DEVELOPMENT OF SPECTROPHOTOMETRIC MEASUREMENT AND CONTROL OF MINIATURIZED INTENSIFIED SYSTEM

by

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Thesis submitted in fulfillment of the requirements
for the degree of
Master of Science

June 2009

ACKNOWLEDGEMENT

First, I would like to thank the Almighty God upon the accomplishment of my studies. I would like to express my genuine gratitude to my supervisor, Deputy Dean of School of Chemical Engineering, Dr. Syamsul Rizal Abd Shukor for his wonderful supervision and the enormous time and effort he spent guiding and assisting me despite being extremely busy. And also for his endless support in each and every step of my research. I will always remember him as a great person with a smiling face. I would also like to extend my gratitude to my co supervisor, Dean of School of Chemical Engineering, Prof. Dr. Abdul Latif Ahmad for his support and encouragement. I was really honored to have the opportunity to work under the supervision of them.

I would also like to express my appreciation to the Deputy Dean, Dr. Zainal Ahmad for his continuous support, kind guidelines and assistance rendered throughout my studies. I should also express my utmost appreciation to Dr. Norashid Bin Aziz for his fruitful comments throughout my research. My sincere thanks to all the respective lecturers, staff and technicians, School of Chemical Engineering for their cooperation and support. My sincere thanks to Mr. Shamsul Hidayat Shaharan for the fabrication of my experimental rig and Mr. Mohd. Faiza Ismail, Mr Aziz Ismail, Mr. Mohd Rasydan Omar and Mr. Syed Nor Izwan Said Muliyana for their valuable and kind assistance with my laboratory works. I highly appreciate all the help and supports from Mrs. Aniza Abd. Ghani for her assistance in the official work during my studies.

The financial support provided by Universiti Sains Malaysia (School of Chemical Engineering) as a short term grant (No. 6035132) and also eScience Fund (No. 6013358) is gratefully acknowledged

I would like to express my deepest gratitude to all my adored friends, in Malaysia and in Iran for their support, kindness and moral support towards me. Thank you for always being there for me. I hope we all have a very bright future ahead.

Last but definitely not least, my deepest and most heart-felt gratitude to my beloved mum, Mrs. Ashraf Seifattari and my adored dad, Mr. Houshang Barzin for their endless love and support. I would like to dedicate this Master thesis to them. To my wonderful sisters, Yalda and Neda, my kind brothers in law Mr. Amir Jafari and Mr. Babak Fattahi and my lovely nephews, Nastaran, Dorsa and Niloofar for their love and care. To those who are directly and indirectly involved in this research, your contribution given shall not be forgotten. My appreciation to all of you.

Reza Barzin

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LIST OF ABBREVIATION

AR	Absorption Ratio
BCP	Bromocresol Purple
CMV	Constrained Minimum Variance
CSTR	Continuous Stirred-Tank Reactor
DNA	Deoxyribonucleic Acid
DR	Direct Synthesis
DS	Direct Synthesis
FPAA	Field Programmable Analog Arrays
FPGA	Field Programmable Gate Arrays
GUI	Graphical User Interface
HPLC	High Pressure Liquid Chromatography
HR	Half Rule
IAE	Integral Absolute Error
IMC	Internal Model Control
ISE	Integral Of The Squared Error
ITAE	Integral Of The Time-Weighted Absolute Error
MCPs	Micro Plant Systems
MM	Method of Moments
MPC	Model Predictive Control
MV	Minimum Variance
NIR	Near Infra Red
PCR	Polymerase Chain Reaction

PP	Pole Placement
PR	Phenol Red
QGPC	Quadratic Generalized Predictive Control
RD	Reactive Distillation
SDR	Spinning Disc Reactor
SEAS	Spectrophotometric Elemental Analysis System
SIT	Simulation Interface Toolkit
SoC	System-On-A-Chip
SP	Set Point
SSIMM	Standard Slit Interdigital Micro Mixer
STQGPC	Self-Tuning Quadratic Generalized Predictive Control
TRD	Time Residence Distribution
UV	Ultra Violet
VIS	Visible
Z–N	Ziegler–Nichols

LIST OF SYMBOLS

		Unit
A	Absorbance	
G_c	Controller transfer function	
G_p	Actual transfer function of process	
G_m	Actual transfer function of Measurement	
G_v	Actual function of final control element	
G_K	Low pass filter transfer function	
$\widetilde{G}_p$	Model of process transfer function	
$\widetilde{G}_m$	Model of measurement transfer function	
$\widetilde{G}_p$	Model of final control element transfer fuction	
K_p	Process gain	
K_c	Controller gain	
K_m	Measurement gain	
K_v	Valve gain	
S_s	Desired closed loop transfer function	
Y_{sp}	Set-point	
Y	Controlled variable	
C	Concentration	mol/lit
b	Path length	m
R	Spectrometric absorbance ratio	
e	Molar absorbance ratio	

K'_a	Dissociation constant	
pK_a	Negative log of apparent dissociation	
t	Time	s
M	Moment of system	

Greek symbols		Unit
ε	Molar absorptivity	m^2/mol
θ	Process time delay	s
λ	Wave length	nm
τ_D	Derivative term	s
τ_D^2	Second derivative term	s
τ_I	Integrative term	s
τ_m	Measurement time constant	s
τ_p	Process time constant	s
τ_v	Valve time constant	s

PEMBANGUNAN PENGUKURAN SPEKTROFOTOMETRIK UNTUK KAWALAN PROSES SISTEM TERINTENSIF KECIL

ABSTRAK

Proses intensifikasi pergamatan dianggap sebagai cara terbaik kearah industri kimia yang lebih selamat, lebih bersih dan lebih murah. Walaupun pelbagai usaha dibuat kearah rekabentuk proses dan fleksibiliti konsep PI berserta dengan percubaan untuk membuktikan parameter kekunci rekabentuk bagi pelbagai unit proses, namun hanya sedikit kajian dilaporkan berkenaan kawalan proses bagi sistem terintensif terutamanya sistem terintensif terkecil. Tambahan pula ketiadaan pengukuran dan unsur pengawalan akhir yang sesuai menjadi masalah utama dalam mengawal peranti terintensif ini.

