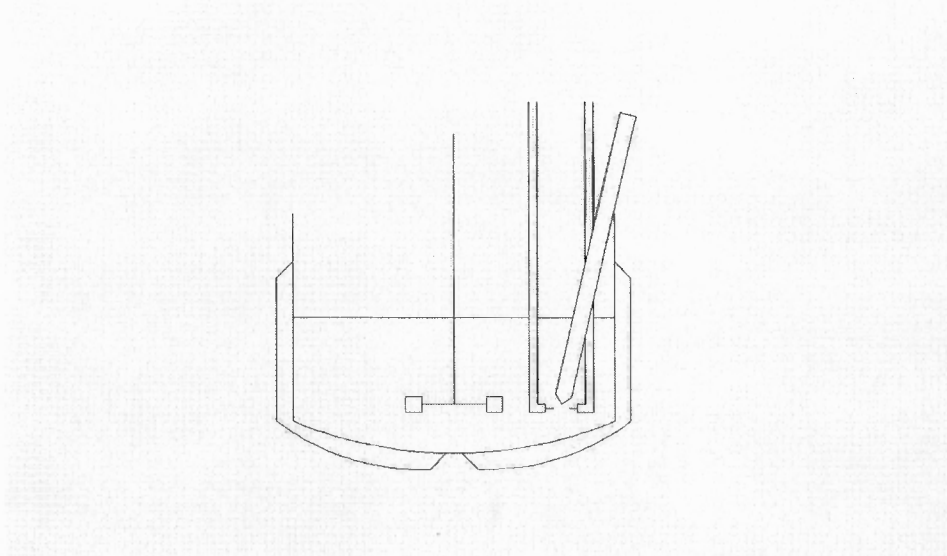
Figure 1.1   Schematic of submerged impinging jets mixer

As for confined impinging jets mixer, two or more jets with very small inner-diameter (0.5mm~2mm) are placed inside a small reactor vessel in such a way as to make the liquid jets impact with each other. Liquids containing different reactants are fed into the chamber through the jets at a very high velocity so as to promote rapid mixing and minimize mixing effects on the overall reaction process.

The impinging jets can be oriented to form different angles between them. For example, if there are only two jets opposite to each other in the reactor chamber, they form a 180 degree angle.   Different arrangements are possible (Figure 1.2).
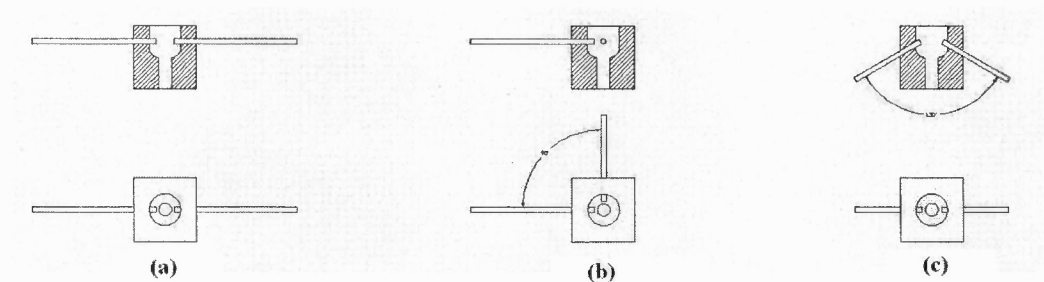
Figure 1.2   Schematic of confined impinging jets mixers: (a) CIJ with 180-degree jets angle; (b) CIJ with 90-degree jets angle; (c) CIJ with 120-degree jets angle

1.3   Mixing-Sensitive Competitive Reactions Systems

Competitive reaction systems are simultaneous reactions in which one of the reactants can participate in two parallel reactions.   For instance, in the following reaction system in which three reactants, A, B, and C are involved, both reactants A and C can react with B and produce the products P and Q, respectively:

$$A + B \xrightarrow{\ k_1\ } P \qquad\qquad\qquad 1.1(a)$$

$$C + B \xrightarrow{\ k_2\ } Q \qquad\qquad\qquad 1.1(b)$$

If all reactants are in iso-stoichiometric concentrations (the molar ratio of reactants A, B, and C is 1:1:1), B can, in principle, react with A only, with C only, or participate in both reactions in different ratios. Each reaction has its own reaction kinetic rate constant (k). If the value of k for one of the above reactions is larger than the other, one would expect that one reaction will proportionally consume more of the limiting reactant B, and form more of the corresponding product. However, if the time required to achieve homogenization at the small scale is large in comparison to the reaction time, local depletion of one of the reactant may occur, and the product composition will depend on how fast the reactants are "micromixed". In other words, the reaction system is mixing sensitive.

This applies to the reactive system above as well. If the value of k_1 for the first reaction is much greater than k_2, for the second reaction [Equation 1.1(b)], then the second reaction is the slow reaction in the system. Thus very few product Q will be formed if mixing is perfect since B can react with both A and C, and it will preferentially react with A because of the favorably kinetics. However, when reactant segregation is intense because of imperfect mixing (i.e., the reactions take place independent of each other), the yield of Q is not a function of the kinetics and is given by:

$$X_Q = \frac{C_Q}{C_P + C_Q}$$

1.2

where X_Q can be, theoretically, as high as 0.5 if segregation is so intense that the reactions take place independent of each other. In practice, X_Q can vary between near zero to a significant fraction, as high as 20-30%, if segregation is significant.

Several mixing-sensitive reaction systems have been used in the past, as shown in Table 1.1.

Table 1.1 Competitive reactions with mixing-dependent product distributions [1]

Case No.	Competitive Reaction System
Case 1	Benzene and toluene with nitronium ion
Case 2	Cobalt (III) complexes with chromium (II) ion
Case 3	Alkaline ester hydrolysis and neutralization
Case 4	Alkaline ester hydrolysis and precipitation
Case 5	Diazo coupling with decomposition of reagent
Case 6	Iodate / iodine reaction with neutralization
Case 7	Acetal hydrolysis with neutralization

The methyl and ethyl esters of monochloroacetic acid are categorized as Case 3 in Table 1.1. If ethyl chloroacetate ($ClCH_2COOC_2H_5$) is used as the ester, the competitive reactions are as follows (third Bourne reaction):

$$HCl + NaOH \xrightarrow{\ k_1\ } NaCl + H_2O \qquad\qquad 1.3(a)$$
$$(A) \qquad (B) \qquad\qquad (P) \quad (R)$$

$$ClCH_2COOC_2H_5 + NaOH \xrightarrow{\ k_2\ } C_2H_5OH + ClCH_2COONa \qquad 1.3(b)$$
$$(C) \qquad\qquad (B) \qquad\qquad (Q) \qquad\qquad (S)$$
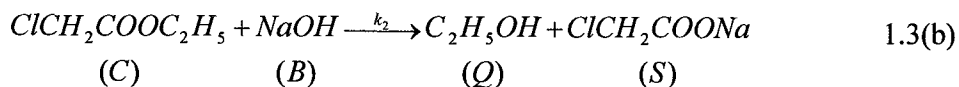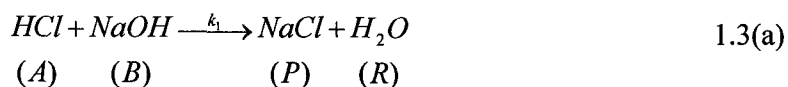
This is the system of parallel reactions that was used in this work to study the mixing characteristics of the sonicated confined jets reactor. When all reactants are in iso-stoichiometric ratios [molar ratio: 1(NaOH):1(HCl):1(ClCH2COOC2H5)] sodium hydroxide (NaOH) acts as the limiting reagent in the system.

