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THESIS

KINETICS STUDY OF THE ALKALINE HYDROLYSIS OF ETHYL ACETATE IN CSTR USING SIMULTANEOUS TEMPERATURE SCANNING AND COMPOSITION MODULATION TECHNIQUE

CHONTHIDA NAUMMANEERAT

A Thesis Submitted in Partial Fulfillment of
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This work presents a new technique for reaction kinetic studies of liquid phase reactions in a CSTR. The technique simultaneously varies the reaction temperature (Temperature Scanning) and reactant feed concentration (Composition Modulation) while collecting the output concentration. Alkaline hydrolysis of ethyl acetate was chosen to demonstrate the technique. Time-evolved output concentration of the system was used as a basis for comparison in the analysis. The reaction kinetics in the form of power-law model and Arrhenius equation with different sets of parameters including reaction order, activation energy, and preexponential factor was simulated under transient conditions as experimentally performed. The set of parameters resulting in the minimum sum of squared errors was selected. These values were comparable to those reported in literature. The technique saves time and experiment resources.

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Student’s signature Thesis Advisor’s signature

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Chonthida Nuammaneerat
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LIST OF ABBREVIATIONS

Ar = The preexponential factor

C = The concentration of any chemical species in the reactor or at the exiting reactor

C_A^{δ} = The concentration of feed pulse dose (mol/L)

Ea = The activation energy (kJ/mol)

F = The molar flow rate of any chemical species out of the reactor (mol/s)

k = The reaction rate constant respecting to any chemical species

N = The number of moles in the reactor at time t

R = The rate of reaction (The number of moles of any chemical species reacting (or production) per unit time per volume (mol/L.s)

T = The temperature of reactor (°C)

T = Time (s)

t^{δ} = Feed duration (s)

t_w = Feed initiation time (s)

v = The volumetric flow rate of a chemical species into the reactor (cm^3/min)

V = Vessel size (cm^3)

V^{δ} = Volume of feed pulse (cm^3)

γ, β = The order of reaction with respect to NaOH and ethyl acetate, respectively

δ_A = Feed rate (mole/s)

$_{A, B, C, D}$ = Any chemical species of reaction, i.e. NaOH, Ethyl Acetate, Ethanol and Sodium Acetate, respectively.

$_i$ = The initial values of a parameters in the system

LIST OF ABBREVIATIONS (Continued)

0 = The values of inlet parameter of the system

m = Condition of the mixing tank

R = Condition of the reactor

s = Condition of at steady state

KINETICS STUDY OF THE ALKALINE HYDROLYSIS OF ETHYL ACETATE IN CSTR USING SIMULTANEOUS TEMPERATURE SCANNING AND COMPOSITION MODULATION TECHNIQUE

INTRODUCTION

The kinetics study of reactions is a common task for chemical engineers. It is necessary for: designing chemical reactors, drawing inferences on the mechanism of the reaction, quantifying the rate of reaction for chemical process, improving reactor control and design, identifying the optimum reaction conditions and designing better catalysts. In general, the kinetics studies of chemical reactions have been performed under steady-state conditions. This is time-consuming because a typical experiment provides data for an experimental condition (inlet concentration, reaction temperature, time, etc).

Kinetics experiments, however, may be performed by continuously varying one of the operating parameters such as reactant concentration (composition modulation), reaction temperature (temperature scanning), or even flow rate (reverse flow operation). This type of experiment is called an “unsteady state” or “transient” kinetics study. This transient technique is an efficient tool using various types of automated reaction systems. It is rapid and reduces the time and resources associated with carrying out steady-state experiments. Moreover, research has shown that transient operated chemical reactors are better than steady-state ones (Lian and Haidong, 1993; Silveston, 1998; Arprey *et al.*, 1999; Wojciechowski and Arprey, 2000; Domke *et al.*, 2001; Suman, 2004).

“Temperature scanning” (TS) is a methodology that uses the variation of temperature to a system of interest such as a chemical reactor, an analytical instrument, etc. In reaction kinetics, this temperature is the reaction temperature. The TS technique defines the operating conditions required to generate interpretable signals from a reactor operated under conditions different from those of an isokinetics procedures (Wojciechowski, 1997). By collecting a large number of the rate-data from transient experimentation, TS technique also allows us to model or to predict the reaction kinetics with high accuracy. On the contrary, in the isokinetics method, each steady-state condition investigated provides single rate-data point. Reaction rate is influenced by both temperature and chemical composition. Hence, reaction rate regression requires experimental validation at various reactant concentrations as well as temperatures.

The composition modulation (CM) or forced concentration oscillation is another powerful technique to investigate the transient behavior of chemical and physical system (Urakawa *et al.*, 2006). This technique can be defined that a system perturbed by a periodic change of parameter affecting the chemical and physical state of the system, i.e. influent concentration, resulting in a periodic pattern of the output response. During each periodic perturbation cycle, the affected parameters relax to new quasi-steady state values around which they oscillate. The periodically alternating response can be detected by sensitive analytical instruments, in which some noise will unavoidably occur. Square-wave stimulation is typically applied for composition modulation in kinetic study. This type of stimulation is easy to generate experimentally by switching between two flows of different concentration levels fed to the reactor. Apart from investigations of reaction kinetics, there have been reports on improved reaction performance via composition modulations such increased reaction rate or selectivity (Lian and Haidong, 1993; Silveston, 1998; Lange *et al.*, 1999; Suman, 2004).

With the objective of obtaining accurate reaction kinetics using minimal resources, this work explores the estimation of reaction kinetic parameters using a new technique called “TS-CM CSTR”, where the temperature scanning is performed simultaneously with the pulsation of inlet reactant concentration. Each reacting system generates unique characteristic responses underlying by rate-data. The transient experimental results using the alkaline hydrolysis as a model reaction in a CSTR are analyzed in order to obtain the kinetic parameters as well as to compare them with those reported in literature (Bamford and Tipper, 1972; Robison and Tester, 1990).

OBJECTIVES

1. To develop a new technique to estimate the kinetic parameters for liquid-phase reactions under transient condition in CSTR.

2. To verify the new technique with the model reaction under transient condition in CSTR.

Scope of the investigation

1. To obtain the reaction kinetics for the alkaline hydrolysis of ethyl acetate based on the power law model via the developed technique, under transient condition in CSTR.

2. Test and analyse the computational results from the developed technique with the experimental results for the alkaline hydrolysis of ethyl acetate under transient condition in CSTR.

Impact of Results

The newly-developed technique will be an important tool for the estimation of the kinetic parameters and the orders of reaction for the power law models, which will save time and resources for kinetic researchers. In addition, this technique may be further applied with Langmuir-Hinshelwood models for heterogeneous reaction.

LITERATURE REVIEW

1. The overview of kinetics study

Chemical kinetics study is the study of rates of chemical reactions, also known as reaction rate. It includes the investigations of how different experimental conditions can influence the speed of a chemical reaction. The main factors that affecting the reaction rate include: the physical state of the reactants, the concentrations of the reactants, the temperature at which the reaction occurs, and whether or not any catalysts are present in the reaction. The study of reaction kinetics can help optimize the design and operation of chemical reactors. The dependence of the reaction rate on the concentrations of various species involved in the reaction has been described via the algebraic equation or “the rate law.” This is one of the important factors involved in the selection of a reaction system that operates, in which the safest and most efficient manner can be maintained; the key to economic success or no failure of a chemical plant.

How fast a number of moles of one chemical species are being consumed to form another chemical species, or products, can be described as the reaction rate (Fogler, 2005). An example reaction:

$$aA + bB \rightarrow cC + dD \tag{1}$$

Alternatively, equation (1) can be expressed as

$$A + \frac{b}{a}B \rightarrow \frac{c}{a}C + \frac{d}{a}D \tag{2}$$

From the stoichiometry of the reaction, the relation of reaction rates of the various species involved can be expressed as follows:

$$\text{Rate of appearance of C} = \frac{c}{a}(\text{Rate of consumption of A}) \tag{3}$$

$$r_{\mathrm{C}} = \frac{c}{a}(-r_{\mathrm{A}}) = -\frac{c}{a}r_{\mathrm{A}} \tag{4}$$

Similarly for all of species in equation (1), the relative rates of reaction can be expressed as:

$$\frac{-r_{\mathrm{A}}}{a} = \frac{-r_{\mathrm{B}}}{b} = \frac{r_{\mathrm{C}}}{c} = \frac{r_{\mathrm{D}}}{d} \tag{5}$$

For a model reaction that was employed throughout this study, the alkaline hydrolysis reaction of ethyl acetate and the reaction rate are described in equations (6) and (7):

$$\mathrm{NaOH} + \mathrm{CH_3COOC_2H_5} \rightarrow \mathrm{C_2H_5OH} + \mathrm{CH_3COO^-Na^+} \tag{6}$$

$$\frac{r_{\mathrm{CH_3COOC_2H_5}}}{-1} = \frac{r_{\mathrm{NaOH}}}{-1} = \frac{r_{\mathrm{CH_3COO^-Na^+}}}{1} = \frac{r_{\mathrm{C_2H_5OH}}}{1} \tag{7}$$

1.1 The Reaction Order and the Rate Law (Fogler, 2005)

From the reaction in equation (1), it was assumed that the limiting reactant is species A that was taken as the basis of the calculation. Along the path of reaction, species A is being consumed as a result of the chemical reaction to generate products (species C and D). The rate of consumption of A, $-r_{\mathrm{A}}$, can be indicated in equation (8) as the product of *a reaction rate constant*, k_{A} and a function of the concentrations (activities) of the various species involved in the reaction. It is noted that the relationship depends on both temperature and composition.

$$-r_{\mathrm{A}} = [k_{\mathrm{A}}][C_{\mathrm{A}}, C_{\mathrm{B}}, \ldots] \tag{8}$$