MATLAB® 2006a dan SIMULINK® *toolbox* digunakan dalam kajian simulasi untuk memahami masalah kawalan proses bagi sistem model kecil terintensif terkecil. Kaedah sintesis terus digunakan untuk merekabentuk pengawal yang menghasilkan pengawal PIDD bukan konvensional bersama penapis laluan rendah tertib pertama. Kaedah penurunan model digunakan untuk menurunkan tertib pengawal kepada pengawal PID konvensional, untuk mengatasi masalah apabila pengawal PIDD digunakan. Berdasarkan keputusan simulasi, satu eksperimen bagi sistem terintensif terkecil direkabantuk dan dibangunkan. Satu eksperimen dihubungkan antara muka pergguna bergraf melalui perisian LabVIEW® 8.2 Student Edition berserta dengan pengawal dalam persekitaran MATLAB®. Keputusan simulasi menunjukkan masa lengah proses, pengukuran masa malar dan masa malar bagi gelung tertutup memainkan peranan penting dalam kawalan sistem terintensif

terkecil. Pengawal tidak mampu berperanan untuk proses dengan $\theta/\lambda > 1$. Ujian gelung-buka menunjukkan prestasi yang baik dengan sistem pengukuran yang mengurangkan masa lengah proses dan juga pengukuran masa malar. Ujian gelung tertutup juga menunjukkan prestasi pengawal yang sangat pantas untuk pengesanan titik set dan ujian penolakan gangguan.

DEVELOPMENT OF SPECTROPHOTOMETRIC MEASUREMENT FOR PROCESS CONTROL OF MINIATURIZED INTENSIFIED SYSTEM

ABSTRACT

Process intensification deemed the most suitable pathway to safer, cleaner and cheaper chemical industry. Nevertheless, despite the great effort that has been directed towards the process design and feasibilities of PI concept as well as attempting to establish key design parameters of various process units, relatively few works have been reported on the control of intensified system especially miniaturized intensified systems. In addition, the unavailability of suitable measurement and final control elements seems to be one of the main problems in controlling these new developed intensified devices.

MATLAB® 2006a and SIMULINK® toolbox were used for simulation study in order to have better understanding of the control problem of miniaturized intensified system. A direct synthesis method was applied for designing the controller which results in unconventional PIDD controller plus first order low pass filter. Based on the simulation results, the miniaturized intensified experimental rig was designed and developed. The experimental rig is linked with graphical user interface via LabVIEW® 8.2 Student Edition software with embedded controller in MATLAB® environment. Simulation results shows that process time delay, measurement time constant and desired closed loop time constant play critical role in control of miniaturized intensified systems where controller is not able to handle the process with $\theta/\lambda > 1$. Open-loop test demonstrated the outstanding performance of designed measurement system reducing the process time delay to 1.2 second as well as

measurement time constant to 5-10 milliseconds. Closed loop test also indicated very fast controller performance for both set-point tracking (with corresponding settling time of 4.2 seconds) and disturbance rejection tests.

CHAPTER 1

INTRODUCTION

1.1 Modern Chemical Industry

Advanced chemical engineering industries always move in the direction of producing high quality products at lower cost with more rapid response to the daily increasing customer demand which is also tolerating the constraints from public regarding to the safety and being environmental friendly. The production of high quality products needs precise control in the process parameters such as flow pattern, temperature, pH, residence time, but due to the inherent limitations of conventional systems it is difficult to satisfy these requirements using conventional process plants (Hasebe, 2004). For instance temperature control for highly exothermic reaction can hardly be achieved using normal continuous stirred tank reactors (CSTR) systems due to their inherently poor mixing and heat transfer. Heat transfer and mixing problem is more complicated for high viscosity fluid reactions such as polymerization reactions which cause further difficulties in the heat and mass transfer using conventional reactors. Moreover in order to achieve high quality products for selective reactions, accurate residence time is essential. But due to the large volume of conventional chemical systems it seems to be impossible to achieve the desired residence time.

Safety has always been one of the most critical factors in chemical engineering industry. Processing the highly toxic or explosive materials using conventional large volume devices, can oftenly end up with a tragedy. Because even a single small mistake, either in designing or the control of the process can end up with a massive explosion or releasing the highly toxic chemicals to the environment similar to that

happened in Bhopal where poisonous intermediate (methyl isocyanate) was released because of the explosion killing 4000 people (Moulijn et al., 2008).

Scaling up is one of the other main problems that slows down the process of response to the market demand. Production at industrial scale necessitates the need for scaling up from lab scale to industrial scale. Even if the process design is aided by advanced and powerful computational tools, there are many complicated steps still required for scaling up from laboratory size to mini plant size and later to industrial plants. Scaling up process is usually very expensive and time consuming and also some properties such as mixing are totally different in small and large scale that makes the scaling up process further complicated.

1.2 Process Intensification

In order to achieve the production objectives in modern chemical industry, there is a new trend in chemical engineering which is able to facilitate the achievement of those objectives namely *process intensification* (PI). PI is a revolutionary approach to design, development and implementation of process and plant. It is a strategy of making dramatic reductions in the size of unit operations within chemical plants, in order to achieve given production objectives (Nigam and Larachi, 2005). PI can be done in two different ways, intensification via downsizing process equipments or intensification done by methods, where generally both will results in much faster processes comparing to the conventional processes.

In general PI consists of novel apparatus and techniques that comparing to the conventional technology can dramatically improve the manufacturing and processing industries. This can be achieved by decreasing the equipment size/production

capacity ratio, energy consumption, or waste production. Moulijn et al., (2008) defined process intensification as “producing much more with much less”.

PI was introduced by Colin Ramshaw in 1970s at ICI New Science Group. Now, after three decades, there are numerous researches that have been conducted on the process intensification to facilitate development of new apparatus as well as new methods for PI industry. Large number of new devices have been designed and manufactured based on the PI concept and further researches are being carried out on optimizing the design concept. Examples of the developed PI equipment are rotating packed bed columns (HiGee), spinning disc reactor, oscillating flow reactor, different types of microreactors, supersonic gas liquid reactor and static mixer catalysts to name a few. Among the PI equipments there are few number of equipments which have been existed in chemical industry even before the existence of PI technology but their potential had not been fully exploited such as compact heat exchangers, structured packed columns, static mixers, etc.