The first reaction is a neutralization reaction between a strong acid and a strong base. At a temperature of 298 K, the kinetic rate constant of neutralization (k_1) has been reported to about $1.3 \times 10^8 m^3/(mol \cdot s)$ which makes the neutralization nearly instantaneous[1]. The second reaction is an ester hydrolysis reaction, whose kinetics has been reported to be given by the equation:

$$k_2 = 2.0 \times 10^5 \times \exp(-\frac{3.891 \times 10^4}{RT}) \qquad\qquad 1.4$$

At 298 K, k_2 is about $0.030 m^3/(mol \cdot s)$ [1]. Although both reactions are fast, the first reaction is much faster than the second, since the value of k_1 is much greater than that of k_2. If mixing was perfect, only sodium chloride (NaCl) would be present, in practice, in the final solution. However, if mixing is not perfect and segregation occurs, appreciable amounts of ethanol (C_2H_5OH) are formed since once

HCl has been locally depleted by reacting with the NaOH in the added stream, the NaOH will start reacting, with the ethyl chloroacetate. Therefore, the variable that can be used to evaluate the mixing performance is the yield of ethanol, X_Q, defined as:

$$X_Q = \frac{n_{C_2H_5OH}}{n_{C_2H_5OH} + n_{NaCl}} = \frac{C_{C_2H_5OH}}{C_{C_2H_5OH} + C_{NaCl}} \qquad 1.5$$

When the reactant are reacting in iso-stoichiometric ratios and all the NaOH is consumed at the end of the reaction, the denominator in this equation is equal to the moles of NaOH initially added, i.e.:

$$X_Q = \frac{n_{C_2H_5OH}}{n_{NaOH}} \qquad 1.6$$

Equation 1.6 provides a convenient way to calculate conversion of the slow reaction. The molar quantity of sodium hydroxide (n_{NaOH}) is known initially when the sodium hydroxide (NaOH) solution is prepared. The molar quantity of ethanol ($n_{C_2H_5OH}$) is obtained based on concentration of ethanol and volume of final solution.

1.4 Previous Research on Competitive Reactions System

Bourne and Yu [3] were the first to use the sodium hydroxide, hydrochloric acid and ethyl chloroacetate (or in substitution methyl chloroacetate, $ClCH_2COOCH_3$) reaction

systems to study mixing. Their research was aimed at finding the effects of chemicals feed sequence, feed position, initial solution concentration, tank bottom, and geometric scale-up on the conversion of slow reaction [3]. Many other investigators have used their approach. In this group, Armenante and Akiti used the competitive reactions (Equation 1.3) to study mixing in stirred tank. They used computational fluid dynamics (CFD) and a modeling approach to predict the behavior of the reacting system, and validated this approach using experimental data [4].

As for the impinging jets system, a number of researches have used this reactor to produce micrometer-sized and nanometer-sized particles. The basic principle is to take advantage of the different solubilities of drugs in inorganic solvents and organic solvents and precipitate particles using rapid antisolvent precipitation in the impinging jet system. Under such circumstances, two streams with high kinetic energies colliding with each other, which makes the mixing times much shorter than the agglomeration times. Lindrud et al. [5] used a submerged impinging jets reactor together with sonication unit to produce nanoparticles of some organic chemicals. Experiments on nanoparticles crystallization are realized in the confined impinging jets system by Marchisio et al. [6], who used barium chloride ($BaCl_2$) and sodium sulfate (Na_2SO_4) to produce nanoparticles of barium sulfate ($BaSO_4$). In their research, the effects of initial solution concentrations, volumetric flow rates, and scale-up factors were studied. [6] Johnson and Prud'homme studied the formation of copolymer nanoparticles in impinging jets [7, 8]. In the pharmaceutical industry, smaller particle sizes can improve the bioavailability of final

drug products. Some papers demonstrate the method to produce drug nanoparticles in the confined impinging jets mixer. The drugs studied include PROSCAR®, Simvastatin, Lovastatin, Triton X-100, Omeprazole, and others [9, 10].

The competitive reactions systems listed in Table 1.1 have been used to study mixing in impinging jet systems. For example, Johnson and Prud'homme used two competitive reactions systems in their work, i.e., the neutralization of sodium hydroxide and hydrochloric acid vs. base hydrolysis of ethyl chloroacetate (Equation 1.3) and the neutralization of sodium hydroxide and hydrochloric acid combined with the acid catalyzed hydrolysis of 2,2-dimethoxypropane [DMP, CH₃C(OCH₃)₂CH₃]:

$$NaOH + HCl \longrightarrow NaCl + H_2O \qquad \text{1.7(a)}$$

$$CH_3C(OCH_3)_2CH_3 + H_2O \xrightarrow{H^+} CH_3COCH_3 + 2CH_3OH \qquad \text{1.7(b)}$$
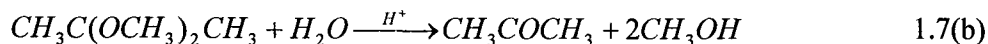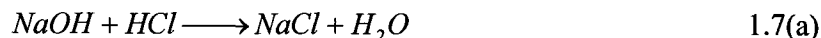
Their work shows how a number of operating factors affect the conversion of slow reaction [11].

1.5   Objective of this Work

The objective of this research work is to study experimentally the mixing effectiveness of a sonicated confined impinging jets instrument using parallel competitive reactions, i.e., the reactions system shown in Equation 1.3. In particular, the effect of operating parameters such as the volumetric flow rate of one of the reactants and the sonication power were studied. The results are also presented as a

function of a modified Damköhler number, i.e., the ratio of the system's mixing time to the reaction time, which was calculated to draw additional conclusion about liquid mixing process.

CHAPTER 2

THEORETICAL BACKGROUND

2.1 Mixing Scale

The streams fed into the confined impinging jets chamber typically have a high velocity, which means their Reynolds number is high enough to categorize their flow state as turbulent. In turbulent flow, the molecules diffuse so complex that it is impossible to study the process well. In a turbulent mixing process, the mixing process is conveniently characterized by different mixing scales: macromixing, mesomixing, and micromixing. Macromixing refers to the large-scale mixing in the whole vessel. Mesomixing reflects the coarse-scale turbulent exchange between the fresh feed and its surroundings. If there are reactions in the mixing process, fast chemical reactions usually happen near fresh feed points. Mesomixing is associated with a coarse scale relative to the micromixing scales (Kolmogorov and Batchelor microscales). Micromixing refers to mixing occurring in small scale eddies in the viscous-convective range [1]. The liquid mixing in confined impinging jets mixer is typically dominated by the meso- and especially micromixing effects. Because of the small size and high energy dissipation rates in impinging jets systems, these reactors are effective in enhancing mixing at the microscale level and thus affect reactions whose product composition is affected by micromixing, such as fast competitive reactor systems. In turn, these reactions can be used as the 'ruler' to determine the mixing scale [7, 8, 9, 10,11].

2.2   Competition between Reaction and Mixing and Damköhler Number

When one of the competitive reactions systems listed in Table 1.1 is used in liquid

mixing process, there is competition not only in the reaction system but also between

the mixing process and reaction process. The time needed to homogenize the system a

the microscale level is called the (micro)mixing time (τ_M) and the time associated

with completing the reaction to a predefined meaningful extent is called reaction time

(τ_R). It is these two times that determine which process acts as the controlling one in

the overall process. For instance, if the mixing time is much shorter than the reaction

time, the process is controlled by how long the reaction will take to complete since the

reactants are rapidly well mixed, as far as the reaction is concerned. If the reaction

time is shorter than mixing time, the process becomes controlled by how fast the

reactants are mixed, which makes this mixing-controlled process. To calculate the

reaction time, one needs to know the value of reaction kinetic rate constant and the

reaction mechanism, such as zero-order reaction, first-order reaction, and so on. The

general equation for reaction time calculation is

$$\tau_R = \frac{1}{k_n \times (C_{A0})^{n-1}} \qquad\qquad 2.1$$

where n is the nth-order of reaction and C_{A0} is the initial concentration of reactant.   If

the initial concentration approximately remains, the reaction time is only affected by

the kinetic rate constant. For the competitive reactions system of Equation 1.3, the