Equation (8) is called the kinetic expression or *rate law*. k_A is the specific rate of reaction or the rate constant which refers to a particular species in the reaction and should be subscripted with respect to species; similarly for the reaction rate, $-r_A$. For the alkaline hydrolysis of ethyl acetate (equation 6) in which the stoichiometric coefficient is 1 for all species involved in the reaction:

$$1\mathrm{NaOH} + 1\mathrm{CH_3COOC_2H_5} \rightarrow 1\mathrm{C_2H_5OH} + 1\mathrm{CH_3COO^-Na^+} \qquad (9)$$

The rate constants can be written as

$$k = k_{\mathrm{NaOH}} = k_{\mathrm{CH_3COOC_2H_5}} = k_{\mathrm{CH_3COO^-Na^+}} = k_{\mathrm{CH_3OH}} \qquad (10)$$

1.2 Power Law Models (Fogler, 2005)

The power law model is one of the most common general forms of the dependence of the reaction rate on the concentrations of the species presented (C_i). Here, the rate law is the product of concentrations of the individual reacting species, each of which is raised to a power (be stand for reaction order of each species). This dependence is always necessary to be postulated from theory and confirmed by experiments at the proposed form. For example, the alkaline hydrolysis reaction of ethyl acetate:

$$-r_{\mathrm{NaOH}} = kC^{\gamma}_{\mathrm{NaOH}}C^{\beta}_{\mathrm{CH_3COOC_2H_5}} \qquad (11)$$

γ and β are the orders of reaction, referring to the powers to which the concentrations are raised in the kinetic rate law. For this particular example, the reaction is γ order with respect to NaOH and β order with respect to ethyl acetate. The overall order of the reaction, n, is defined as:

$$n = \gamma + \beta \qquad (12)$$

The units of $-r_A$ are in terms of concentration per unit time while the units of the rate constant, k, can vary with the order of the reaction, n, as shown below:

$$k = \frac{(Concentration)^{1-n}}{Time} \tag{13}$$

To illustrate the estimation of the units of the rate constant, we consider a reaction involving only one reactant:

$$\mathrm{A} \rightarrow \mathrm{Product} \tag{14}$$

For some order reactions, those are:

- Zero-order (n = 0):

$$-r_{\mathrm{A}} = k_{\mathrm{A}} \qquad ; k = \mathrm{mol/dm^3.s} \tag{15}$$

- First-order (n = 1):

$$-r_{\mathrm{A}} = k_{\mathrm{A}} C_{\mathrm{A}} \qquad ; k = \mathrm{s^{-1}} \tag{16}$$

- Second-order (n = 2):

$$-r_{\mathrm{A}} = k_{\mathrm{A}} C_{\mathrm{A}}^2 \qquad ; \mathrm{k} = \mathrm{dm^3/mol.s} \tag{17}$$

- Third-order (n = 3):

$$-r_{\mathrm{A}} = k_{\mathrm{A}} C_{\mathrm{A}}^3 \qquad ; \mathrm{k} = \mathrm{(dm^3/mol)^{2}\ .s^{-1}} \tag{18}$$

Note that the rate laws are a function of the reaction chemistry and not the type of reactor in which the reactions occur. For instance, kinetics study on esterification for biodiesel production by using 10%HPW/Al_2O_3, 10%HSiW/Al_2O_3 and 10%H_2SO_4/Al_2O_3 as catalyst to convert high free fatty acid oil and methanol into methylester and water (Tadarun and Napawan, 2006). Experiments were conducted at 60°C, 70°C and 80°C, the mole ratio of crude palm oil to methanol was 1:20 (methanol in excess). In order to identify the kinetics parameters for the collection of experimental data, POLYMATH was employed to determine parameters in the model, which would be presented by the followings:

Reaction: $\text{Free Fatty acid} + CH_3OH \underset{k_2}{\overset{k_1}{\rightleftarrows}} \text{Methylester} + H_2O$

Rate equation:

$$rate = \frac{-dC_{\mathrm{FFA}}}{dt} = -KC_{\mathrm{FFA}}^{\alpha} + k_2 C_{\mathrm{methylester}}^{\delta} C_{\mathrm{H_2O}}^{\gamma}$$

where $K = k_1 C_{\mathrm{methanol}}^{\beta}$

k_1 = forward reaction rate constant

k_2 = reverse reaction rate constant

C_{FFA} = concentration of free fatty acid, (mol/L)

C_{Methanol} = concentration of methanol, (mol/L)

$C_{\mathrm{Methylester}}$ = concentration of methylester, (mol/L)

$C_{\mathrm{H_2O}}$ = concentration of water, (mol/L)

α = reaction order with respect to free fatty acid

β = reaction order with respect to methanol

δ = reaction order with respect to methylester

γ = reaction order with respect to water

From experimental results, the determination of k_1, k_2, α, β, δ and γ was made at the optimum temperature of 80°C using 10% HPW/Al_2O_3 as solid catalyst. It was found that the forward reaction rate constant was 5 $(\mathrm{mol/L})^{0.6999}$ s^{-1}, backward reaction rate constant was 94 $(\mathrm{L/mol})^{0.0001}$ s^{-1}, reaction order of free fatty acid, methanol, methylester and water were 0.3, 0.0001, 0.0001 and 1, respectively.

1.3 The Reaction Rate Constant (or specific reaction rate, *k*) (Fogler 2005; Houston 2001; Walas 1989)

It is well known that the quantity of *k* is not constant and is independent of the concentrations of the species involved in the reaction. It is strongly dependent on temperature and also depends on the presence of catalyst. In addition, for gas-phase reactions, it depends on total pressure of the reacting system. For liquid-phase reactions, it can be a function of different parameters such as ionic strength and choice of solvent. However, these factors have little effects on *k* compared to reaction temperature, except for supercritical solvent such as super critical water, etc. Nontheless, it is generally assumed that the quantity of *k* depends only on temperature for most reaction conditions.

The temperature dependence of reaction rate constant was first proposed by the Swedish chemist named “Arrhenius,” which is known as the Arrhenius equation, shown in equation (19). It has been verified by numerous experiments that the temperature behavior of most reaction rate constants can be predicted within experimental accuracy over fairly large temperature ranges.

$$k = Ar \exp\left(-Ea/\mathrm{R}T\right) \tag{19}$$

where *Ar* is a temperature-independent constant, often called the preexponential factor. It has the units of *k*, usually based on the units of concentration, and thus depends on the order of reaction. *Ea* is called the activation energy, R is the gas constant (8.314 J/mol.K = 1.987 cal/mol.K) and *T* is the absolute temperature (K). For practical purposes (including liquid-phase kinetics investigation), the Arrhenius equation is a sufficiently accurate representation of data (Walas, 1989).

1.4 The Activation Energy (*Ea*)

The activation energy can be generally expressed as a barrier to energy transfer (from the kinetic energy to the potential energy) between reacting molecules that must be overcome. It is explained via the reaction coordinates as shown in Figure 1. This represents the potential energy of the reacting molecules as a function of the reaction pathway from reactants to an intermediate, and to the final products. The schematic of this reaction is (Fogler, 2005):

$$A + BC \leftrightarrow A\text{-}B\text{-}C \rightarrow AB + C$$

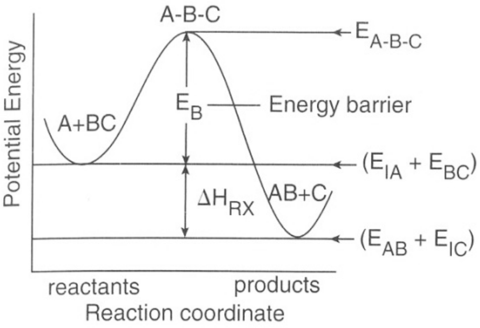


Figure 1 Progress along reaction path.

Source: Fogler (2005)

Figure 1 shows the progress of the potential energy of the three-molecule system (i.e., A, B, C). The reaction progress is going from reactant species A and BC to products AB and C. At first, molecules of A and BC are far apart. The energy of the system is the energy of chemical bonding BC. Moving along the reaction coordinate (*x*-axis) to the right, A and BC approach each other and the BC bond starts to break away. The energy of the reacting pair increases reaching the top of the energy barrier. At the top of the barrier, or at the transition state, there exists an intermediate A-B-C. After that, during the transformation, A and B are getting close and the AB bond starts to form. Finally, the AB and C move away from each other and the energy of the reacting pair decreases to value representing the AB bond energy. At the end of the reaction, the products AB and C are formed, and the energy of system is the energy of bond AB and C. Therefore, it can be mentioned that the activation energy, *Ea* is approximated by the barrier height (E_B).

For the conventional method, the estimation of the activation energy can be obtained from the relationship between the reaction rate constant and reaction temperature. When the experimental data are plotted as ln k against $1/T$, the slope of the resulting straight line is $-Ea/\mathrm{R}$. Figure 2 presents a slight temperature dependency of reaction rate constant for the unimolecular decomposition of acetonedicarboxylic acid in aqueous solution (Walas, 1989). The rate constant for this reaction is described as shown in equation (20).

$$k = 7(10^{20})\, e^{-55,400/T} \qquad \mathrm{sec}^{-1} \tag{20}$$

The calculation of *Ea* need not be graphical. Whenever if the reaction temperature and the reaction rate constant are known, *Ea* and *Ar* can be obtained via equation (20).

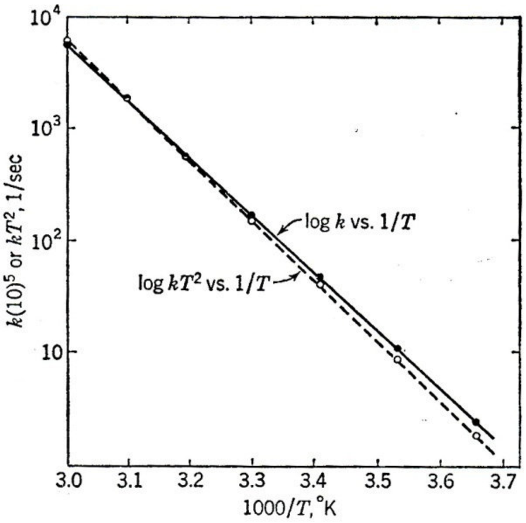


Figure 2 Temperature dependence of reaction rate constant of decomposition of acetonedicarboxylic acid in aqueous solution.