1.2.1 Advantages of Process Intensification

Many researches were conducted to demonstrate the superior performance of these new chemical engineering devices over conventional chemical devices. Higher mass and heat transfer can be achieved in miniaturized intensified system as a result of their high surface per volume characteristic. Advantages such as high mixing performance, even in very high viscosity liquids, lower reaction time , less energy consumption, reduced impurity level, less waste and by product, elimination of scaling up, fast response to the market demand and finally better company image, are some of the advantages that can be achieved using PI technology. Furthermore PI

can lead to production of new products that could not be produced using conventional devices (Moulijn et al., 2008).

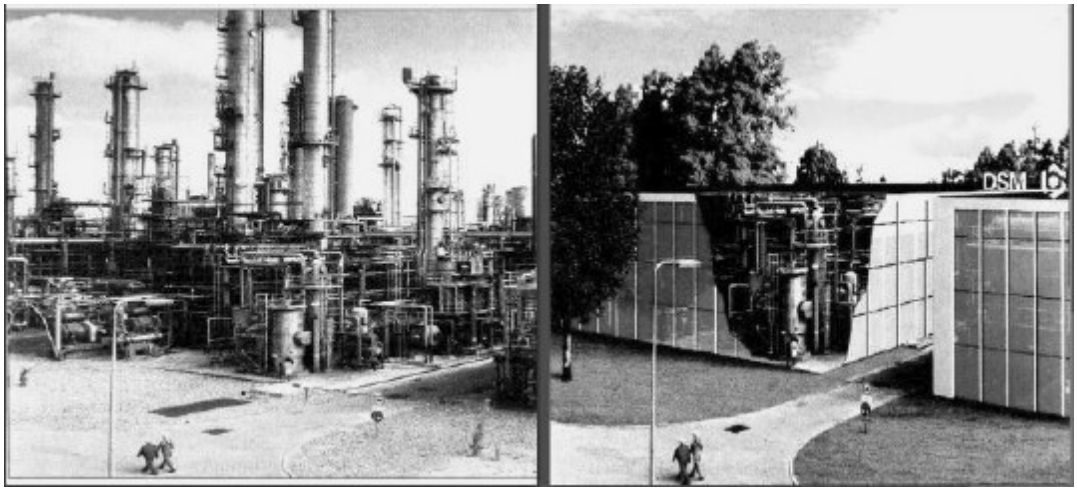

Figure 1.1: One vision of how a future plant employing process intensification may look (right) versus a conventional plant (left)(Charpentier, 2005)**.**

Dramatical size and time reduction can be achieved using PI technology even at industrial level as shown in Figure 1.1. For instance, a conventional methane steam reformer plant for production of 20 million standard cubic feet per day of hydrogen needs a large volume of 30 m × 30 m × 30 m. Contact time for the mentioned industrial scale process is about 1 second. Using a PI technology for the same hydrogen production plant with equal production capacity, can be done in much smaller size of 3.9 m × 5.8 m × 3.9 m, and 100 times faster (contact time equal to 900μs) comparing to conventional plant (Tonkovich et al., 2007). Capitalizing on PI technology can provide the possibilities of utilizing continuous rather than conventional batch systems with much smaller volume. For example phosphorus trichloride production takes place in 3 batch reactors aggregation to 34 m^3 volume where the production capacity is 500 tons per month. Utilizing PI technology would bring down the reactor volume to 0.5 m^3 to produce 700 tones per month (CCD India, 2008).

Different PI systems can be applied to different industrial problems for example spinning disc reactors can be used for exothermic polymerization reactions because of high mixing and heat transfer characteristics even for high viscosity liquids (Boodhoo and Jachuck, 2000a, b) and also its unique design makes it ideal for photocatalytic and photopolymerization reactions (Boodhoo et al., 2004; Yatmaz et al., 2001). Fine chemical and pharmaceutical industries are another attractive area for using intensified systems because intensified systems do not require costly scaling up process and consequently the product can be used directly from laboratory stage. Miniaturized intensified systems has also been used for production of highly toxic or highly explosive materials (such as TNT) due to their small process volume because for case of any system breakdown, released amount can be easily contained (CCD India, 2008).

Actually there are some disadvantages for example; the idea for intensified systems is to design equipment to minimize the inventory of hazardous material so that the safety and environmental consequences of loss of containment are reduced in the event of a large leak from the process equipment. However, as a result of having small holdups, there are several problems on the dynamic controllability of these processes.

1.3 Microreactors

Microreactors are an example of miniaturized equipment and one of the most attractive devices among intensified systems which opened up new pathway on the chemical engineering production. Microreactors provide an environment for mixing of two or more chemical components using various principles with respect to the reaction requirements. Mixing in microreactors can be divided into active and

passive mixing techniques (Kockmann et al., 2006) where for active mixing, energy input from exterior is used whereas for passive mixing, flow energy is used which results in faster mixing comparing to the active mixing (Hessel et al., 2005). Different micro-mixing technologies can be applied for different microreactors according to the particular reaction nature. Figure 1.2 shows example of commercially available microreactors.