kinetic rate constant of neutralization k_1 is $1.3 \times 10^8 m^3/(mol \cdot s)$ which is so large that the reaction happens, for practical purposes, instantaneously when the acid solution and base solution are contacted together. As for ester hydrolysis, the kinetic rate constant k_2 is $0.030 m^3/(mol \cdot s)$ resulting a much slower reaction compared with neutralization. The scales of mixing time and reaction time reflect the competition between mixing and reaction. Figure 2.1 shows an example of a possible ranking of time scales for mixing and reaction. The left-hand axis represents the mixing process, while the right-hand axis characterizes reaction rates.
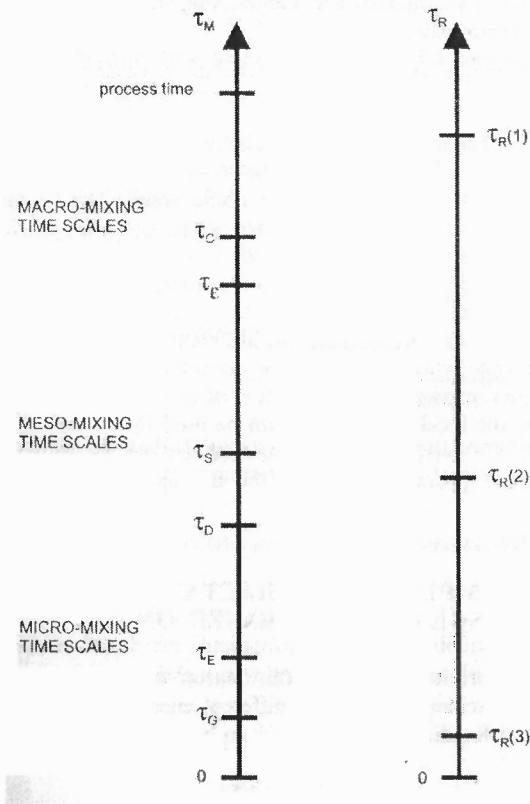
Figure 2.1   Competition between reaction and mixing (τ_R: reaction time; τ_M: mixing time; τ_C: circulation time; τ_ε: energy dissipation time) [1]

In Figure 2.1, for the reaction characterized by τ_R (1), the only relevant time is the reaction time since mixing at all scale is rapid in comparison. The second reaction,

τ_R (2), requires attention to be given to the macro- and mesomixing steps to ensure that these mixing step do not become controlling. The third one, τ_R (3), can be micromixing-dependent. [1] In the competitive reactions system of neutralization and ester hydrolysis (Equation 1.3), the reaction time of neutralization is similar to τ_R (3) in Figure 2.1. As the chemical mechanism of neutralization is changing ions, the reactions time is small enough to be categorized as a mixcromixing-dominated process. If it were possible first to mix a 1N acid solution with a 1N base solution, the half-life of neutralization would be some 7.7×10^{-12} s. This time is very short compared to attainable mixing times ($>10^{-4}$s), which implies that mixing is controlling [1]. As for the ester hydrolysis reaction, the reaction time is typically short but of the same order of magnitude as the micro- and possibly meso-scale of turbulence. This means that depending on how rapid the mixing process is at these scales the overall process could be a function of a critical mixing time. The ethanol yield(X_Q), also called conversion of slow reaction, i.e., how much ethyl chloroacetate has reacted at the end of the process is a measure of the effectiveness of the mixing process at the microscale and mesoscale levels: the greater this conversion, the poorer the mixing process is.

The non-dimensional Damköhler number is a measure of the relative importance of these two processes in the overall process. The Damköhler Number is defined as the ratio of mixing time (τ_M) to reaction time (τ_R).

$$Da = \frac{\tau_M}{\tau_R} \qquad\qquad 2.2$$

The reaction time of neutralization is neglected because of the reaction instantaneity. Only the reaction time of ester hydrolysis is studied in the liquid mixing process. Johnson and Prud'homme gave the equations to calculate the reaction time of ester hydrolysis and mixing time. For ethyl chloroacetate hydrolysis reaction, the reaction time is: [11]

$$\tau_R = \frac{1}{k_2 \times C_{NaOH,initial}} \qquad\qquad 2.3$$

For impinging jets systems, the mixing time is proportional to: [11]

$$\tau_M \propto \frac{1}{2\sqrt{2}} \frac{v^{\frac{1}{2}}\Delta^{\frac{y}{2}}d^{\frac{1}{2}}}{u^{\frac{3}{2}}} \qquad\qquad 2.4$$

Thus, the Damköhler number becomes: [11]

$$Da = \frac{\tau_M}{\tau_R} \propto \frac{1}{2\sqrt{2}} \frac{v^{\frac{1}{2}}\Delta^{\frac{y}{2}}d^{\frac{1}{2}}}{u^{\frac{3}{2}}} k_2 C_{NaOH,initial} \qquad\qquad 2.5$$

In their work, Johnson and Prud'homme studied the effect of scaled-up on the mixing process in impinging jets systems. Three confined impinging jets mixer with different dimensions were used in their research. Parameters, such as v, Δ, and d, depend on the geometry of the system and were easily obtained by measuring the distance between the jets, the jet tube diameters and other geometric dimensions. In this work, only one size of confined impinging jets mixer is utilized so that the equation of Damköhler Number can be simplified as:

$$Da = \frac{\tau_M}{\tau_R} \propto \frac{k_2 C_{NaOH,initial}}{u^{\frac{3}{2}}} \qquad 2.6$$

In particular, in order to associate an actual value to Damköhler number rather than express a proportionality between Damköhler number and the characteristics of the system, a modified Damköhler Number, Da', defined as follows, was used here:

$$Da' \equiv \frac{k_2 C_{NaOH,initial}}{u^{\frac{3}{2}}} \qquad 2.7$$

The Damköhler number can be thought of as a way to measure the relative scales of the mixing process and the reaction process. If the process is mixing controlled, the mixing time is very large compared to the reaction time and this makes the Damköhler number small, implying a high degree of mixing. If the reaction time

is smaller than mixing time, the number increases to reflect a less effective mixing

level.

CHAPTER 3

EXPERIMENTAL APPARATUS, MATERIALS, AND METHOD

3.1 Experimental Apparatus

The experimental apparatus system consisted of two feed tanks (one for the NaOH solution and the other for the HCl/ethyl chloroacetate solution), two gear pumps, two rotameters, the confined impinging jets mixer, the sonication unit, and piping and fittings. Table 3.1 lists the models and types of gear pumps, rotameters, and sonication unit.

Table 3.1 Experimental Components and Models

Component	Model			
Gear Pump 1	LEESON®	A6C17FB4K	1725 rpm	60Hz
Gear Pump 2	LEESON®	A6C17FB4K	1725 rpm	60Hz
Rotameter 1	Gilmont®	GF-6341-1135		
Rotameter 2	ColeParmer®	Model Unknow		
Sonication unit	Omni-Ruptor®	Omni-Ruptor250	115Volts	60Hz

The configuration of the confined impinging jets reactor system is shown in Figure 3.1.

(a)   (b)

(c)
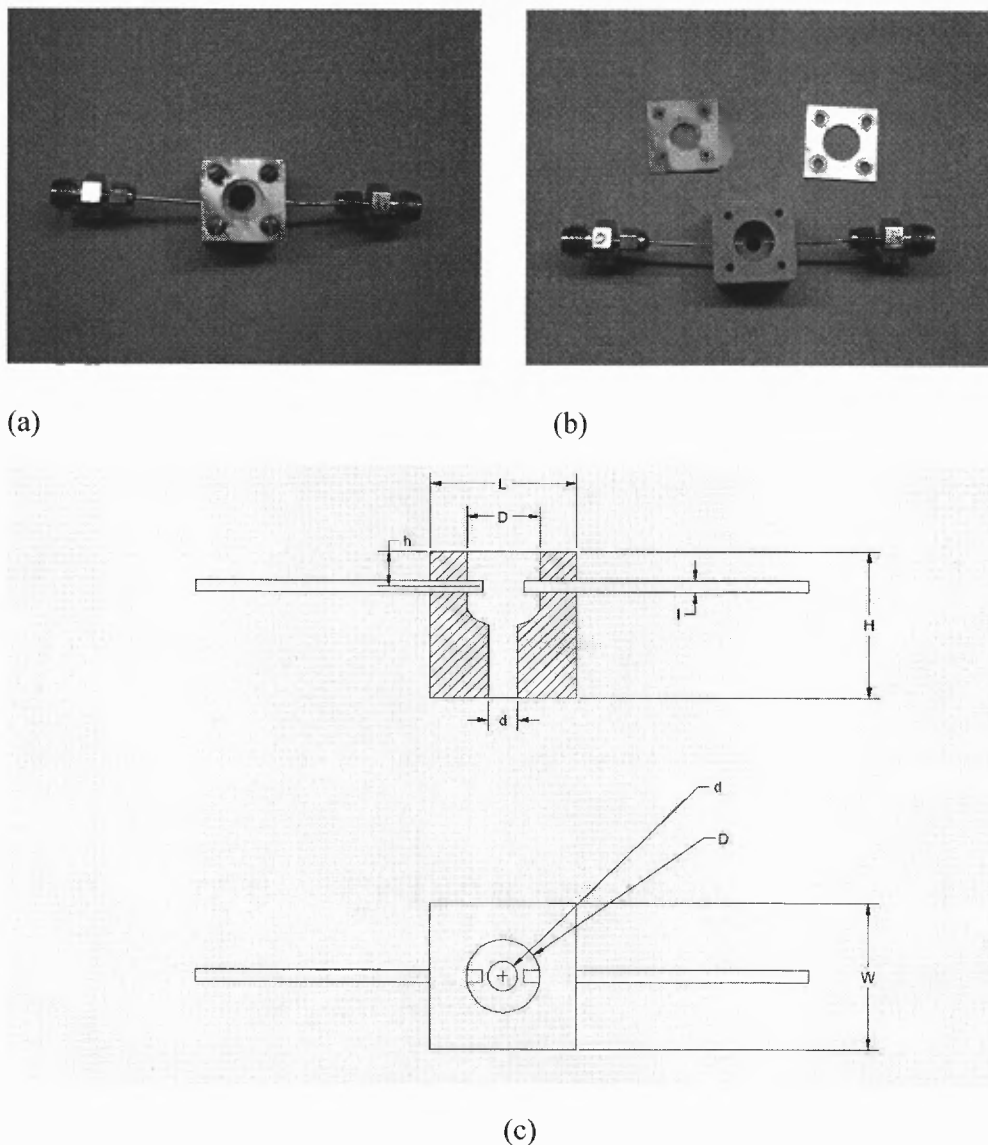
Figure 3.1 Schematic of the confined impinging jets mixer and its dimensions: (a) confined impinging jets assembly with a steel gasket; (b) steel gasket and rubber gasket de-fixed from the chamber; (c) dimensional symbols of the confined impinging jet reactor.