Source: Walas (1989)

The kinetic measurements are usually performed over the moderate-temperature ranges that the activation energy appears to be independent of temperature. However, in a few instances an effect of temperature has been detected.

For example, a careful reexamination of the original data and more recent data on the hydrolysis of sucrose in hydrochloric solution revealed the effect of temperature on the activation energy, as shown in Table 1.

Table 1 The effect of temperature in the hydrolysis of sucrose by hydrochloric acid

T, $^{\circ}$C	20	35	50
Ea, cal/g mol	25,430	24,470	22,950

Note: In this data the Arrhenius equation was assumed.

Source: Walas (1989)

In addition, it was found that the total pressure of the system can have an influence on the activation energy. For example, the reaction $2NO_2 \rightarrow N_2 + 2O_2$, the activation energy significantly increases with increasing total pressure as shown in Table 2.

Table 2 The effect of pressure in the decomposition of nitrogen dioxide

P, atm	0.03	0.79	36.3
Ea, cal/g mol	54,500	58,700	65,000

Source: Walas (1989)

Catalysts can also change the activation energy by changing the mechanism of reaction. This contribution, however, does not focus on this particular aspect. The activation energy of some reactions is shown in Table 3. It is noted that *Ea* is generally positive (Pilling and Seakins, 1995).

Table 3 Activation energy of some reactions

Reaction	**Activation Energy** (kcal/g mol)
1st Order gaseous decompositions:	
Nitrogen tetraoxide	13.9
Ethyl peroxide	31.5
Dimethylethyl acetic acid	60.0
2nd Order gaseous reactions between stable molecules:	
$NO + O_3 \rightarrow NO_2 + O_2$	2.5
$2NOCl \rightarrow 2NO + Cl_2$	24.0
$2HI \rightarrow H_2 + I_2$	44.0
2nd Order gaseous reactions involving atoms or radicals:	
$H + HBr \rightarrow H_2 + Br$	1.2
$CH_3 + i\text{-}C_4H_{10} \rightarrow \ldots$ products	7.6
$CH_3 + C_2H_6 \rightarrow \ldots$ products	10.4
3rd Order gaseous reactions:	
$2NO + O_2 \rightarrow 2NO_2$	0 (or negative)
$H + H + H \rightarrow H_2 + H$	0
$2NO + Cl_2 \rightarrow 2NOCl$	~ 4

Source: Walas (1989)

1.5 The preexponential factor (*Ar*)

The *Ar* parameter is sometime called *the frequency factor* or *the preexponential factor* (Walas, 1989). It is proportional to the number of molecular collisions per unit time, as *Ea* describes the fraction of collisions that have enough energy to result in a chemical transformation. A selection of the preexponential factor (*Ar*) is provided for first-order and for second-order gaseous reactions in Table 4.

Table 4 The preexponential factor (*Ar*) of some 1st and 2nd order gaseous reactions

Reaction (Valid Temperature range)	
1st Order gaseous reactions:	*Ar*, (s^{-1})
$CH_3CHO \rightarrow CH_3 + HCO$ (500-2,000 K)	3.8×10^{15}
$N_2O \rightarrow N_2 + O$ (1,000-3,600 K)	6.1×10^{14}
$C_2H_5 \rightarrow C_2H_4 + H$ (250-2,500 K)	2.8×10^{13}
$H_2S \rightarrow HS + H$ (1,965-19,700 K)	6.0×10^{14}
2nd order gaseous reactions:	*Ar*, (cm^3 / mol .s)
$CH_3 + H_2 \rightarrow CH_4 + H$ (300-2,500 K)	6.7×10^{12}
$H + H_2O \rightarrow OH + H_2$ (250-3,000 K)	9.7×10^{13}
$O + CH_4 \rightarrow OH + CH_3$ (298-2,575 K)	1.0×10^{14}
$OH + O \rightarrow O_2 + H$ (220-500 K)	1.4×10^{13}

Source: Houston (2001)

Most reactions investigated obay the simple Arrhenius form. A few exceptions, however, do exist. For example, experimental data of the $OH + CO \rightarrow H + CO_2$ reaction over the temperature range from 300 to 2000 K suggested that $k(T) = (3.25\times 10^{10}\ cm^3\ mol^{-1}\ sec^{-1})(T^{1.5}\exp(+250/T))$. It was found that the preexponential factor is not independent of temperature and the activation energy is negative. Thus, some reactions may require a more complicated relationship between k and T than the simple Arrhenius form (Houston, 2001). However, in this work, the simple Arrhenius model is assumed.

2. The Temperature Scanning (TS) technique

The Temperature Scanning (TS) technology was first developed by Wojciechowski (1997) at Queen’s university, Kingston. He proposed that this methodology can improve the reaction kinetics studies by obtaining the same reaction rate information more rapidly than the conventional steady-state technique. TS methodology is one category of transient operation that applies dynamic thermal methods to various types of reactor i.e. continuously-stirred tank reactor (CSTR), plug-flow reactor (PFR), etc. TS reactors can be operated simply by introducing the temperature-ramping rate to the reaction system. It can also produce rate-data which cover a wide range of moving-boundary conditions. These rate-data are easily collated in a series of standard sets of isothermal results, at a speed much faster than any conventional method. TS technique is highly adaptable for sophisticated automation for high-through research such as automated data acquisition and statistical data analysis.

For conventional method of kinetics investigation, output temperature and concentration isothermal obtained from a series of steady-state experiments are correlated with the rate of reaction. Results from such steady-state experiments will then be interpreted for reaction kinetics. TS method, on the other hand, correlates histories of output concentration and rate-data with reaction temperature. Therefore, a large collection of rate-data (via online measurements) can be acquired from each experiment. The reaction kinetic parameters are determined via regression analysis, which requires experimental reaction rate-data at various reactant compositions and temperatures. In this work, the composition modulation was applied simultaneously with TS technique to help decrease the number of experiments required for reaction kinetics investigation.

Arprey *et al.* (1999) studied reaction kinetics using TS for steam-reforming of methanol over $Cu/ZnO/Al_2O_3$ catalyst in plug-flow reactor (PFR). They implemented an experimental program on the kinetics of this reaction on one catalyst at a fixed pressure and feed composition in the period of four hours of fully automated reactor operation. In order to compare the results obtained using the TS method to those obtained using the conventional isothermal method by the Hydrogen Research Group at RMC group, their work confirmed the rate measured satisfying to the rate model developed by RMC group. Their rate expression derived from a Langmair-Hinshelwood mechanism involving the forward and reverse processes of the three reactions involved as followed:

$$CH_3\,OH + H_2O \leftrightarrow CO_2 + 3H_2 \tag{21}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \tag{22}$$

$$CH_3OH \leftrightarrow CO + 2H_2 \tag{23}$$

The methanol conversions were monitored by a mass spectrometer in this automated reactor operation. This TS-PFR produced a large set of data much faster than the isothermal methods of reactor operation to date. Figures 3 and 4 show the overall methanol conversion and reactor exit temperature versus time, respectively. In Figure 3, the ethanol conversions at different values of space–time that are defined on the right hand side of the figure in the unit of sec. They were calculated as the volume of catalyst (litter) divided by the volumetric flow rate (litter. s^{-1}) of feed gas. Figure 4 shows the distinct separation in the reactor exit temperature between each runs, which is caused by the level of conversion varied with the flow rate, or another word due to diversities of the endothermicity of the reaction at different conversion.

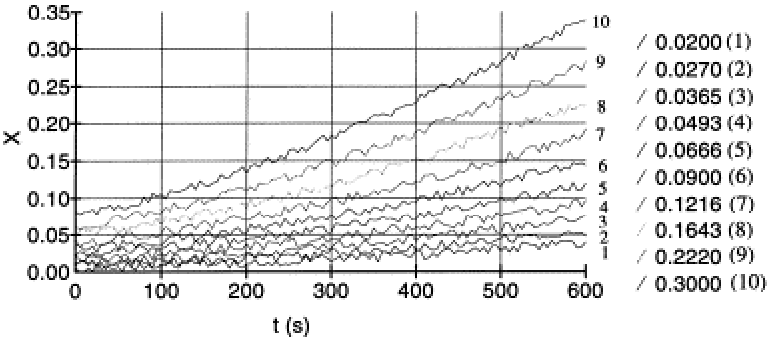


Figure 3 Raw conversion (X) as a function of clock time (t), experimental data using TS for steam-reforming of methanol over Cu/ZnO/Al_2O_3 catalyst in PFR.

Source: Wojciechowski (1999).

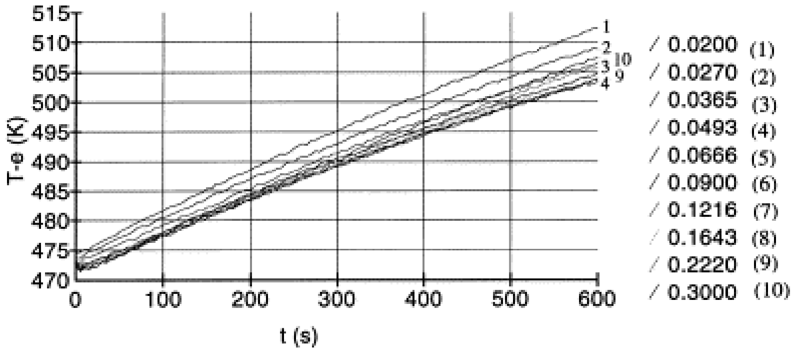


Figure 4 Reactor exit temperature (T-e) as a function of clock time (t), experimental data using TS for steam-reforming of methanol over Cu/ZnO/Al_2O_3 catalyst in PFR.

Source: Wojciechowski (1999).