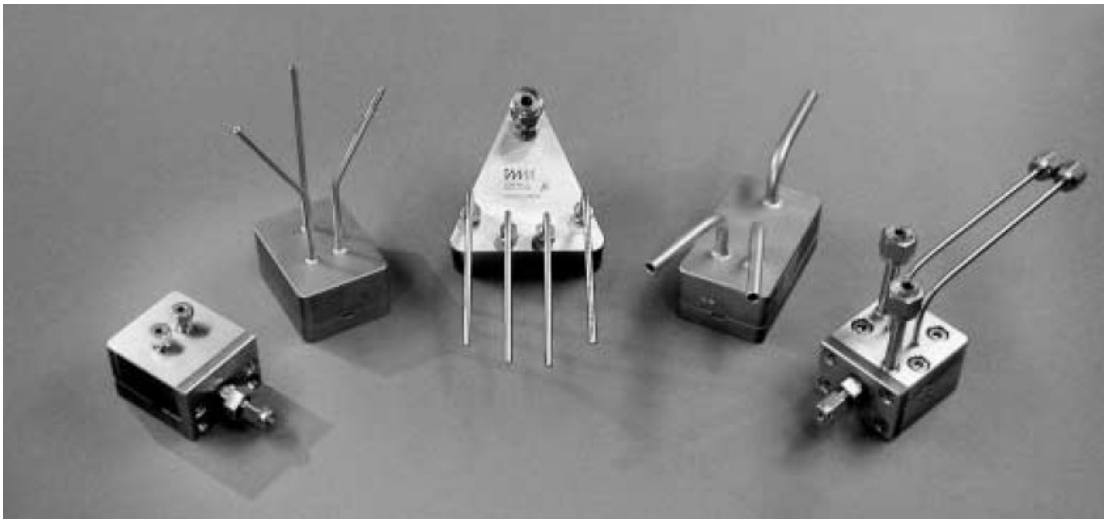

Figure 1.2: Caterpillar split-recombine micromixer (IMM, 2007)

Unique characteristics of microreactors make them suitable for wide range of reactions. For example having very small hold up and very fast mixing performance as fast as 10 ms (Hessel et al., 2003) make them suitable for selective reactions such as selective hydrogenization reactions (Rebrov et al., 2009). Owing to small volume and high surface to volume ratio, precise temperature control can be achieved for exothermic reactions in microreactors and this makes them highly attractive for catalytic reaction (Nakamura et al., 2004). Microreactors are also ideal devices for synthesis of very expensive chemicals or biological researches due to its perfect mixing ability in very small quantities and continuous manner.

1.4 Problem Statement

In the quest of automation and control of product quality, and also deciding on the best operating conditions, suitable process control design is essential (McGreavy, 1983). Unfortunately, despite the great effort that has been directed towards the process design and providing feasibility of PI concept as well as attempting to establish key design parameters for various process units, little investigation have been reported on the control of such systems. Unless these devices are to be controlled properly, advantages of having PI technology would not be achieved and current developed devices would not be complete for commercialization.

Due to the different nature and required control strategy, intensified systems can be classified into two categories. Frist category is the hybrid systems which is the result of integration of several operations in a single apparatus. They do not require highly swift control action (in comparison with low volume intensified systems) such as reactive distillation columns but they are rather complex systems. The second category is the low volume intensified systems in which having a small hold up enabling the reactors to be highly responsive such as spinning disc reactor or other miniaturized intensified systems such as microreactors. Consequently, low volume intensified systems require swift control systems in order to perform proper control action.

Low volume devices such as microreactors, spinning disc reactors, static mixer reactor and monolithic reactor seems to be the candidates for control faliure. The problems in controlling the miniaturized intensified systems are presented below:

1. Having very short residence time due to the small volume whilst maintaining almost the same throughput as the conventional devices, results in very fast responsive devices. Consequently the measurement

errors that could easily be neglected in conventional devices can introduce significant error in intensified systems.

2. Typical measurements and final control elements might not be suitable for the fast responsive low volume intensified systems. Conventionally available measurement systems usually have very large volume comparing to very small hold up of the low volume intensified systems.
3. Final control elements also are not fast enough to cope with low volume intensified systems in order to do proper control action. It is obvious that when a new technology is been developed, new compatible instruments should also be developed to suite the requirements of the new developed technology.

In other word, new developed intensified systems might not be able to operate using conventional measurement and final control elements. Consequently, development of new final control elements and new measurement systems (well-suited to intensified systems requirement) is vital.

Miniaturized intensified systems require some criteria for measurements that conventional measurements could not meet. As an example, the measurement should be very fast in order to quickly provide favorable measurement for process control of the intensified system. The process time for miniaturized intensified systems is within the range of a fraction of a second to few seconds. Thus the measurement devices with tens of second measurement time constant would be too slow to perform proper measurement for intensified systems. Secondly, since miniaturized devices deal with very narrow flow channels and low flow rates, measurement systems should be capable of performing the measurement even for very small quantities. And finally, measurement should also be installable in such small

environment to be able to continuously acquire data from the process. As an example, in the case of pH measurement for miniaturized intensified systems, conventional pH meters are too big to be installed in the systems. Therefore spectrophotometric measurement can be used as a suitable alternative measurement system for low volume intensified systems. It can satisfy all the 3 mentioned requirements because data acquisition can be performed as fast as 1 millisecond and also it can be used for small quantities of chemicals, depending on the cell selection and finally it can be used for continuous measurement using the flow through cell connected to the fiber optics.

1.5 Scope of The Study

The research comprises of two parts namely simulation and experimental studies. For the simulation part, a feedback control loop developed using Simulink toolbox is applied to a process model developed using matlab. Final control element is also included in the model. Direct Synthesis (DS) method is used to analytically design the controllers and the designed controller are then reduced to conventional PID form. Large number of simulations are carried out with various probable ranges of the component characteristic for the propose of evaluating the performance and identifying the difficulties in controlling the system.

On the experimental part, a spectrophotometric measurement is incorporated on an experimental rig representing acid base reaction system which is used for the study. U-V visible spectrophotometric measurement is used to measure the pH of the product from the reaction through an online computer acquisition system. A computer system al also built for the purpose of the studying the performance.

The proposed process model is then experimentally validated through open loop study. The performance of the proposed measurement system also tested using the open loop study. The simulation study also is validated through online closed loop study.

1.6 Objectives

This research project is planned and carried out to address the following objectives:

- To design suitable controller for miniaturized intensified systems.
- To study the compatibility of conventional measurement for application in intensified systems via simulation studies.
- To design and develop experimental rig with fast measurement and corresponding low process time delay in order to achieve swift control action.
- To develop suitable measurement systems for low volume intensified systems.
- To study the control system on a developed intensified process using the designed controller and measurement system on a developed experimental rig.