The reactor chamber was carved out of from a cube of polyoxymethylene (Deldrin) 25 mm in size (length=L, width=W, and height=H). The reactor chamber was a cylinder, 12.5 mm in diameter (D), with a hemispherical bottom [Figure 3.1(c)]. The diameter D of the chamber was the same as the diameter of the sonication probe

to be inserted from the top. Two stainless steel metal tubes were inserted at a distance, h, 6 mm below the top of the chamber in order to produce impinging jets during the reactor operation. The inner diameter, I, of the jets was 0.5mm. The distance between two jets was 7mm. The chamber was provided with a cylindrical outlet opening at the bottom of the chamber with a diameter, d, of 5mm.
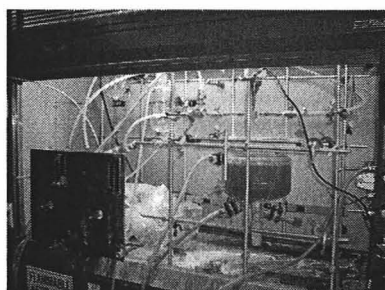
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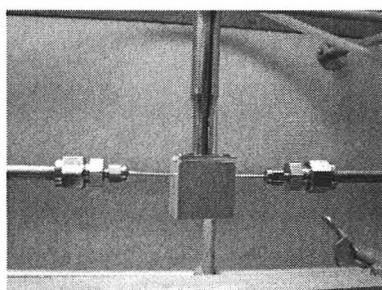
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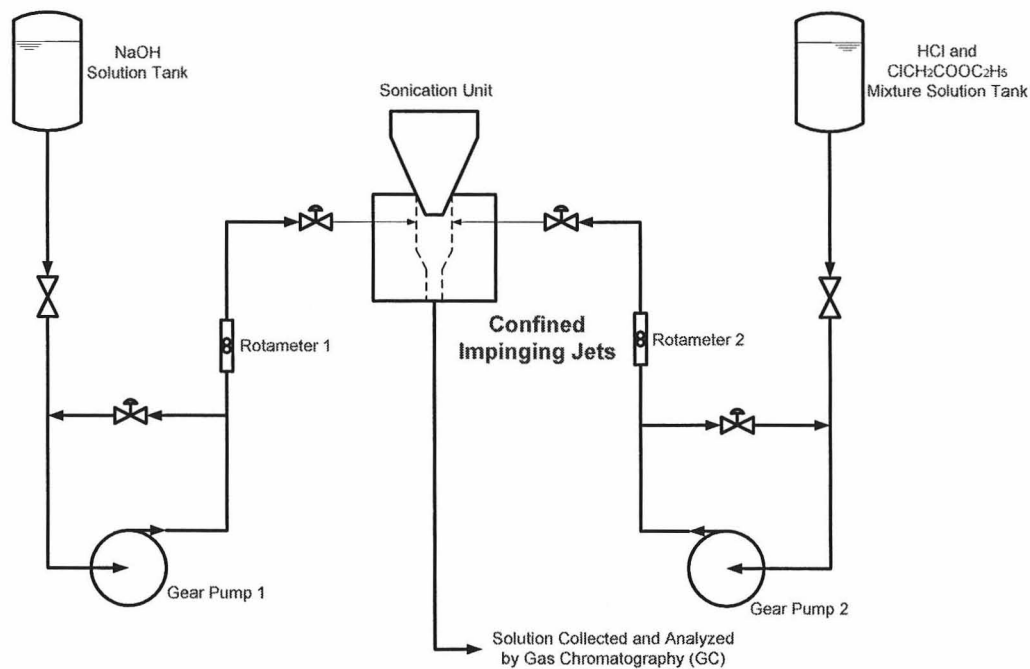
(c)

Figure 3.2 Schematic of experimental apparatus: (a) experimental system; (b) confined impinging jets reactor with sonication probe; (c) system flowchart.

3.2 Materials

The reactants used in this work were sodium hydroxide (NaOH), hydrochloric acid (HCl), and ethyl chloroacetate ($ClCH_2COOC_2H_5$). Ethanol (C_2H_5OH) was formed in the process. Sodium hydroxide reacts with hydrochloric acid and ethyl chloroacetate to form sodium chloride and ethanol (Equation 1.3). Ethanol was used to prepare standard solutions when the concentration of ethanol in the product solution at the end of each experiments. A list of materials is provided in Table 3.2.

Table 3.2   Chemicals and Their Properties and Manufacturers

Chemical/Lot No.	Manufacturer	Physical Properties
Sodium Hydroxide(NaOH) /07920MR	Aldrich Chemical Company Inc.	Assay: 97+%; F.W.:40.00; m.p.:318°F; Density:2.130
Hydrochloric Aid(HCl)/707189	Fisher Scientific Company	Minimum Concentration: 36% (wt)
Ethyl Chloroacetate (C4H7ClO2) /24717BB	Sigma-Aldrich Inc.	Assay: 99%; F.W.:122.55; F.p.:54°C(129.2°F); b.p.:141~144°C; m.p.:-26°C; Density: 1.15
Ethanol (C2H5OH) / Lot No. Unknown	Unknown	Assay: 95%

3.3 Experimental Method

A typical experiment consisted of preparing the reactant solutions with the desired concentration, i.e., an NaOH solution and an HCl/ethyl cholroacetate solution, charging them to the feed tanks, set the pumps to deliver the desired flow rates, simultaneously starting the pumps to operate the system at steady state, collecting the solution containing the reaction products at the reactor outlet, and analyzing this solution to determine the concentration of one of the products, i.e., ethanol.

One of the main objectives of this work was to study the effect of volumetric flow rates on the final conversion of the competitive reaction system in order to understand the mixing performance of the impinging jet reactor under conditions similar to those used in the precipitation of griseofulvin in another study from this research group. [13] In that work the volumetric flows of the reactants was not balanced, i.e., the volumetric flow rates of the streams entering the system was not equal. This was the case in the present study as well.

Since sodium hydroxide acted as the limiting reactant, the mass flow rate of the NaOH solution fed to the reactor (and hence its volumetric flow rate) was always kept unchanged in all experiments at 25.517 g solution/min (i.e., 25.517 mL NaOH solution/min). The only operating parameter that was varied was the flow rate of HCl/chloroacetate mixture solution. Three different ratios of the mass flow rates of the reacting solutions were studied here (expressed as mass flow rate of HCl/chloroacetate solution to mass flow rate of NaOH solution), i.e., 3.21:1, 5.64:1 and 13.99:1. Three corresponding volumetric flow rates of the HCl/chloroacetate

mixture solution were 84.6mL/min, 144mL/min, and 357mL/min, respectively. In all cases, the molar flow rate of all the reactants needed to be kept constant. Since the flow rated changed, this required changing the concentration of the reactants in solution. Details of the mass ratio, concentrations, volumetric flow rates and other flow data are listed in Table 3.3.