Wojciechowski and Arprey (2000) also implemented the TS technique for carbon monoxide oxidation over platinum supported catalyst. Two mechanistic rate models used in this work are:

1) the Langmuir-Hinshelwood dual site molecular adsorption model (MAM)

2) the Langmuir-Hinshelwood dual site molecular dissociative model (DAM)

From TS-PFR experiments, the authors confirmed that the oxidation of carbon monoxide over platinum supported on alumina is a process in which rate expression could be derived from a Langmuir–Hinshelwood dual-site mechanism as previously proposed in literature. It was suggested that dissociated oxygen and molecular carbon monoxide adsorb on the same type of site and interact as adsorbed species in the rate-limiting step as the rate of this process is very well described by the fundamentally derived rate expression for the DAM. The parameters of the DAM rate expression indicate that atomic oxygen covers most of the surface at temperatures below 520 K. As temperature increases, the total surface coverage decreases slowly while the proportion of the surface covered by oxygen decreases rapidly. However, the authors referred that the MAM model presumed a reaction of carbon monoxide molecules with adsorbed molecular oxygen, and could fit experimental rates well for individual feed ratios but not over the range of feed ratios used in their study.

Domke *et al.* (2001) investigated the kinetics of ethylbenzene pyrolysis using a TS-PFR at various pressures, flow rates and steam-to-oil ratios. Raw data were collected at the end of PFR undergoing temperature ramping. The major product from this thermal cracking was styrene. It was observed that its selectivity was raised with increasing temperature. Several forms of the possible rate expression were analyzed. The rate expression best representing the collection of rate-data was an irreversible reaction with an Arrhenius rate constant as shown below:

$$r_{i,\text{calc}} = k_i P_{\text{EB}}^n = Ar_i \exp\left(Ea_i / RT\right) P_{\text{EB}}^n \qquad (24)$$

where the preexponential factor (Ar_i), activation energy (Ea), and order of reaction (n) were determined by minimizing the sum of residuals. The fitted rate expressions yielded the calculated conversions satisfying to those reported in literature.

3. The TS reactors operating procedure (Rice and Wojciechowski, 1997)

TS reactor operation involves ramping of the feed temperature while collecting composition and temperature data at the output of the reactor. This ramping rate must be set such that the time between successive analyses is shorter than the time required for a kinetically increment of temperature to be induced in the reactor. In the case of pilot plant, TS has already been used in much simplified form in some long-duration experiments, its space time is kept constant and its isothermal conditions are maintained for a certain period of time before introducing transient conditions. These results provided multiple isothermal conversion data which can be used to calculate multiple rates at various conversions and temperatures.

4. The definition equations for the TS-continuously-stirred tank reactor (CSTR)

CSTR is one type reactor commonly used in industrial processing due to the well-mixed property. It means that every variable (i.e., temperature and concentration) has no gradient everywhere inside the reactor and at the exit stream. In this work, we would consider only the mass balance for an ideal reactor model. This means that different molecules will have the same residence time and history.

Consider a CSTR for which the temperature of reactor can be ramped by controlling the amount of heat input to the reactor. In order to get an expression for the reaction rate, we will need the net rate of accumulation of reactant A according to the reaction in equation (1), that is

$$\textbf{Accumulation = input – Output + Generation} \tag{25}$$

$$\frac{\mathrm{d}N_{\mathrm{A}}}{\mathrm{d}t} = F_{\mathrm{A0}} - F_{\mathrm{A}} + \int_{V_{\mathrm{R}}} r_{\mathrm{A}} \mathrm{d}V \tag{26}$$

Since a liquid-phase reaction is considered, Eq. (26) can be rewritten in terms of concentration as there is no volume change ($F_{\mathrm{A0}} = C_{\mathrm{A0}}v_{\mathrm{A0}}$ and $F_{\mathrm{A}} = C_{\mathrm{A}}v_{\mathrm{A0}}$) (Fogler, 2005).

$$\frac{\mathrm{d}C_{\mathrm{A}}}{\mathrm{d}t}=\frac{1}{\tau}(C_{\mathrm{A0}}-C_{\mathrm{A}})+r_{\mathrm{A}} \quad ; \quad r_{\mathrm{A}}=-k_{\mathrm{A}}C_{\mathrm{A}}^{\gamma}C_{\mathrm{B}}^{\beta} \tag{27}$$

where the residence time = $\tau = V_{\mathrm{R}} \big/ \left(v_{\mathrm{A0}}+v_{\mathrm{B0}}\right) = V_{\mathrm{R}}/v_0$; s^{-1} (28)

Other chemical species involved in the reaction, they can be described in the same manner (Fogler, 2005):

Reactant B:

$$\frac{\mathrm{d}C_{\mathrm{B}}}{\mathrm{dt}}=\frac{1}{\tau}(C_{\mathrm{B0}}-C_{\mathrm{B}})+r_{\mathrm{B}} \quad ; \quad r_{\mathrm{B}}=-k_{\mathrm{A}}C_{\mathrm{A}}^{\gamma}C_{\mathrm{B}}^{\beta} \tag{29}$$

Product C:

$$\frac{\mathrm{d}C_{\mathrm{C}}}{\mathrm{d}t}=\frac{1}{\tau}(0-C_{\mathrm{C}})+r_{\mathrm{C}}=r_{\mathrm{C}}-\frac{1}{\tau}C_{\mathrm{C}} \quad ; \quad r_{\mathrm{C}}=k_{\mathrm{A}}C_{\mathrm{A}}^{\gamma}C_{\mathrm{B}}^{\beta} \tag{30}$$

Product D:

$$\frac{\mathrm{d}C_{\mathrm{D}}}{\mathrm{d}t}=\frac{1}{\tau}(0-C_{\mathrm{D}})+r_{\mathrm{D}}=r_{\mathrm{D}}-\frac{1}{\tau}C_{\mathrm{D}} \quad ; \quad r_{\mathrm{D}}=k_{\mathrm{A}}C_{\mathrm{A}}^{\gamma}C_{\mathrm{B}}^{\beta} \tag{31}$$

Note that reaction rates in the mass balances in equations (27-31) are interchangeable according to the stoichiometry, equation (5) and can be directly substituted by the specific rate of A.

For this TS-CM CSTR, in which the reaction temperature can be varied by controlling the amount of heat input to the reactor, the energy balance is not taken into account in the mathematical modeling because we assume instantaneous mixing. The reaction temperature is only required for the Arrhenius equation. The reactor temperature (T_R) was maintained at the desired temperature during steady state (T_{Rs}) and at a controlled ramping rate (u) during transient operation ($t > t_w$). The governing equation for the reactor temperature is given as:

$$T_R = T_{Rs} + u(t - t_w) \tag{32}$$

where u is the ramping rate of temperature (°C/s) introduced at $t = t_w$.

5. The composition modulation (CM) technique

The composition modulation is a powerful technique to investigate the transient behavior of chemical and physical system. When a system is perturbed by a periodic change of parameter affecting a chemical and physical state of the system, for example concentration, pH, or temperature, the response will also be periodic. The periodically alternating response can sensitively be detected and the signal-to-noise ratio can be significantly enhanced by a phase-sensitive detection (Urakawa *et al.*, 2006). Two kinds of composition modulation are typically used in the kinetic studies; sinusoidal and square-wave stimulations. Sinusoidal-wave is simpler to treat theoretically for the quantitative analysis of the response including the overtone. The latter, square-wave, is often easier to generate experimentally, in particular in the case of concentration stimulation, which is generated by switching between two flows of different concentrations. However, the analysis of the responses to a square-wave is more cumbersome when it comes to quantitative analysis. The response of the affected parameters obtained will exhibit frequency dependent amplitude and a phase delay with the stimulation. During each periodic perturbation cycle, the affected parameters relax to new quasi-steady state values around which they oscillate. This research contribution is the demonstration of a new transient technique for kinetic responses to square-wave modulation in CSTR both computationally and experimentally.

In order to reasonably model the well-mixed tank and also to consider the square wave stimulation of the feed rate, $\delta_A(t)$, introduced at $t = t_w$ in units of mole/s and the first order differential equation are used to mathematically describe the concentration change of NaOH in the tank, resulting in following equation:

$$\delta_{\mathrm{A}}(t) = C_{\mathrm{Ami}} v_{\mathrm{m}} + \left(C_{\mathrm{A}}^{\delta} \bullet (V^{\delta} / t^{\delta}) \right) \tag{33}$$

Defining the inlet concentration of NaOH into the mixing tank:

$$C_{\mathrm{Am0}}(t) = \frac{\delta_{\mathrm{A}}}{v_{\mathrm{m}} + (V^{\delta} / t^{\delta})} \tag{34}$$

The unsteady-state mixing tank model with a constant volume (without chemical reaction):

$$V_{\mathrm{m}} \frac{dC_{\mathrm{Am}}}{dt} = v_{\mathrm{m}} (C_{\mathrm{Am0}} - C_{\mathrm{Am}}) \tag{35}$$

According to equation (34), the inlet concentration (C_{AM0}) is varied with time due to the infusion rate described by equation (33). Thus, C_{AM} is perturbed with forced concentration modulation. The system then follows a certain trajectory while undergoing relaxation to a new steady state.

Suman (2004) reported that, for oxo reaction converting olifins and synthesis gas into aldehydes and alcohols carrying out in two CSTRs in series, higher productivity (up to 11.6%) compared to that of steady-state operation was obtained by forcing input composition and/or flow rate fluctuations. These forcing fluctuations were made in the form of systematic sinusoidal disturbances to process. As a result, the unsymmetrical fluctuations in the process output were observed. It was found that the overall heat transfer coefficient has a significant effect on this chemical oscillator system. Especially, when the variations in process inputs are coupled with chemical oscillatory system, the effect of input composition modulation is prominent and complex.