1.7 Organization of the Thesis

This thesis contains six main chapters. The first chapter briefly introduces the research project, the problem statement, and the scope of the study. This is followed by Chapter 2, providing a review of relevant topics on process intensification (PI), and touching on some basic knowledge about the project such as miniaturized intensified systems, microreactors and spectrophotometric pH measurement and also

related studies in detail. Chapter 3 covers the section on the design of the controller and experimental procedure. The chapter presents the controller design calculations and controller reduction methods followed by the experimental procedure describing the preparation of solution as well as the steps that should be taken in order to perform the experiments. This chapter is presented in great detail and arranged in such a way that it can be easily repeated.

Design and development of the miniaturized intensified system as well as interfacing the developed system using computer based control system is presented in Chapter 4. Brief descriptions on the experimental rig components as well as their working principles are also discussed. Data acquisition, converting to equivalent pH value and processing using the simulation software as well as the system interfacing are also described in detail. Chapter 5 converse the results and discussions. Detail comparison on simulation results for different controller performance for different pairing of process component is made in order to determine the difficulties in controlling intensified system.

The experimental study section covers the controllability of intensified systems using the designed control system. In Chapter Six (Conclusion), overall conclusion based on the results and findings made in the present study are given in brief. The recommendations for future research based on the understanding and knowledge generated in the present study are given in the final chapter (Recommendations).

CHAPTER 2

LITERATURE REVIEW

This chapter provides a survey on previous related works on this subject. This chapter includes a brief introduction to process intensification and its advantages followed by a short introduction on the selected intensified device (microreactor) and its principle. Next, problems of controlling intensified system are being reviewed and discussed. Conventional pH measurement system and its difficulties are then introduced followed by the proposed system that is used to perform the fast measurements.

2.1 Process Intensification

The term intensification in chemical engineering applied for a group of processes which offers improved environment in a chemical process that results in better products, and processes which are: smaller, cheaper, safer, slicker. Process intensification (PI) includes novel equipments, process techniques, process development methods when compared to conventional ones, offers substantial improvements in chemical and process engineering (Stankiewicz and Moulijn, 2004). These improvements can be outlined in dramatic improvements in manufacturing and processing, substantially decreasing equipment size/production capacity ratio (as shown in Figure 2.1), energy consumption, or waste production (CCD India, 2008).

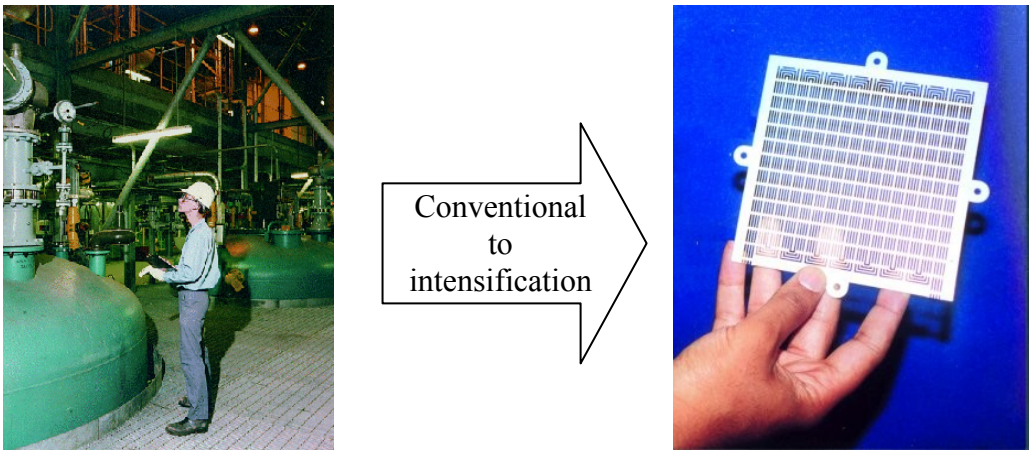

Figure 2.1: Moving from conventional stirred tank reactor to miniaturized PI unit that delivers same job (BHR, 2006)

2.2 Brief History of PI

The birth of PI as a chemical engineering discipline was marked by the paper published in 1983 by Colin Ramshaw from ICI New Science Group, who described their studies on the application of centrifugal field (so-called "HiGee") in distillation process. Ramshaw described PI as "devising an exceedingly compact plant which reduces both the "main plant item" and "installation cost" (Stankiewicz and Moulijn, 2004).

As a result of several researches that were carried out on the PI, the concept of the PI has widely been understood. Large number of universities and research centers are working on this concept and several conferences and symposiums on the PI technology are being organized every year. A large number of intensified systems has already being used for industrial applications (CCD India, 2008).

2.3 Philosophy of Process Intensification

Nigam and Larachi, (2005) and Stankiewicz and Moulijn (2004)defined PI as "strategy for making dramatic in chemical engineering plants to achieving the production objectives". PI can help to overcome instruments limitation as well as

performing new processes that seems to be impossible using normally used equipments.

Similar revolution in the electronics industry in the past decades has made dramatic transformation in the people life style all around the world. This revolutionary idea was the miniaturization of electronic devices which results in invention of transistors and consequently portable radios that could be carried anywhere. Later, using the same idea results in invention of chips, where with this technology enables us to use hand-held computers, cell phones, and many other hand-held electronic devices (Wegeng et al., 2000).

Process intensification can also take us to the similar technological journey because PI has potential to make dramatic changes in the whole chemical engineering industry by making new devices with much smaller size and lower price with the ability to operate in more environmental friendly situations and above all producing better products.

Intensification can be done either through using new methods (PI software) or new devices (PI hardware). Obviously in many cases, overlap between these two domains can be observed. Because using a new method may require a novel types of equipments also to be developed and vice versa, using novel equipment may lead to using a new method also. The examples of PI hardware and PI software are presented in Figure 2.2.