Table 3.3 Mass Ratio, Flow Rate, and Concentration of Reactants

		Mass Ratio of Solutions	Mass Flow Rate (g solution/min)	Volumetric Flow Rate (mL solution/min)	Molar Flow Rate (mol/min)	Solution Concentration (mol/mL)
Sodium Hydroxide Solution			25.517	25.517	1.523×10^{-3}	5.968×10^{-5}
Mixture Solution	Hydrochloric Acid	3.32:1	84.6	84.6	1.523×10^{-3}	1.800×10^{-5}
	Ethyl Chloroacetate				1.523×10^{-3}	1.800×10^{-5}
Sodium Hydroxide Solution			25.517	25.517	2.344×10^{-3}	9.187×10^{-5}
Mixture Solution	Hydrochloric Acid	5.64:1	144	144	2.344×10^{-3}	1.628×10^{-5}
	Ethyl Chloroacetate				2.344×10^{-3}	1.628×10^{-5}
Sodium Hydroxide Solution			25.517	25.517	5.290×10^{-3}	2.073×10^{-4}
Mixture Solution	Hydrochloric Acid	13.99:1	357	357	5.290×10^{-3}	1.482×10^{-5}
	Ethyl Chloroacetate				5.290×10^{-3}	1.482×10^{-5}

If there were no reactions taking place, the final solution would contain the equal molar concentrations, 1.38×10^{-5} mol/mL of NaOH, HCl, and $ClCH_2COOC_2H_5$, which meets the iso-stoichiometric principle.

Due to different volumetric flow rates, the corresponding stream jet velocity and Reynolds number are listed in Table 3.4.

Table 3.4 Volumetric Flow Rate of Chemicals and Corresponding Jet Velocity and Reynolds Number

	NaOH Solution	Mixture Solution
Volumetric Flow Rate (mL/min)	25.517	84.6
Jet Velocity (m/s)	2.167	7.185
Reynolds Number	1211.996	4018.296
Volumetric Flow Rate (mL/min)	25.517	144
Jet Velocity (m/s)	2.167	12.229
Reynolds Number	1211.996	6839.653
Volumetric Flow Rate (mL/min)	25.517	357
Jet Velocity (m/s)	2.167	30.318
Reynolds Number	1211.996	16956.639

The effect of sonication power on the mixing degree was also investigated. Six sonication powers levels were examined: 0 W (no sonication), 50 W, 100 W, 150 W, 200 W, and 250 W. Experiments at different power levels were run at the same volumetric flow rates and formed a set of 18 experimental data set that were studied here. Triplicate experiments were conducted for each experimental condition in order to determined reproducibility, i.e., mean values and standard deviations.

The running time for each experiment was also recorded to calculate the final solution volume. Most of the running times were 30 seconds to 1 minute, in order to save the chemicals.

3.4 Analytical Method

The ethanol yield(X_Q) was derived from the concentration of ethanol so produced, which was found in the final solution. Samples from this solution were collected and analyzed for their ethanol concentration via gas chromatography (GC). In addition, the concentration of the residual ethyl chloroacetate reactant in the final solution was also measured via gas chromatography, so that the correctness of the mass balance could be verified.

A HP 5890 gas chromatograph equipped with two FID detectors and a *Rtx-200* (Crossbond trifluoropropylmethyl polysiloxane) column was used for the analysis. The analysis was conducted using helium as the carried gas at a initial temperature of 55°C. The temperature was kept at 55°C for the initial 10 minutes. After that time, the temperature of column over was increased at the rate of 25°C/min to final temperature 150°C. 1 μL of the sample (sometimes 0.5μL or 2μL, See Appendix A) to be analyzed were injected, the resulting chromatograph was collected by the computer installed with EzChrom Elite Chromatography Data System (Control Software), and analyzed for the peaks corresponding to ethanol and ethyl chloroacetate. Equation 2.2 and 2.3 were used to calculate the concentrations of ethanol and ethyl chloroacetate. A

standard solution containing 1000 mg/L of 99% ethyl chloroacetate and 300 mg/L of

95% ethanol was prepared and used for calibration purposes.

$$C(C_2H_5OH) = \frac{Area_{sample} \times C_{standard} \times 95\%}{Area_{standard}} = \frac{Area_{sample} \times 300\,mg/L \times 95\%}{Area_{standard}} \qquad 2.2$$

$$C(ClCOOC_2H_5) = \frac{Area_{sample} \times C_{standard} \times 99\%}{Area_{standard}} = \frac{Area_{sample} \times 1000\,mg/L \times 99\%}{Area_{standard}} \qquad 2.3$$

Based on the running time, the volumetric flow rates, one could obtain the

mole of ethanol and sodium chloride. Thus the yield of the slow reaction (X_Q) was

calculated.

CHAPTER 4

RESULTS AND DISCUSSION

The raw data in this work include running times for each experiment, and the corresponding GC peak areas for ethanol and ethyl chloroacetate, from which the conversion of ethyl chloroacetate to ethanol and the reaction yield of ethanol produced through the slow reaction were calculated using the equations given in Chapter 3. The ethanol yield could then be obtained for each of the experiments conducted under different operating conditions.

4.1 Ethanol Yield Obtained under Different Operating Conditions

The ethanol yield – the critical parameter to evaluate the mixing effectiveness of the reactor – was obtained as a function of the volumetric flow rate of HCl/ethyl chloroacetate mixture solution and sonication power. The full set of data is provided in Appendix A. Table 4.1 lists the ethanol yield for each triplicate experiment and the corresponding standard deviation.

Table 4.1   Ethanol yield as a function of operating parameters, i.e., volumetric flow

rate of the HCl/ethyl chloroacetate mixture solution and sonication power.

Volumetric flow rate of Mixture Solution (mL/min)	Sonication Power (W)	Ethanol Yield - Average (%)	Ethanol Yield - Standard Deviation (%)
84.6	0	18.349	1.745
	50	7.422	2.428
	100	7.210	2.398
	150	6.765	2.969
	200	5.173	1.496
	250	5.592	2.788
144	0	4.041	1.460
	50	7.089	4.069
	100	6.258	3.123
	150	5.064	2.134
	200	4.324	3.043
	250	3.970	2.877
357	0	1.447	1.250
	50	1.078	1.056
	100	1.816	0.702
	150	2.007	0.920
	200	2.740	0.595
	250	2.521	0.489

4.2   Effect of Sonication Power on Ethanol Yield

Figure 4.1 shows the effect of sonication power on ethanol yield at different

volumetric flow rates of the HCl/ethyl chloroacetate mixture solution (84.6mL/min,

144mL/min, and 357mL/min).
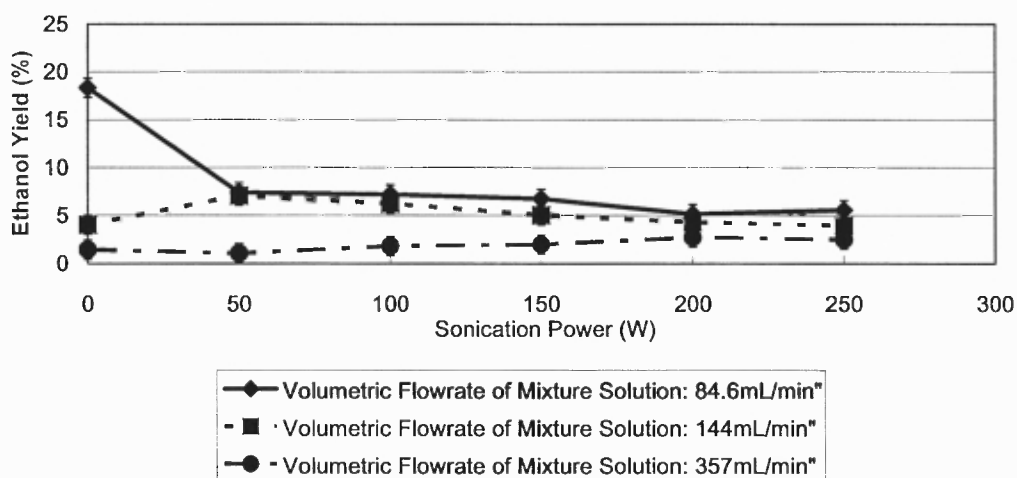
Figure 4.1   Plot of ethanol yield as a function of sonication power for different volumetric flow rates of the mixture solution.