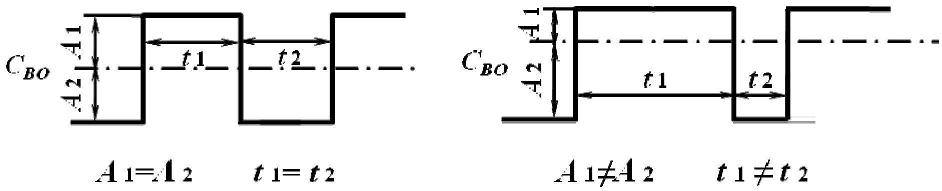
Lian and Haidong (1993) investigated the transient behavior of benzene oxidation over V_2O_2 catalysts in an isothermal fixed-bed reactor under forced concentration modulation. Two types of concentration perturbations were applied; regular and irregular forms as shown in Figure 5. The relation of the irregular square wave in Figure 5 can be expressed as follow:

$$t_1 A_1 = t_2 A_2 \tag{36}$$

where

$$C_{B0} = \frac{t_1(A_1 + A_2)}{(t_1 + t_2)} \times 100\% \tag{37}$$

Hence up-step t_1 and down-step t_2 periods and amplitudes of oscillation operation (A_1 and A_2) can be determined through C_{B0} (the time-averaged feed concentration of benzene). Selectivity and yield of maleic anhydride for experiments with different patterns of concentration perturbation (C_{B0} constant) were compared with the steady-state values. It was found that the irregular square-waves of benzene concentration enhanced the production yield of maleic anhydride from the steady-state operation more than the regular square-waves.



(a) (b)

Figure 5 Two different types of square wave concentration modulation: a) regular square wave and b) irregular square wave

Source: Lian and Haidong (1993)

6. Kinetics of alkaline hydrolysis of ethyl acetate

In order to test and analyze the application of this newly developed transient technique in CSTR, the alkaline hydrolysis of ethyl acetate was chosen as a model reaction for the investigation of reaction kinetics based on the power law model. This reaction is simply assumed without side reactions and without reverse reaction, as shown in equation (6). As the reaction proceeds, hydroxyl ions are consumed and acetate ions are produced.

The relationship of reaction rate of the various species involved in the reaction is obtained from the ratio of stoichiometric coefficients, as shown in equation (7). Thus, the rates of disappearance and generation are rewritten as:

$$-r_{\mathrm{H_3COOC_2H_5}} = -r_{\mathrm{NaOH}} = r_{\mathrm{C_2H_5OH}} = r_{\mathrm{CH_3COO^-Na^+}} \qquad (38)$$

The reaction can be considered as an equi-molar, first order with respect to both sodium hydroxide and ethyl acetate, i.e. second order (overall), within basic solution at pH ranging from 11-14 and the reaction temperature in the range of 25-80°C (Robison and Tester, 1990). From the power-law model in equation (11), the specific reaction rate of NaOH (Species A) is written that:

$$-r_{\mathrm{A}} = k_{\mathrm{A}} \mathrm{C}_{\mathrm{A}}^{1} \mathrm{C}_{\mathrm{B}}^{1} \qquad (39)$$

The steady state conditions of this reaction system depend on reactor temperature, concentration of reagents, flow rate and the volume of the reactor. This particularly-simple chemical reaction has been used in research work to demonstrate the deviation of a chemical reactor from an ideal CSTR. The alkaline hydrolysis of ethyl acetate can be monitored by following the change in the conductance of reaction mixture with time because the hydroxyl ions have a very much higher specific conductance than acetate ions. By means of calibration line, the conductivity is the functions of concentration and temperature, thus the data collected in the form of electrolyte conductivity would be transformed into NaOH concentration.

In most cases of published kinetics data for alkaline hydrolysis, the second order rate constant agree well for experiments performed in strongly basic solutions (NaOH) at pH values ranging from 11 to 14 and temperatures from 25-80°C. If the concentration of hydroxyl ions is kept constant, or in excess, the order of reaction is pseudo-first in ester concentration. Table 5 lists some Arrhenius parameters for various conditions of ethyl acetate hydrolysis reactions. In Table 5, the first two published kinetic data (Bamford and Tipper, 1972) were obtained from experiments carried out with 1 M NaOH at 25°C. Later literature data reported by Robison and Tester (1990), the non-buffer experiments with ethyl acetate were performed in the temperature range of 25 to 60°C and pH of 11, and the buffer experiments were studied at room-temperature pH of 5.6 and temperatures from 110-190°C. In this work, it was assumed that $[\mathrm{OH}^-] = 10^{-\left(14 - \mathrm{pH}_{25^\circ\mathrm{C}}\right)}$, without the effect of water dissociation reaction.

Table 5 Published alkaline hydrolysis kinetic data

Conditions	Preexponential factor, *Ar* (L/mol·s)	Activation Energy, *Ea* (kJ/mol)
70 % acetone solvent*	1.26×10^6	42.30
Water*	2.45×10^7	47.30
Non-buffer experiment**	4.00×10^7	48.90
Buffer experiment**	1.01×10^6	38.40

Source: * Bamford and Tipper (1972); ** Robison and Tester (1990)

MATERIALS AND METHOD

Materials

1. Equipments

1. Computer and Software (MatLab Program)
2. Mixing tank (330 cm^3)
3. Continuous Stirred Tank Reactor: CSTR (330 cm^3)
4. Magnetic stirrer hotplates
5. Magnetic stirring bars
6. pH meter (pH 211; HANNA Instrument)
7. Conductivity measuring cell (Cond 330i/ SET, TatraCon 325; WTW)
8. Temperature sensors
9. Syringe (5 and 25 cm^3)
10. Tube (L/S 14 and 25, Tygon® Chemical; Masterflex®)
11. Solution reservoirs
12. Peristaltic pumps (easy-Load® II; Masterflex®)
13. Syringe pump
14. Analytical Balance (within 0.0001 g)
15. Micropipette (100-1,000 µL)
16. Pipette (10 cm^3)
17. Volumetric flasks (2,000 cm^3)

2. Reactants

1. Ethyl acetate (QRëC™, Grade AR, 99.5%)
2. NaOH solution (0.02, 0.8, and 3 M)
3. Deionized (ID) water

Methods

1. Algorithm of the developed TS-CM technique

The transient technique developed in this work involves TS and CM simultaneously imposed to a CSTR initially operating at steady state. This is called “TS-CM CSTR”. To verify the possibility to apply this technique for the estimation of reaction kinetic parameters, the procedure is described as followed:

1) Design the system though TS and CM approaches, including mixing tank, reactor and analytical instruments. And choose a model reaction which can base on power law and Arrhenius equation in CSTR for the investigation of reaction kinetics.

2) Setup and perform the transient experiments of model reaction.

3) Develop the computational procedures using software (MatLab7) to estimate kinetic parameters for the model reaction. It will construct the relation between rate of reaction versus reactant concentration and reaction rate constant versus temperature reactor (The correlation of Arrhenius equation) by varying the kinetic parameters (i.e., the reaction order, the activation energy, and the preexponential factor).

Estimation of reaction kinetic parameters employed a series of time-evolved output NaOH concentration generated via the dynamic simulation of the aforementioned mathematical model. Each simulation is associated with different values of reaction parameters i.e., reaction order, activation energy, and preexponential factor. The ranges of parameters were 0-2, 0-2, 2.40×10^7-4.05×10^7 L/mol-s, and 49,000-47,000 J/mol for γ, β, Ar and Ea, with the step size of 0.2, 0.2, 5×10^5, and 100, respectively. For each set of reaction kinetic parameters, the sum of squared errors was calculated from the comparison between the calculated concentration of NaOH versus time and the experimental data. The sum of squared errors is defined as:

$$\mathrm{SSE} = \sum (C_{\mathrm{Aex}} - C_{\mathrm{Acal}})^2$$

The set of parameters yielding the minimum SSE was the reaction kinetic parameters for the system.

5) Discuss and conclude whether the error and the reaction kinetic parameters attained of the computationally developed technique is acceptable.

2. The Calibration of Conductivity measuring cell

Perform the calibration of conductivity measuring cell as follow:

- Prepare NaOH solution at various concentrations (0.001, 0.002, 0.003, …, and 0.012 M)

- Find-tune conductivity on the basis of the conductance of NaOH solution for the temperature range of 30-50°C

- Measure conductivity of different solutions

3. TS-CM CSTR configurations and operations

The system for TS-CM CSTR includes a mixing tank, a reactor, and analytical instruments. Single-pulse and multi-pulse experiments for the determination of reaction kinetics parameters of alkaline hydrolysis of ethyl acetate were performed by injecting a controlled dose of concentrated NaOH into a CSTR operating at steady-state with two separate input streams of an NaOH solution and an ethyl acetate one. The schematic diagram of the experimental setup is shown in Figure 6. A mixing tank, a 330 cm^3 glass vessel, was fitted with a thermometer and a measuring pH probe (pH 211 by HANNA Instrument). For an experiment, 0.02 M of NaOH solution was fed from the solution reservoir into the mixing tank placed on a hotplate magnetic stirrer at the volumetric flow rate of 74 cm^3/min using a peristaltic pumps (easy-

Load® II by Masterflex®). 0.012 M of ethyl acetate solution was fed at the volumetric flow rate of 67.5 cm^3/min into another mixing tank, a CSTR, fitted with a thermometer and a conductivity measuring cell (Cond 330i/ SET & TatraCon 325 by WTW). The vessel was placed on a hotplate magnetic stirrer and stirred vigorously. The outflow of NaOH solution from the mixing tank was transferred into a CSTR while it was maintained at the desired temperature (31.2°C) (see Figure 6). At this point, the sensing instrument, i.e. pH meter and conductance measuring sensor, and temperature sensor, were started to collect data. When the system reached steady state, 5 cm^3 of 0.8 M NaOH solution was injected into the mixing tank while the temperature of CSTR was started to ramp from 31.2°C to 45°C with the ramping rate of approximately 0.02°C/sec. The operation terminated when the new steady state of the mixing tank and the CSTR were established.

For the multi-pulse experiment, three loops of square-wave modulation of NaOH concentration were introduced to the system together with the temperature ramping. The operation of multi-pulse experiment was similar to that of single-pulse experiment. The concentrations of bulk NaOH and ethyl acetate solutions were 0.02 M and 0.015 M, respectively. The inlet flow of mixing tank was 70 cm^3/min, and the inlet flow rate of ethyl acetate solutions fed into the CSTR was 73 cm^3/min. The CSTR was maintained at 29.5°C. A syringe pump was programmed to feed 1 cm^3 of 3 M NaOH every 19 minutes at the volumetric flow rate of 60 cm^3/h (20 minutes of cycle time). The reactor temperature was ramped up along the duration of the first pulse followed by a ramp down and up again during the second and third pulse, respectively. After the 3rd pulse, the perturbation of both reaction temperature and inlet NaOH concentration terminated. The pattern of temperature fluctuation is discussed later.