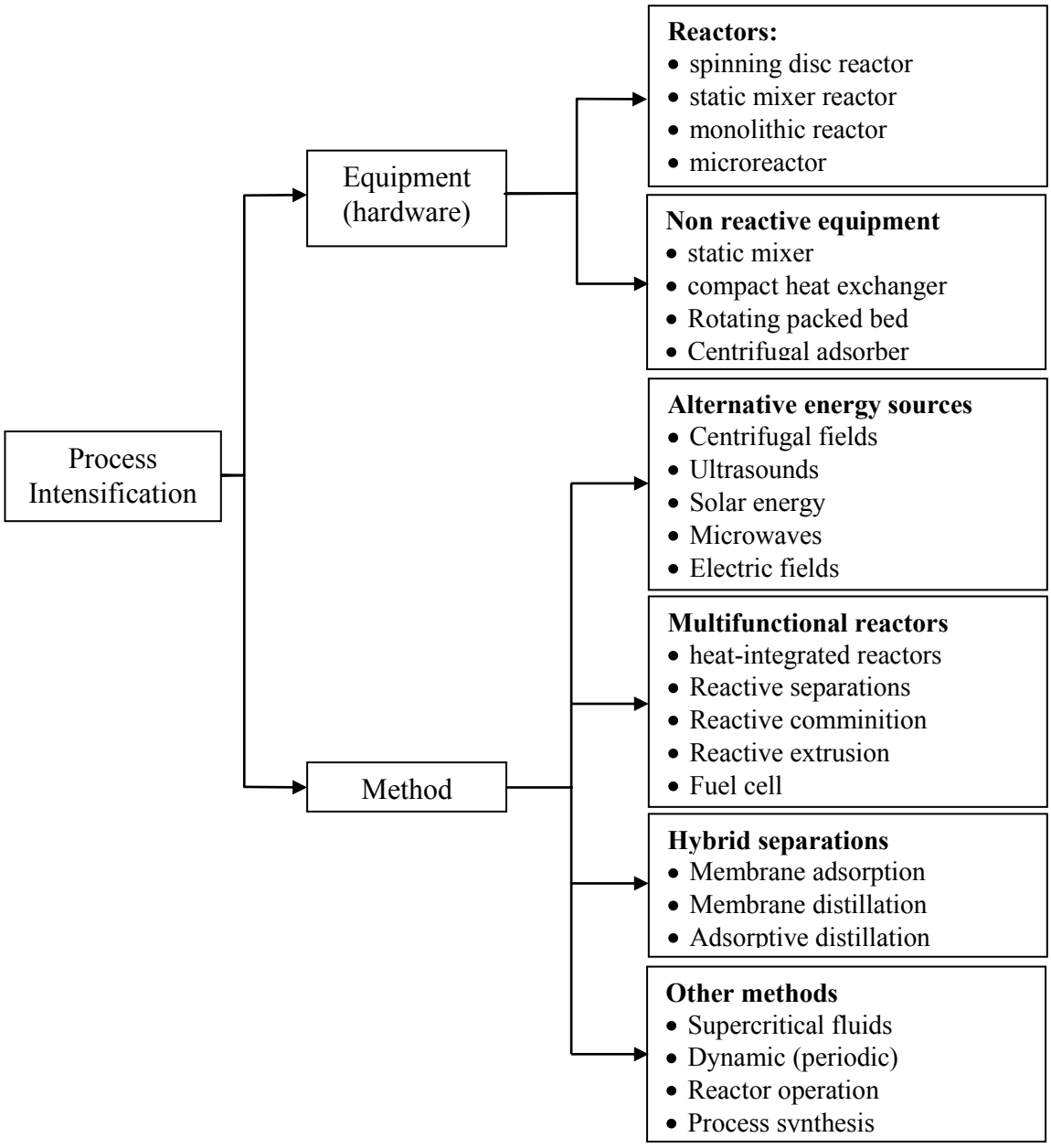

Figure 2.2: Process intensification and its components (Stankiewicz, 2003).

2.4 Advantages of Intensified Systems over Conventional Systems

Process intensification offer opportunities to operate under conditions that might not be achievable in conventional equipment. Using process intensification, not only will it increase productivity and product quality but also in some cases it can change the impossible to possible. In other words PI can provide a route to bypass

thermodynamic barriers which using conventional equipment conducting the process seemed to be impossible (Charpentier, 2005). As mentioned previously, large number of advantages can be obtained using PI technology where a number of them are discussed in the following part.

2.4.1 High Heat and Mass Transfer

Intensification through miniaturization can significantly decrease the resistance to heat and mass transfer. Shorter diffusion length in miniaturized intensified systems such as microreactors results in high mass transfer even at very low Reynolds, Re numbers (Kockmann et al., 2006). Increasing the heat transfer surface area per unit volume in miniaturized intensified systems up to 10,000 - 50,000 m^2/m^3 facilitates high heat transfer rate with a heat transfer coefficient as high as 25,000 W/m^2K has been reported for a microreactor (Kiwi-Minsker and Renken, 2005). High heat transfer (as high as 15,000-20,000 W/m^2K) could also be achieved for other intensified units such as spinning disc reactor (SDR) (Protensive, 2008). Thus, devices designed through this technology are capable to meet the required high heat transfer for extreme reactions that could not be addressed using conventional devices. High heat transfer rate also enable isothermal operation to be conducted for highly exothermic processes. It can also help to overcome the mass and heat resistance in high viscosity processes such as polymerization (Toledo et al., 2005).

Using intensified systems facilitate very good temperature control for highly exothermic reactions that can easily prevent formation of hot spots and consequently increases the selectivity of product (Kolb and Hessel, 2004). Owing to their high heat transfer and precise heat control characteristics of intensified systems, they can operate under much more aggressive condition with corresponding lower pressure

drops and less energy consumption while producing less waste and by products (Charpentier, 2005)

2.4.2 High Mixing Quality

Mixing of high viscosity fluids such as polymerization processes has always been very difficult to be conducted in conventional batch reactors, due to their poor mixing level (Boodhoo et al., 2003). Some problems such as poor temperature control cannot be avoided due to this poor mixing performance. Mixing quality as well as mixing time can be improved by several order of magnitude using intensified systems. Perfect mixing could be achieved in liquid-liquid, gas-liquid and solid-liquid using either micromixers that are conventionally used for low flow rates or micro structured mixers that are used for high flow rates (Hessel et al., 2005). Utilizing intensified systems provide aggressive mixing environment that can easily operate high viscosity fluids in fraction of a second. High mixing performance of intensified systems has been demonstrated in many literatures (Hessel et al., 2005; Kockmann et al., 2006; Xia and Wan, 2007).