Without sonication (0 W), the ethanol yield was about 18% at a mixture flow rate of 84.6 mL/min. When the sonication was applied, the value of the ethanol yield decreased appreciably to about 8% (50 W sonication). However, when the sonication power level was increased, the yield changed only very slightly.

At a mixture flow rate of 144 mL/min, the yield first increased at a sonication power of 50W, and then decreased slightly. At the highest flow rate (357mL/min), the yield curve was approximately horizontal, implying that the sonication power was not critical.   This can be better observed by examining the average ethanol yield values listed in Table 4.1.

4.3   Effect of Sonication Power on Ethanol Yield

Figure 4.2 shows a plot of the ethanol yield as a function of the volumetric flow rate of the HCl/ethyl chloroacetate mixture solution for different sonication powers.

Figure 4.2   Plot of ethanol yield as a function of volumetric flow rate of mixture solution for different sonication powers

Six curves are presented in this figure showing how the yield changed with different mixture flow rates. Although in most sonicated cases the points on each curve appear to be relatively close to each other, it is evident that the yield always decreased with the increasing mixture flow rates.   The yield changed dramatically with the mixture flow rate only when the reactor was not sonicated, in which case the yield decreased from 18% to 4.041% as the flow rate increased from 84.6 mL/min to 144 mL/min.   However, at a flow rate of 357mL/min, the yield was 1.4% even with no sonication.

In order to better show the effect of mixture volumetric flow rate on yield for the case in which sonication was applied, some of the data in Figure 4.2 were re-plotted in Figure 4.3. This figure clearly shows that increasing the flow rate had a dramatic effect on ethanol yield and hence mixing effectiveness: the higher the flow rate, the better the mixing efficiency. Sonication also had an effect, as one can see from Figure 4.2, but only in comparison to no sonication at all. One even a moderate level of sonication was introduced no benefits were introduced by further increasing the sonication level. In fact, although sonication had a positive effect at low to medium mixture flow rates (up to 144 mL/min), it actually had a limited or even negative effect at the higher flow rate (357mL/min). Therefore, moderate sonication and a high mixture flow rate appear to be most effective in reducing the ethanol yield and hence improve mixing in the reactor.
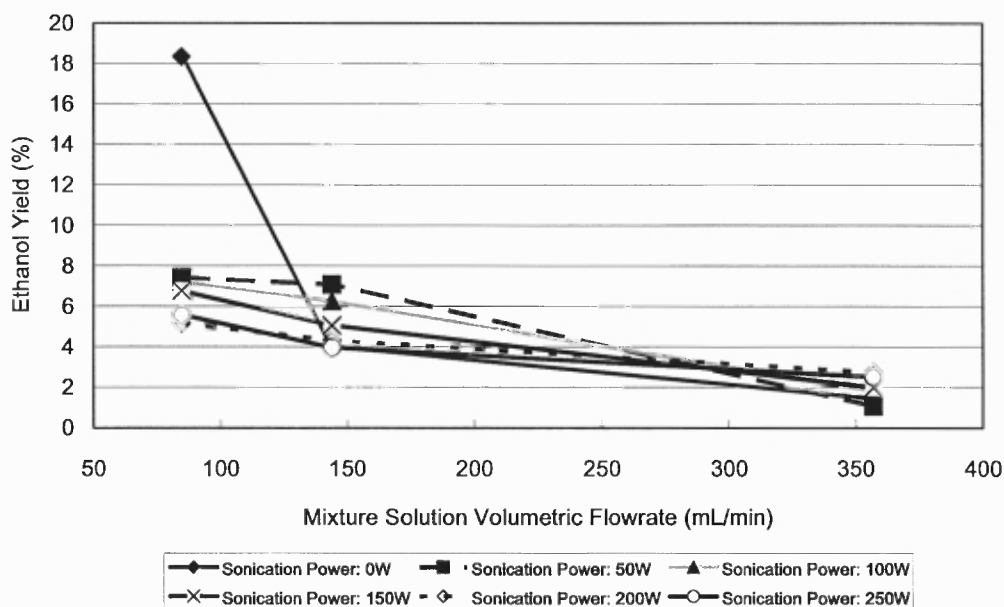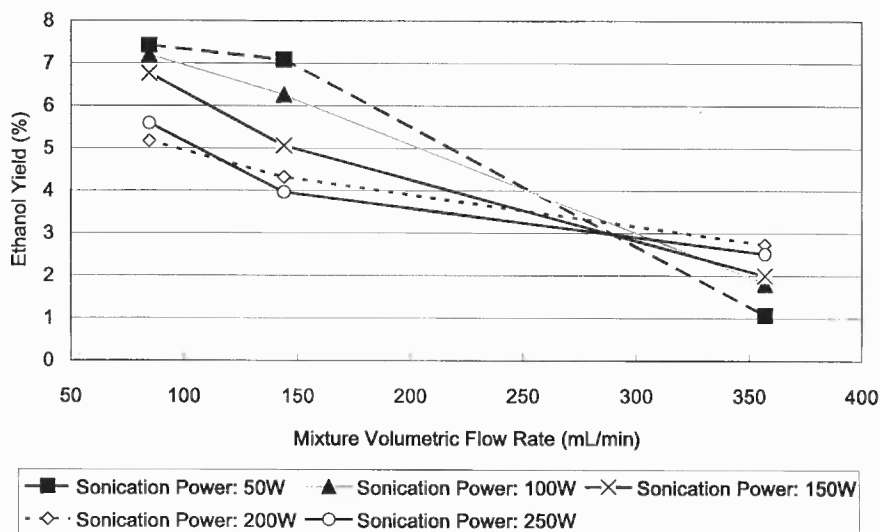

Figure 4.3 Plot of ethanol yield as a function of volumetric flow rate of mixture solution for different applied sonication powers

4.4 Ethanol Yield as a Function of the Modified Damköhler Number

As already mentioned in Chapter 2, the dimensionless Damköhler number represents the ratio of mixing time to reaction time in liquid mixing process. If the Damköhler number is very high, then the mixing time is much larger than the reaction time, and mixing will be the controlling process. This is a common case when the reaction rate is very fast. In such a case, a small, high mixing intensity reactor such as the reactor studied here can be a better choice than a larger, slow-mixing reactor such as a stirred tank.

Here the ethanol yield was plotted as a function of the modified Damköhler number (Da'), as calculated from Equation 2.7. The results are shown in Figure 4.3. Since the reactions and the reaction times were fixed (and hence the reaction time), the only parameter that could be changed in the Damköhler number was the mixing time, which is inversely proportional to the flow rate, and hence, for constant jet diameters, the jet velocities. Furthermore, since one of the flow rates in the impinging jets reactor was fixed the reactor mixing time depended only on the flow rate of the other jet, i.e., the mixture flow rate, which could take three values. Therefore, the modified Damköhler numbers (Da') associated with each mixture flow rate, were found to be equal to 0.0796, 0.0552, and 0.0319 respectively.
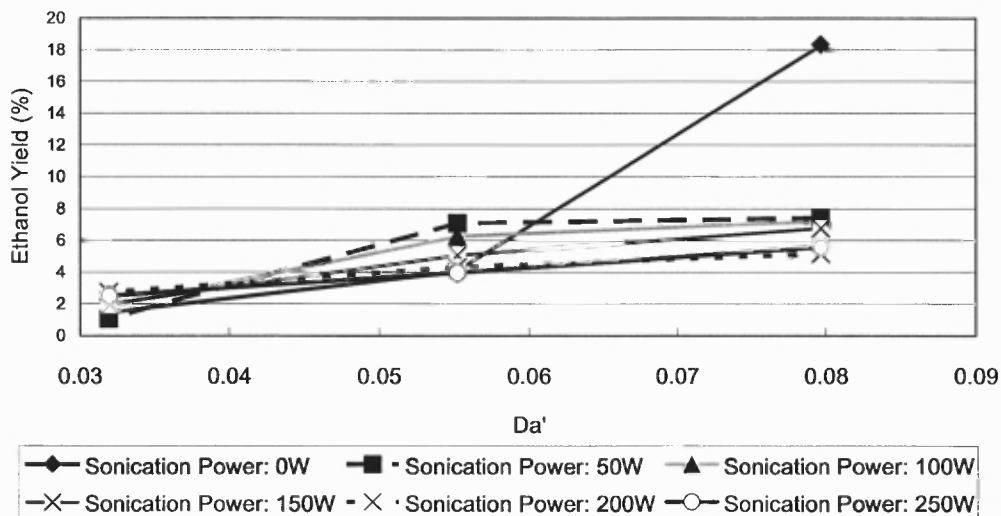
Figure 4.4 Plot of the ethanol yield as a function of the modified Damköhler number (Da') for different sonicaton powers.