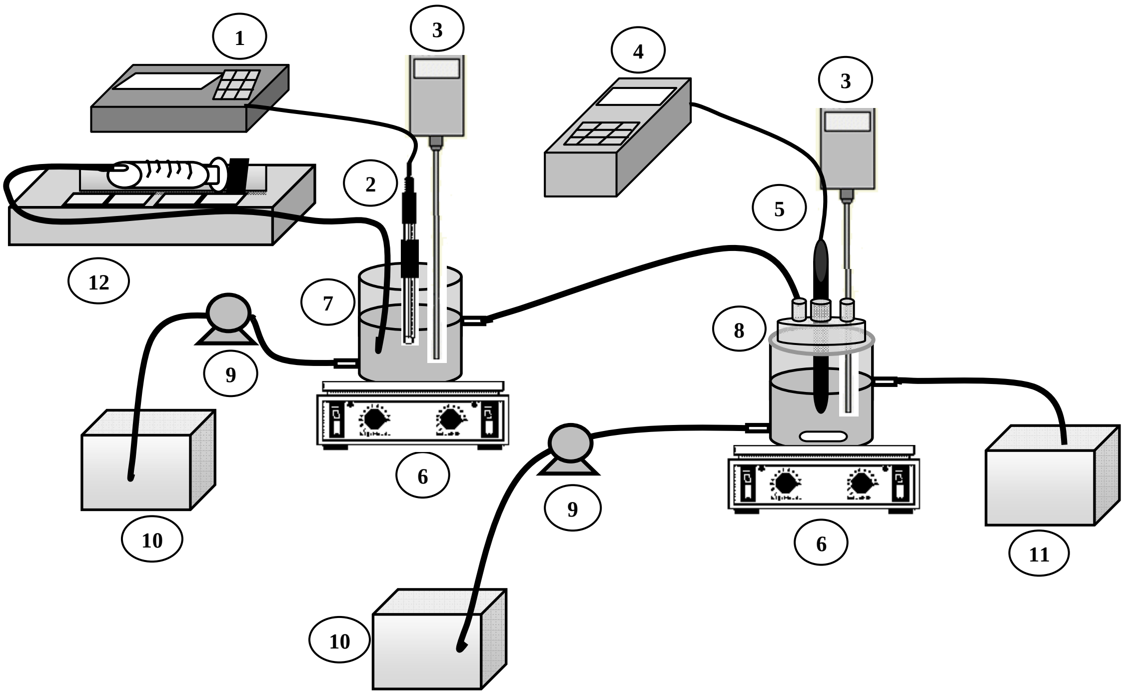


Figure 6 Experiment set-up: 1) pH meter, 2) pH measuring probe, 3) Thermometer sensor, 4) Conductivity measuring cell, 5) Conductivity measuring probe, 6) Magnetic stirrer hotplates, 7) Mixing tank, 8) CSTR, 9) Peristaltic Pump, 10) Solution reservoir, 11) Sample reservoir, 12) Syringe pump

RESULTS AND DISCUSSIONS

To demonstrate and validate the new transient technique for studies on reaction kinetics, a system comprising a mixing tank, a CSTR, continuous and pulsing feed system, a heater for temperature ramping and a data acquisition system was arranged. Experimental results are divided into two sections, which are the response of single NaOH-pulse injection and multiple NaOH-pulse injections experiments; both were accompanied with a ramp of reaction temperature. To obtain the kinetic parameters of the presumed power-law model, the explicit Runge-Kutta fourth-order algorithm was used as the ordinary differential equation solver for simulating transient response of the arranged system. The experimental data was compared with the computer simulation in the form of time-evolved output concentration in order to verify the applicability of the TS-CM CSTR.

1. The response of single-pulse injection into mixing tank accompanied to a ramp of reactor temperature

1.1 The time-evolved concentration from the mixing tank

The mixing behavior was first analyzed from the concentration pulsing experiment. The data collected in the form of pH value were transformed into NaOH concentration (C_A) using the correlation of $[\mathrm{OH}^-] = 10^{-\left(14 - \mathrm{pH}_{25^\circ\mathrm{C}}\right)}$. The inlet signal of concentration modulation is represented in the small right-hand-side picture embedded in Figure 7. The variation of the output NaOH concentration response, caused by injecting a pulse of 0.8 M NaOH (0.004 moles) at t_w = 90 s and t^δ = 3 s, demonstrated a pattern of exponential decay after a sharp increase upon injection. After 1,000 s, the added NaOH was completely flushed out by the flow and the system returned to its initial steady state. This pattern of exponential decay agrees with a dynamical simulation of a NaOH-pulse injected at t = 90 s into a mixing tank, as correlated with equations (28-30), which is indicative of a well-mixed condition without dead volume. The error in terms of the number of NaOH molecules (injected versus integration from output response) is about 0.16%. Because of the similar configurations of the CSTR and the mixing tank, it is assumed that the reactor is also well-mixed. This pulse response was used in the kinetic experiment as a source of inlet concentration perturbation of the CSTR.

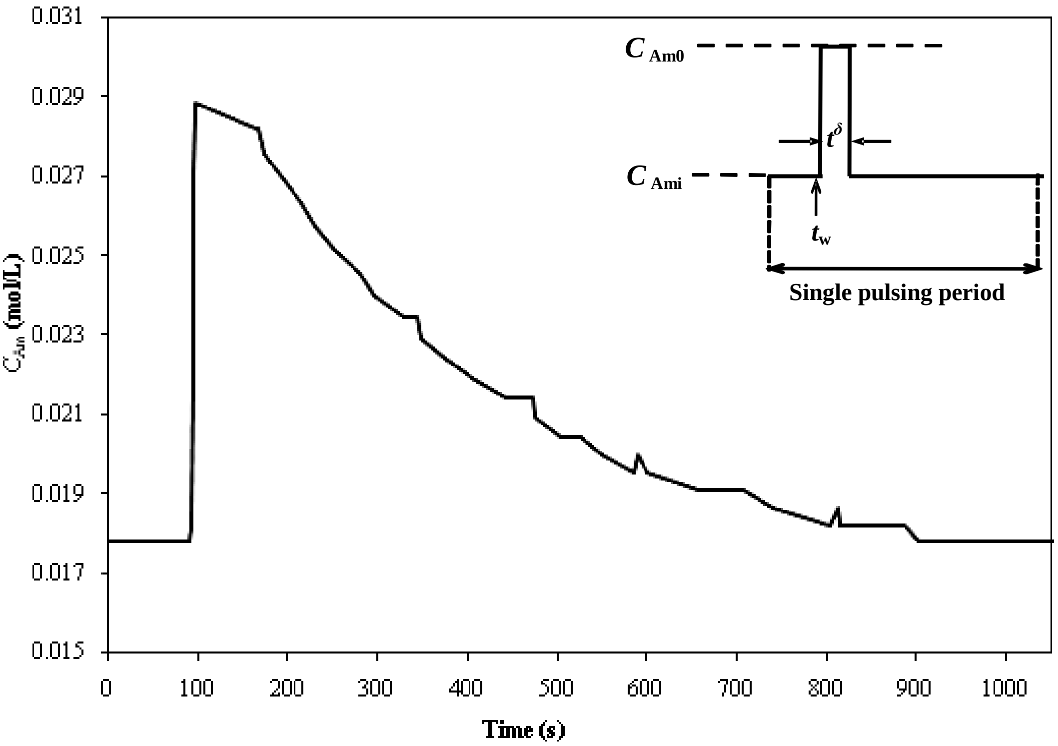


Figure 7 Variation of NaOH concentration with time from a NaOH-pulse experiment accompanied by ramping reactor temperature.

1.2 The variation of the temperature in TS-CM CSTR with time

During an experiment, the reaction temperature was ramped up from the initial steady-state value (31.2°C) to the final temperature at 45°C by means of a hotplate. The temperature response is shown in Figure 8. The duration of this transient period was predetermined by the pulse experiment (Figure 7), such that there would be a combined effect of transient concentration and temperature throughout the experiment. This temperature history together with the pulsing of NaOH will be used as forcing functions in the computer simulation for determination of reaction kinetics.

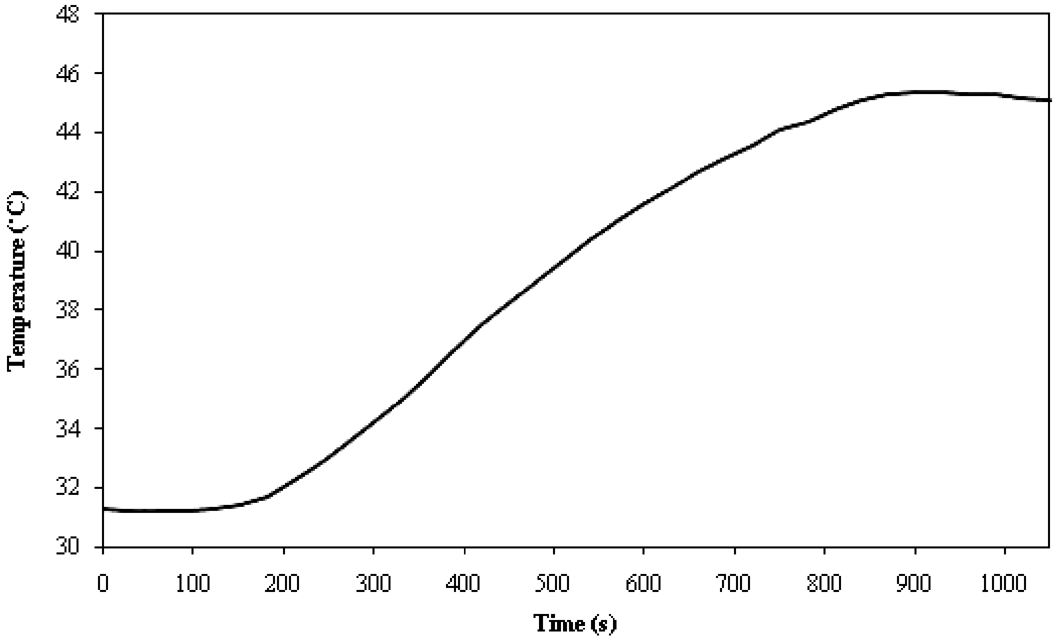


Figure 8 Variation of the temperature in TS-CM CSTR with time from a NaOH-pulse experiment accompanied by ramping reactor temperature.