2.4.3 Lower Cost

Process intensification can substantially decrease the capital cost for processes (Brechtelsbauer et al., 2001). Capital cost reduction up to 60% has been reported (BHR, 2006). The reasons for this huge total cost reduction are outlined below:

- Land cost: that is resulting from higher yield and smaller equipments (up to 99.8% reduction in reactor volume) (BHR, 2006).
- Other investments cost due to integrated processing units, cheaper equipments, and reduced piping (Stankiewicz and Moulijn, 2004).

- Significant reduction in using raw material due to higher yield (93% yield first time out) (BHR, 2006) and producing high selectivity products (Charpentier, 2005)
- Cost of utility due to higher energy efficiency where in one case BHR group reported more than 70% reduction in energy usage (CCD India, 2008)
- Cost of waste processing due to the productions of less waste in intensified systems.
- Process time reduction up to 99.9% (Oxley et al., 2000)
- Reducing inventory up to 99% (Oxley et al., 2000)
- Reducing impurity level up to 93% (Oxley et al., 2000) that eventually results in product with higher quality and consequently higher price.

2.4.4 Safety

Due to their special design characteristics and smaller in size, intensified systems can be considered as inherently safe systems (Etchells, 2005). Size reduction especially in low volume intensified systems is one of the most important characteristics of intensified systems. It is obvious that the smaller the holdup caused by the smaller volume, the safer the equipment becomes. It means that having small size and consequently small hold up can inherently prevent dangerous accidents. For instance, assume a microreactor which is processing highly toxic or highly explosive material. During the processing stage, if suddenly the equipment fails, only few milliliters of those hazardous materials will be released which could be easily contained (Charpentier, 2005; Yarbro and Schreiber, 2003). Similar failure in

conventional plants can end up with massive explosion or releasing tons of toxic material to the environment.

High pressure processes can also be carried out safely in miniaturized intensified systems because pressure can be controlled easily in low volume devices and system breakdown will not lead to severe damage. Intensification can also contribute to safe processing by reducing hazardous intermediate inventory using hybrid systems. In hybrid systems, hazardous intermediates can immediately be converted to the final product in continuous manner (Hendershot, 2000). Finally, reducing the number of equipment naturally will improve process safety as expressed by Kletz (1991) that "what you don't have cannot leak".

2.4.5 Elimination of Scale Up

As mentioned in previous chapter, scaling up from laboratory scale to pilot scale and from pilot scale to industrial scale tend to be very costly and time consuming. Several complicated steps are needed to redesign the process because of phenomenon such as heat transfer and mass transfer are different in microscale (small volumes) and macroscale (large volumes). For example, heat removal from an exothermic polymerization reaction in a small volume might not be a difficult issue but not for large volume batch reactor. However, using miniaturization in PI technology, scaling up process could be eliminated as the lab scale unit is the pilot plant scale. Thus, the quality of the processes involves remains the same and reproducible. Consequently, PI technology could save time and money as compared to conventional technology whereby re-adjustment of process parameters are needed due to scaling-up effects (Wille et al., 2004). This approach would seem more advantageous for pharmaceutical and fine chemical industries due to the low

production amount (Charpentier, 2005). It should also be noted that current micro technology allows for very high flow rates operation for instance StarLam 30000 micromixer can be used for flow rates up to 8000 l/h with corresponding 72 ms residence time (IMM Mainz, 2007).

2.4.6 Low Residence Time

Miniaturized intensified systems have very short residence time which is a fraction of a second up to few seconds thanks to their small inner volume capacity. This can be used in processing of very competitive reactions, or fast liquid reactions (Hessel et al., 2004a; Ying et al., 2008), where fast mixing is essential in achieving the desired result. This type of reaction cannot be handled by conventional reactors due to their slow and inefficient mixing performance (Boodhoo and Jachuck, 2000b).

2.5 Miniaturized intensified systems

As shown previously, large number of advantages can be obtained using intensified systems. These advantages like high heat and mass transfer, low residence time, high mixing performance and elimination of scale up can be achieved through miniaturized systems. The research on miniaturized systems can be classified into four categories. First category is called “lab-on a chip” system which deals with efficient operation of chemical laboratories (Anema, 2009; Bhagat et al., 2008). Development of downsized analytical devices belongs to the second category that is usually called “micro-TAS” systems (Petersen et al., 2002). The third category involved in the different micro fabrication techniques (Andersson et al., 2000; Klaassen et al., 1996). And finally, research on development of new production systems using miniaturized devices that is called the micro plant systems (MCPs)

(Jensen, 2001; Shin and Besser, 2006). MCPs include microreactors, micro heat exchangers and monolithic reactors (Hasebe, 2004). Since a microreactor has been chosen as the intensified system for this research study, it is worth to have a deeper insight of the microreactors and their working principles are being reviewed in the following section.

2.5.1 Microreactor

2.5.1.1 Introduction to Microreactors

Ehrfeld et al. (2000) defined microreactor as "miniaturized reaction systems fabricated by using at least partially methods of microtechnology and precision engineering". This rather old-fashioned definition is recently revised where the new definition does not necessitate microfabrication techniques and microtechnology in fabrication of microreactors and smart modern reactor concepts or simple down-scaled designs of traditional reactors – with no relation to microfabrication – were considered now as well. Falling-film reactors (Al-Rawashdeh et al., 2008; Commenge et al., 2006; Lee et al., 2005) packed-bed reactors (Karim et al., 2005; Suh et al., 2009; Yoswathananont et al., 2008) structured catalysts (Fukuhara et al., 2005; Mathure et al., 2008) and capillary-in-tube reactors (Goshima and Terasaka, 2007; Lohrengel et al., 2004) are examples of reactors that are not fit in the old definition of microreactors but nowadays are considered as microreactors. During the last decades, a wide variety of different microreactors has been developed (Bromley et al., 2008; Tietze and Liu, 2008; Wang et al., 2008; Yu et al., 2008).