Figure 4.3 shows that the ethanol yield increases with the increasing modified Damköhler number (Da'), as expected. At low modified Damköhler Number, the mixing time is short compared with reaction time. The corresponding yield is also value, and it is about 1% to 3%. In this situation, very little NaOH reacted with ethyl chloroacetate ($ClCH_2COOC_2H_5$), while the neutralization reaction accounted for a very large percentage of the NaOH used in the whole reaction process.

This is caused by different reaction rate for the two reactions. Neutralization reaction are very fast, and this implies that as soon as the NaOH and HCl are contacted they react. Improved mixing also implies that local depletion of HCl is minimized, thus reducing the opportunity for the ethyl chloroacetate to react with HCl to form ethanol.

In Figure 4.5 the same data shown in Figure 4.4 are reported, with the exception of the no sonication data, in order to better evidence the low ethanol yield at low Damköhler number. This figure clearly shows that the ethanol yield is proportional to Damköhler number.
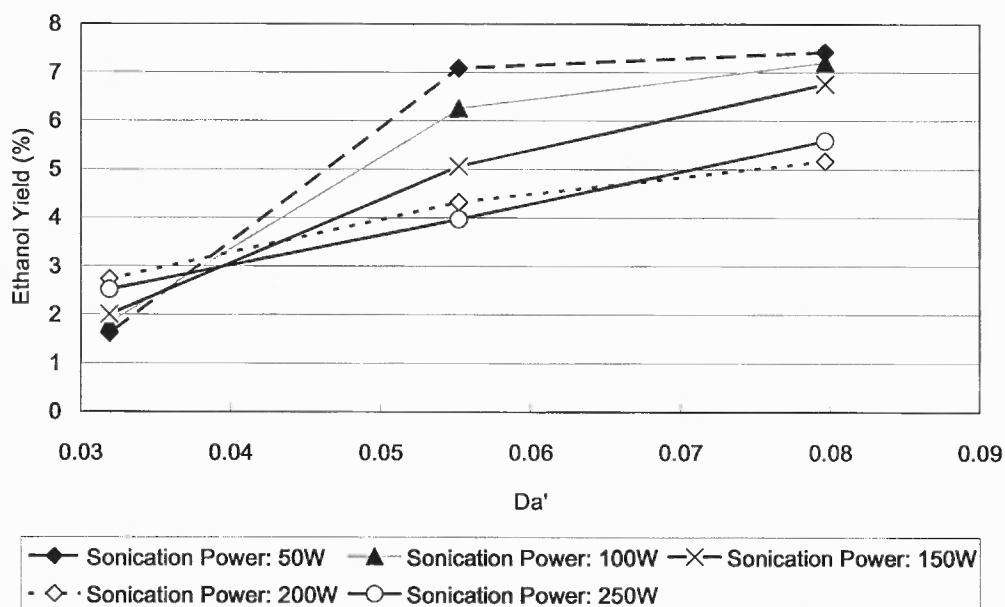
Figure 4.5 Plot of ethanol yield as a function of modified Damkohler number (Da') for different applied sonication powers

4.5 Sources of Experimental Error

The data obtained in this work were associated with experimental error that could be attributed, in part, to some known factors. Firstly, the results could have been affected by the fluctuating value of the flow rate. In this work, the flow rates of the reactant solutions were measured with rotameters and were controlled by the valves on the by-pass systems connected to each pump. Under ideal conditions, the stable position of the stainless steel ball in the rotometer indicated the flow rate. However, during some of the experiments, the ball was not stable in the rotometer, making

reading the flow rate value difficult and introducing error. Occasionally when one of the valves was adjusted slightly to control the flow rate, there was a lag time between the adjustment and the change in flow rate measured by the rotameter. Furthermore, the reactants were fed at a stoichiometric ratio of one. This was achieved by preparing solutions of different concentrations to meet the requirement of different flow rates. However, if the flow rate was not stable during operation, the molar ratio of the reactants in the reactor was not exactly stoichiometric at all times in the reactor and the final conversion could be affected. In order to minimize the effect of unstable flow rate, at least three triplicate experiments for the same operating conditions were conducted (same flow rate and same sonication power).

Secondly, error was introduced during the sample analysis. The product solution was analyzed by gas chromatography to get the concentrations of ethanol and unreacted ethyl chloroacetate. Many ethanol concentrations were below 10 mg ethanol/L, which is a small concentration to determine via GC, since the detection limit was ~ 5 mg/L. Another factor possibly introducing error in the GC measurement was the fluctuating base line which, on occasion, even overlapped the ethanol peak.

CHAPTER 5

CONCLUSIONS AND RECOMMENDATIONS
FOR FUTURE RESEARCH WORK

The sonicated confined impinging jets reactor studied here appears to produce rapid

mixing of the reactants fed to it, thus making the reaction process mixing-independent

or less mixing dependent than other mixing systems such as stirred tanks.

Additional, specific conclusions can be drawn as follows:

- The reaction system used here to measure mixing effectiveness appears to vey

  mixing sensitive and thus appropriate for the study of the mixing effectiveness

  of the impinging jets reactor system used here. This was determined by

  measuring the concentration of the ethanol formed in the slower of the two

  parallel mixing-sensitive reactions used here for this purpose. This

  concentration was found to decrease when the mixing intensity generated by

  increasing the jet flow rate and sonication intensity in the reactor was

  intensified;

- It was experimentally found that improved mixing, quantified by the reduced

  production of ethanol, was achieved by increasing the volumetric flow rate of

  one of the streams fed to the reactor with or without the presence of

  sonication;

- If sonication was applied, mixing was additionally improved, and it was even

  further improved when a higher sonication power was applied. This trend was

  especially evident at lower flow rates;

- At higher flow rates, sonication played a smaller role

- A quantitative comparison of the results based on the use of a modified Damköhler number, Da', showed that as Da' increased the mixing effectiveness decreased.

Suggestions for future research work include:

- Study the effect of initial concentration on conversion: Increasing the concentration can also help reduce some of the analytical issue observed here when mixing was enhanced and the concentration of ethanol in the final product was very low and difficult to measure via GC analysis;

- Study the effect of the velocity of the jet carrying the limiting reactant (NaOH) while also varying the other jet velocity;

- Study the effect of different jet diameter;

- Study the effect of jet angle on conversion.