1.3 CSTR concentration profile

The electrolyte conductivity data were transformed into NaOH concentration (C_A). Figure 9 shows the evolution of the output NaOH concentration from the CSTR with time. The solid line represents the NaOH concentration obtained experimentally. The concentration rapidly increased from 0.0081 to 0.0113 M right after the pulse injection followed by an exponential decline approaching a new steady-state value. The overall trend is similar to Figure 7, except that the front part of the curve is not as sharp due to the chemical reaction. Notice that the final NaOH concentration is less than the initial steady-state value because of the temperature difference of 14°C between the two states (higher reactant consumption rate at higher temperature). Because the entire transient NaOH concentration profile is directly related to the reaction kinetics, a unique solution in terms of reaction order, frequency factor, and activation energy can be found via regression. This characteristic of output response from a TS-CM CSTR results from the combined effects of reaction temperature and the reactant concentration on reaction rate.

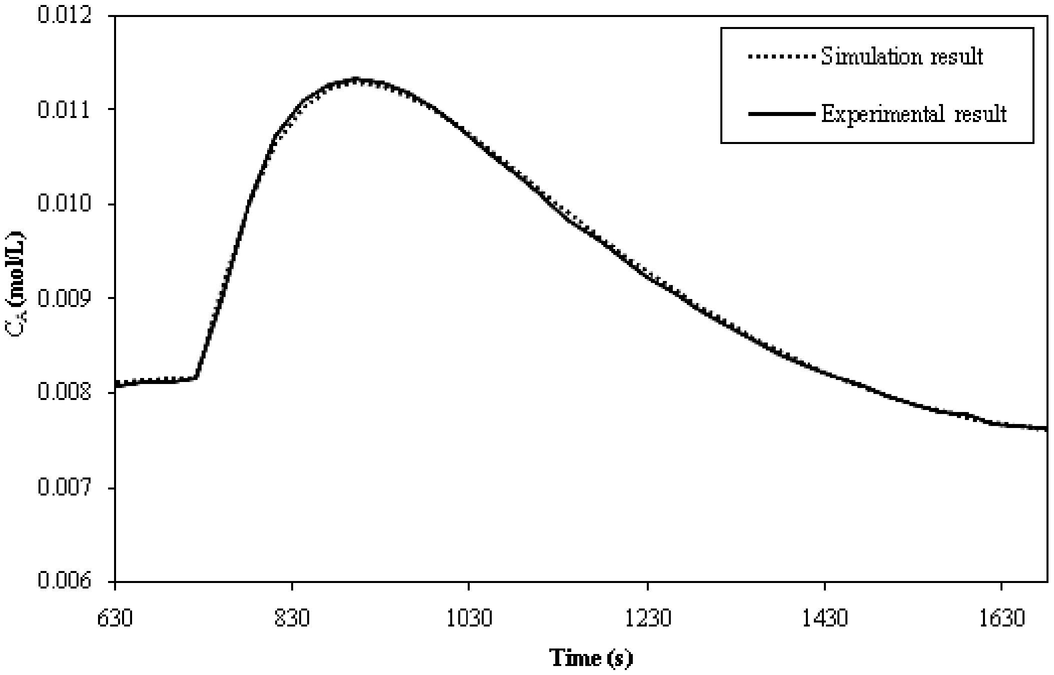


Figure 9 Simulation of $C_{NaOH}(t)$ compared with experimental results from a NaOH-pulse experiment accompanied by ramping reactor temperature.

After performing a transient experiment and collecting the output variable (NaOH concentration) response, γ, β, Ar and Ea can be estimated via the technique previously described. By applying the explicit Runge-Kutta 4^{th}-order algorithm for ordinary differential equations, the dynamic model developed earlier was used to simulate the transient NaOH concentration response in Figure 9, the dotted line represents the computed result of a unique set of reaction kinetic parameters providing the minimum sum of squared errors (SSE = 5.9384×10^{-8}). It is apparent that both simulation and experimental results agree well. Note that SSE accumulates from the steady state prior to the injection to the final steady state. The values of kinetic parameters obtained from the analysis are $\alpha = 1$, $\beta = 1$, $Ar = 4.0 \times 10^7$ L/mol·s, and Ea = 48.5 kJ/mol; comparable to those reported by Bamford and Tipper (1972) and Robison and Tester (1990) as shown in Table 6.

2. The response of multi-pulse injections into mixing tank accompanied to temperature ramping.

2.1 The time-evolved concentration from the mixing tank

For multi-pulse experiment, the inlet concentration of NaOH was forced via feeding of a controlled dose of NaOH into the mixing tank. The feed pattern was predetermined from the previous step response curve such that the outlet NaOH concentration level from the mixing tank prior to each pulse had returned to its initial steady-state value as shown in Figure 10. The time period for eliminating the effect of an NaOH pulse was about 1,200 s. Again, a typical exponential decay pattern corresponding to each pulse indicated well-mixed conditions. This stream of NaOH with varying concentration entered the CSTR where the reaction temperature was forced to change as shown in Figure 12; therefore, both reactant concentration and temperature were changed simultaneously. In principle, the output response is unique for a particular cyclical pattern of perturbation. The inlet signal of concentration modulation is represented in the small right-hand-side picture embedded in Figure 10, in which on-off operation was used as a source of irregular square-wave cycling. There were three pulses of 3 M NaOH (0.003 moles for each pulse) at t_w = 120 s and t^δ = 1 min. The non-pulsing period was predetermined from the previous step response curve such that the effect of each pulse was eliminated before another injection.

Notice that the second and third pulses were introduced after the NaOH concentration in the mixing tank had approached steady state. The steady state value of NaOH concentration after the third pulse was slightly lower than its initial steady state, potentially caused by changes in electrode sensitivity due to temperature difference. For our case, the correction factor due to changes in temperature is very close to 0.01 pH/0.1^{o}C away from the actual pH value. Figure 11 shows the concentration profile of NaOH in the mixing tank according to the corrected pH values.

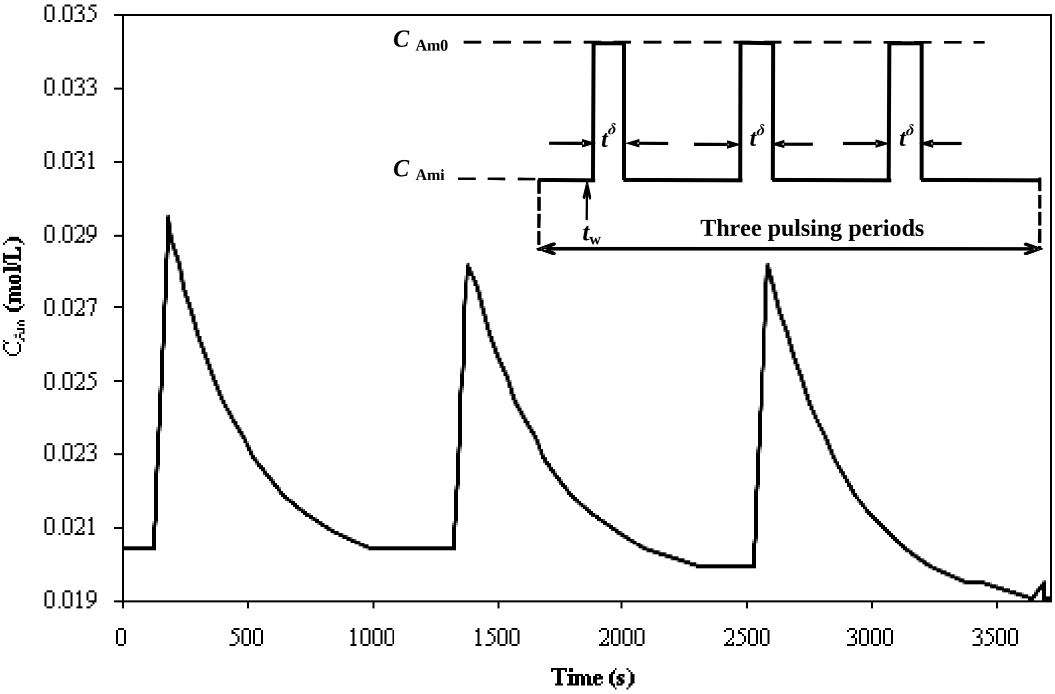


Figure 10 Variation of NaOH concentration with time from multiple NaOH-pulses accompanied by controlled variation of reactor temperature.