Different microreactors use different principle according to its process nature and consequently have different design. The smallest unit in conventional microreactors is *microstructures* that in majority of cases referring to *channel*

structure. Usually parallel channels are combined to an array which is surrounded by inlet and outlet flow regions that sometimes referred to as header. A typical single or multiple flow channel configuration of distinct geometric capture is named as element. There are many mixing element designs such as interdigital channel (Hessel et al., 2003; Hessel et al., 2004a), multiple splitting recombination channel (Mae et al., 2004) and tee-type channel configuration(Hessel et al., 2004b). For catalytic reaction, mixing element are also coated with catalyst to obtain high contact surface (Kataoka et al., 2008; Kiwi-Minsker and Renken, 2005; Mills et al., 2007). Figure 2.3 shows A) SuperFocus and B) triangle interdigital mixing element design.

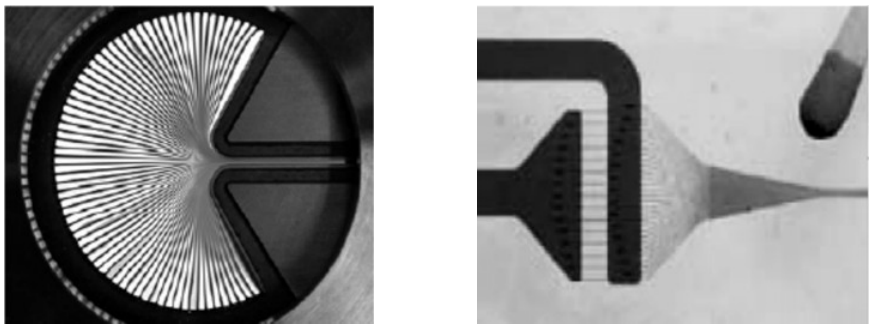

Figure 2.3: Mixing element structure: a) SuperFocus mixer; b) Triangular interdigital micromixer focusing mixer (Mansur et al., 2008).

2.5.1.2 Mixing Techniques for Microreaction Technology

Microreactors use various mixing principles for mixing two or more components. There are many active (Oddy et al., 2001; Yang et al., 2001) and passive (Hessel et al., 2003; Lob et al., 2004; Xia and Wan, 2007) mixing techniques used to perform perfect mixing in microreactors. In active mixing, energy input from the exterior (such as ultrasound, acoustic, bubble-induced vibrations, electrokinetic instabilities, periodic variation of flow rate, etc) is used to perform the mixing while in passive mixing, energy from pumping action or hydrostatic potential, is used to

restructure a flow in a way which results in faster mixing such as interdigital mixers, split-and-recombine, chaotic mixing, nozzle injection in flow, collision of jets (Hessel et al., 2005). Figure 2.4 shows schematic drawing for a number of mentioned passive mixing techniques.

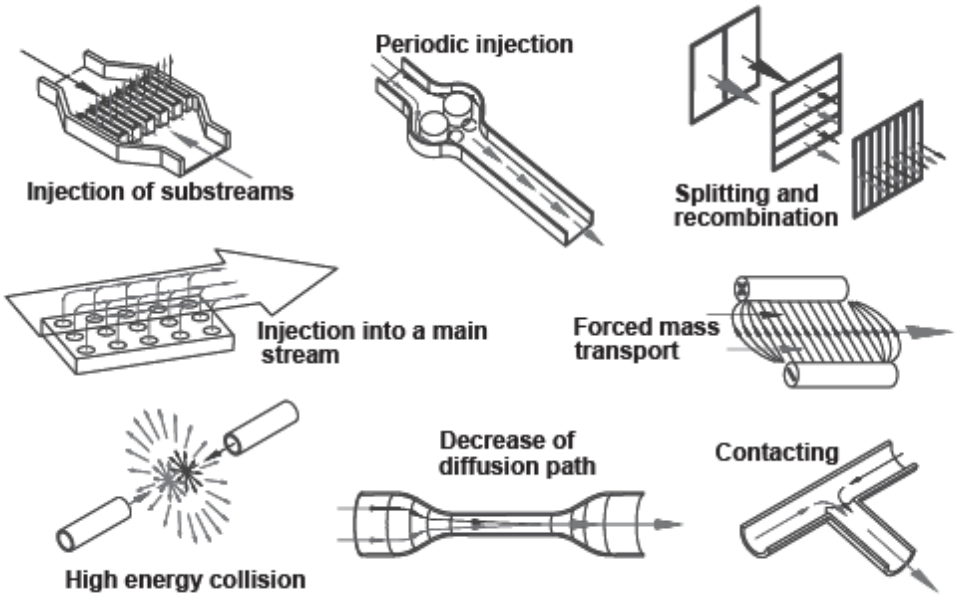

Figure 2.4: Schematic drawings of selected passive and active micromixing principles (Hessel et al., 2005).

One of the most important characteristics of each microreactor is the mixing time. A perfect mixing is essential in providing a complete reaction with a high selectivity and product yield. The relation between mixing process time and reaction time plays the major role where mixing process have to be completed before the reaction completes (Hessel et al., 2005; Kockmann et al., 2006). There were numerous investigations conducted on measurement of mixing time for the various micromixers which use different techniques such as using competitive reactions and optical methods (Kockmann et al., 2006; Panic et al., 2004; Ying et al., 2008). Each technique can be applied to specific group of reactions according to their

characteristics but have certain limitations. In a micromixer, rapid liquid mixing as fast as 10 ms can be achieved (Hessel et al., 2003).

2.6 Control of Intensified Systems

The previous section presented the general picture of process intensification and its numerous advantages over conventional systems. But in order to be able to use those equipments and their advantages, proper control system is essential. As mentioned earlier, PI can be divided into two main groups, the intensification that has been done by means of instruments (hardware) such as microreactors and the intensification that has been done by means of methods (software) such as heat integrated reactors. However different categorization can be obtained from process control perspective. This different categorization is due to the different control strategies which is required for this two categories that is described in the following parts. First category is *hybrid systems* which are intensification though integration of different functions in one apparatus. Second category is intensification that is done through size reduction whilst maintaining the same throughput that are known as *miniaturized intensified systems*. Due to the integration of several function into a single apparatus in hybrid systems, they are rather complicated. Thus they require advance control in order to perform suitable control action. Intensification through miniaturization results in the devices with low volume and consequently very fast responsive systems which necessitate fast control action but not very complex. These different control strategies for each category will be described in the following sections.