APPENDIX

TABLE OF EXPERIMENTAL DATA

Exp No.	Concentration (mol/L)		Volumetric Flow Rate (mL/min)		Sonication Power (W)	Run Time (s)	Peak Area		Conversion (%)
	NaOH Solution	Mixture Solution	NaOH Solution	Mixture Solution			Ethanol	Ethyl Chloroacetate	
1[(1)]	0.05968	0.018	25.517	84.6	0	4'00"51/100	1619	No Signal	18.62
2	0.05968	0.018	25.517	84.6	0	4'00'"56/100	1566	No Signal	18.01
3	0.05968	0.018	25.517	84.6	0	4'00"42/100	1783	No Signal	20.50
4	0.05968	0.018	25.517	84.6	0	4'00"65/100	1415	No Signal	16.27
5[(2)]	0.05968	0.018	25.517	84.6	50	2'41"04/100	552	No Signal	6.33
6	0.05968	0.018	25.517	84.6	100	2'00"65/100	660	No Signal	7.56
7	0.05968	0.018	25.517	84.6	150	2'00"63/100	389	No Signal	4.47
8	0.05968	0.018	25.517	84.6	200	2'00"57/100	287	No Signal	3.30
9	0.05968	0.018	25.517	84.6	250	2'00"27/100	340	No Signal	3.91
10	0.05968	0.018	25.517	84.6	250	2'00"49/100	505	No Signal	5.80
11	0.05968	0.018	25.517	84.6	200	2'00"35/100	405	No Signal	4.65
12	0.05968	0.018	25.517	84.6	150	2'00"59/100	496	No Signal	5.70
13	0.05968	0.018	25.517	84.6	100	2'00"66/100	394	No Signal	4.53
14	0.05968	0.018	25.517	84.6	50	2'00"52/100	564	No Signal	6.49
15	0.05968	0.018	25.517	84.6	50	1'30"86/100	960	No Signal	11.04
16	0.05968	0.018	25.517	84.6	100	1'32"27/100	893	No Signal	10.27
17	0.05968	0.018	25.517	84.6	150	1'30"84/100	880	No Signal	10.12
18	0.05968	0.018	25.517	84.6	200	1'22"92/100	538	No Signal	6.19
19	0.05968	0.018	25.517	84.6	250	2'00"79/100	821	No Signal	9.44
20	0.05968	0.018	25.517	84.6	100	2'00"65/100	561	No Signal	6.45
21	0.05968	0.018	25.517	84.6	50	1'28"85/100	506	No Signal	5.82
22	0.05968	0.018	25.517	84.6	150	1'00"22/100	650	No Signal	7.47
23	0.05968	0.018	25.517	84.6	200	1'03"34/100	570	No Signal	6.55
24	0.05968	0.018	25.517	84.6	250	1'07"98/100	280	No Signal	3.22
25	0.09187	0.01628	25.517	144	50	1'30"66/100	467	No Signal	5.37
26	0.09187	0.01628	25.517	144	100	1'00"66/100	526	No Signal	6.05
27	0.09187	0.01628	25.517	144	100	1'03"95/100	449	No Signal	5.16
28	0.09187	0.01628	25.517	144	200	41"20/100	387	No Signal	4.45
29	0.09187	0.01628	25.517	144	150	50"86/100	396	No Signal	4.55

TABLE OF EXPERIMENTAL DATA
(Continued)

Exp No.	Concentration (mol/L)		Volumetric Flow Rate (mL/min)		Sonication Power (W)	Run Time (s)	Peak Area		Conversion (%)
	NaOH Solution	Mixture Solution	NaOH Solution	Mixture Solution			Ethanol	Ethyl Chloroacetate	
30	0.09187	0.01628	25.517	144	250	34"25/100	298	No Signal	3.43
31	0.09187	0.01628	25.517	144	200	28"23/100	0	No Signal	0
32	0.09187	0.01628	25.517	144	250	50"34/100	0	No Signal	0
33	0.09187	0.01628	25.517	144	150	51"36/100	267	No Signal	3.07
34	0.09187	0.01628	25.517	144	50	1'02"36/100	4597	No Signal	11.96
35[3]	0.09187	0.01628	25.517	144	100	57"27/100	2640	No Signal	6.87
36	0.09187	0.01628	25.517	144	150	50"63/100	2659	No Signal	6.92
37	0.09187	0.01628	25.517	144	200	51"61/100	2554	No Signal	6.64
38	0.09187	0.01628	25.517	144	250	51"14/100	2525	No Signal	6.57
39	0.09187	0.01628	25.517	144	250	38"65/100	2685	No Signal	6.98
40	0.09187	0.01628	25.517	144	200	29"95/100	2932	No Signal	7.63
41	0.09187	0.01628	25.517	144	150	28"38/100	2946	No Signal	7.66
42	0.09187	0.01628	25.517	144	100	28"66/100	3318	No Signal	10.92
43	0.09187	0.01628	25.517	144	50	29"10/100	3267	No Signal	8.50
44	0.09187	0.01628	25.517	144	0	53"86/100	2092	No Signal	5.44
45	0.09187	0.01628	25.517	144	0	35"21/100	954	No Signal	2.48
46	0.09187	0.01628	25.517	144	0	29"78/100	1245	No Signal	3.24
47[4]	0.09187	0.01628	25.517	144	0	58"99/100	987	No Signal	5.75
48	0.09187	0.01628	25.517	144	0	52"71/100	565	No Signal	3.29
49	0.09187	0.01628	25.517	144	50	24"38/100	434	No Signal	2.53
50	0.09187	0.01628	25.517	144	100	33"42/100	394	No Signal	2.30
51	0.09187	0.01628	25.517	144	150	24"49/100	535	No Signal	3.12
52	0.09187	0.01628	25.517	144	200	20"65/100	498	No Signal	2.90
53	0.09187	0.01628	25.517	144	250	16"44/100	493	No Signal	2.87
54	0.2973	0.01482	25.517	357	0	26"44/100	0	No Signal	0
55	0.2973	0.01482	25.517	357	0	29"84/100	0	No Signal	0
56	0.2973	0.01482	25.517	357	0	30"54/100	536	No Signal	3.122
57	0.2973	0.01482	25.517	357	0	26"08/100	480	No Signal	2.80
58[5]	0.2973	0.01482	25.517	357	0	28"00/100	191	16138	1.08
59	0.2973	0.01482	25.517	357	0	40"65/100	197	12141	1.12
60	0.2973	0.01482	25.517	357	50	31"37/100	0	18056	0

TABLE OF EXPERIMENTAL DATA
(Continued)

Exp No.	Concentration (mol/L)		Volumetric Flow Rate (mL/min)		Sonication Power (W)	Run Time (s)	Peak Area		Conversion (%)
	NaOH Solution	Mixture Solution	NaOH Solution	Mixture Solution			Ethanol	Ethyl Chloroacetate	
61	0.2973	0.01482	25.517	357	100	45"66/100	235	11805	1.33
62	0.2973	0.01482	25.517	357	150	42"00/100	244	7298	1.38
63	0.2973	0.01482	25.517	357	200	47"66/100	539	16094	3.06
64	0.2973	0.01482	25.517	357	250	48"81/100	379	11434	2.15
65	0.2973	0.01482	25.517	357	250	45"96/100	542	11022	3.08
66	0.2973	0.01482	25.517	357	200	53"85/100	548	14160	3.11
67	0.2973	0.01482	25.517	357	150	56"02/100	540	11486	3.06
68	0.2973	0.01482	25.517	357	100	1'04"86/100	462	11151	2.62
69	0.2973	0.01482	25.517	357	50	1'35"34/100	372	12588	2.11
70	0.2973	0.01482	25.517	357	50	58"38/100	198	12680	1.12
71	0.2973	0.01482	25.517	357	100	57"31/100	263	12811	1.49
72	0.2973	0.01482	25.517	357	150	50"13/100	277	14963	1.57
73	0.2973	0.01482	25.517	357	200	38"49/100	362	17016	2.05
74	0.2973	0.01482	25.517	357	250	48"05/100	412	19129	2.34
75	0.2973	0.01482	25.517	357	50	47"88/100	354	14701	2.01

Comments:

(1) Standard Solution for Exp No. 1 ~4   Concentration: 300mg/L Ethanol + 1000mg/L Ethyl Chloroacetate;
   Injection Volume: 0.5μL; Peak Area of Ethanol: 3895; Peak Area of Ethyl Chloroacetate: No signal

(2) Standard Solution for Exp No. 5~34   Concentrations of Ethanol: 75mg/L, 100mg/L, 200mg/L, 300mg/L, 500mg/L
   Slope of Calibration Curve: 13.671

(3) Standard Solution for Exp No. 35~46   Concentration: 300mg/L Ethanol + 1000mg/L Ethyl Chloroacetate;
   Injection Volume: 2μL; Peak Area of Ethanol: 17223; Peak Area of Ethyl Chloroacetate: No signal

(4) Standard Solution for Exp No. 47~57   Concentration: 300mg/L Ethanol + 1000mg/L Ethyl Chloroacetate;
   Injection Volume: 1μL; Peak Area of Ethanol: 7690; Peak Area of Ethyl Chloroacetate: No signal

(5) Standard Solution for Exp No. 58~75   Concentration: 300mg/L Ethanol + 1000mg/L Ethyl Chloroacetate;
   Injection Volume: 1μL; Peak Area of Ethanol: 7897; Peak Area of Ethyl Chloroacetate: 7255

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