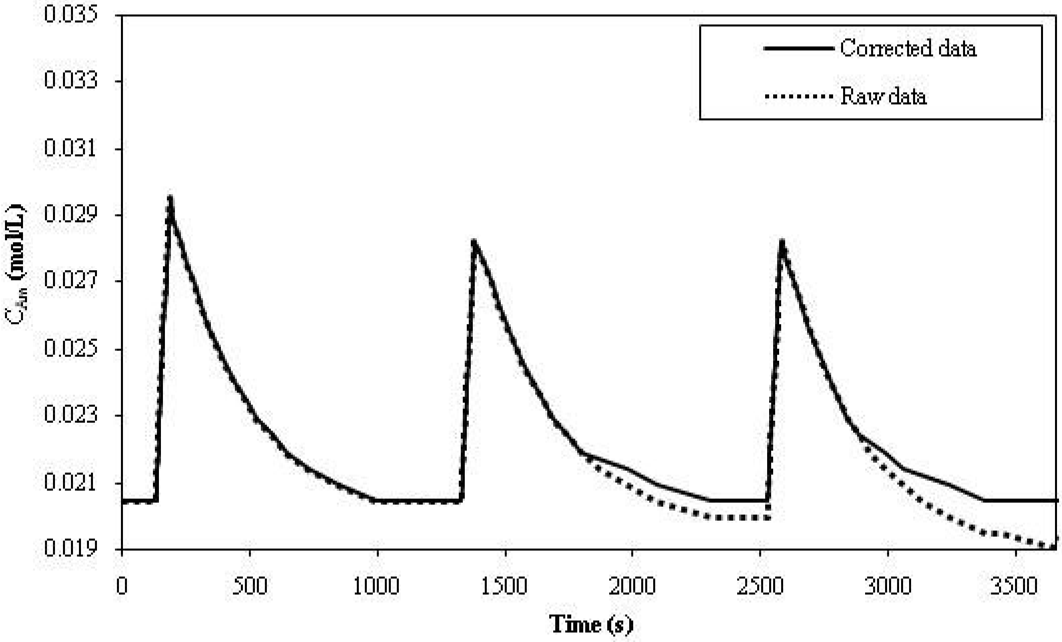


Figure 11 The concentration profile of NaOH in the mixing tank from multi-pulse experiment after and before the correction of pH electrode for the temperature effect.

For this reason, the pulse response of mixing tank model from simulation would be alternatively used as a source of inlet concentration perturbation of the CSTR in the analysis.

2.2 The variation of the temperature in TS-CM CSTR with time

The temperature fluctuation during a multi-pulse experiment in TS-CM CSTR is shown in Figure 12. Prior to feed introduction, the reactor was operated at steady state. At t = 60 s, the reaction temperature was ramped up from the initial steady-state value (30°C) to 44.2°C at t = 1330 s; the time when the 2nd pulse of NaOH was introduced to the mixing tank. After that, the reactor temperature was ramped down reaching 31.9°C at t = 2530 s. Upon the last feed step, the reactor temperature was ramped up again to 44.5°C. In this experiment, the period of temperature ramp was associated with the NaOH concentration pulsing (Figure 10). Note that other temperature patterns can be applied. This temperature profile, together with the output NaOH concentration from the mixing tank, was used as input perturbation in a dynamic simulation of TS-CM CSTR as discussed earlier.

2.3 CSTR concentration profile

The conductivity signal was transformed into NaOH output concentration (C_A) as mentioned above and is represented by a solid line in Figure 13. This concentration profile resulted from a compounding effect of variations of reaction temperature and reactant concentration as previously explained. Three peaks were caused by three separate NaOH infusions. The middle peak is slightly smaller than the other two because of higher reaction temperature (higher reactant consumption rate). By following the same procedure for determining reaction kinetics parameters as applied with the single-pulse experiment, it yielded the minimum SSE of 7.3354×10^{-7} corresponding to $\alpha = 1$, $\beta = 1$, $Ar = 2.90\times10^{7}$ L/mol·s, and $Ea = 47.10$ kJ/mol. The parameter values are close to that obtained from the single-pulse experiment and those reported in literature. The dotted-line in Figure 13 shows that the computed and experimental results are in very good agreement.

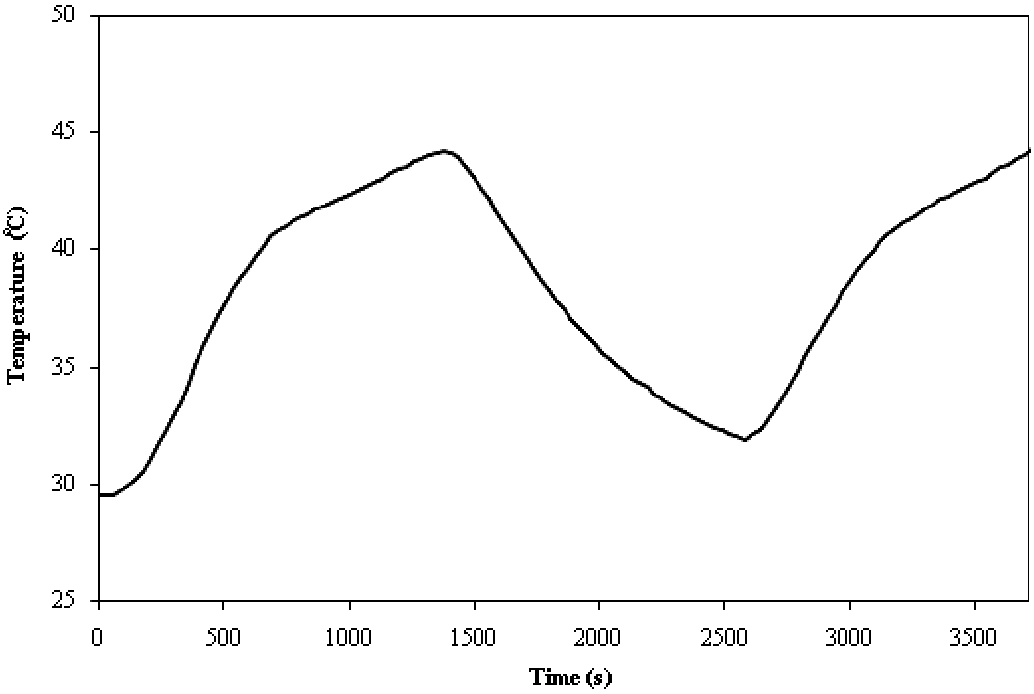


Figure 12 Variation of the temperature in TS-CM CSTR with time from multiple NaOH-pulses accompanied by controlled variation of reactor temperature.

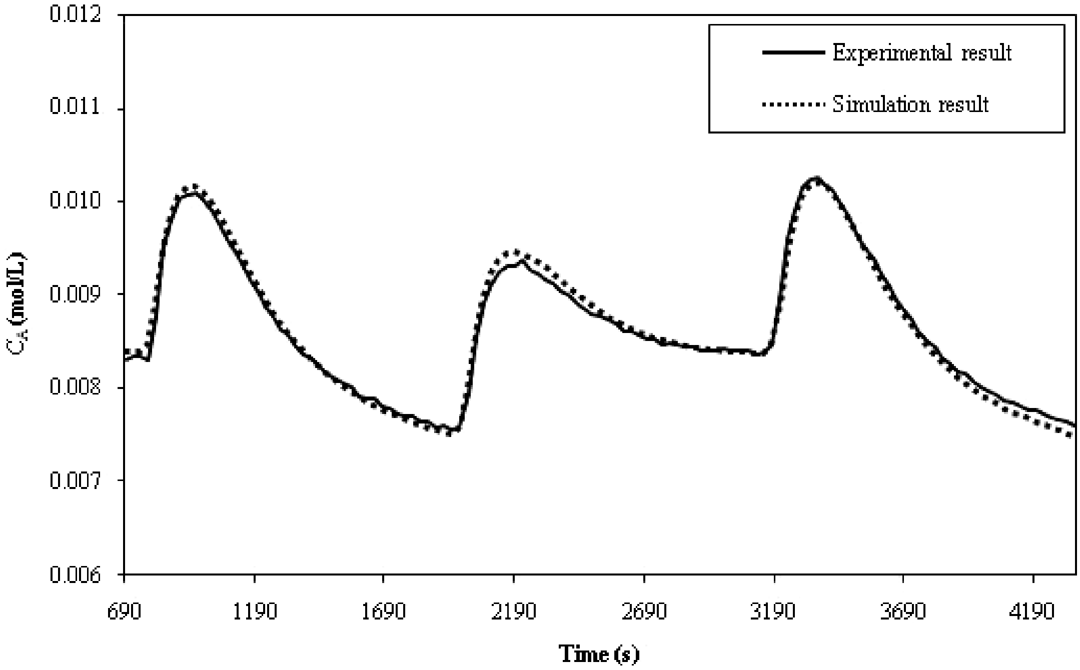


Figure 13 Simulation of $C_{\mathrm{NaOH}}(t)$ compared with experimental results from multiple NaOH-pulses accompanied by controlled variation of reactor temperature.

Table 6 summarizes the kinetic parameters obtained from single-pulse and multi-pulse experiments including reaction orders, preexponential factor, and activation energy. The orders of reaction obtained from the single-pulse experiment and the multi-pulse experiment are the same and are equal to the literature data. The activation energy and preexponential factor from the single-pulse experiment and the multi-pulse experiment were comparable to that reported in literatures. It is noted that the applicability of the power-law model and its parameters is limited to certain extent and is associated with the operating conditions of experiments where the kinetic parameters were obtained from. Another multi-pulse experiment was performed with the concentration level of the ethyl acetate stream at 0.024 M, which was larger than that of the NaOH stream, simulating a condition of excess ethyl acetate. Following the experimental procedure and analysis method of TS-CM technique, it was found that the orders of reaction were different compared to that obtained from previous experiments. The time-evolved concentration from the mixing tank, the temperature variation and concentration profile of TS-CM CSTR versus time are shown in Figures 14, 15 and 16, respectively. Careful inspection of Figure 16 suggested that the experimental steady state prior to perturbations was quite different from the simulated one. It is probable that the form of rate expression used in the analysis was invalid in this range of concentration of ethyl acetate. There may be a significant extent of backward reaction as a result of excess reactant molecules. In this case, the rate expression best representing the experimental data may be determined via model discrimination (mechanistic model, power-law model, etc). However, this is beyond the scope of the current study.

Table 6 Comparison of kinetics parameters of alkaline hydrolysis simulation under TS-MC condition and literature values.

Resource	α	β	*Ar* (L/mol·s)	*Ea* (kJ/mol)
Bamford and Tipper (1972)	1	1	2.45×10^7	47.30
Robison and Tester (1990)	1	1	4.00×10^7	48.90
The single-pulse experiment	1	1	4.00×10^7	48.50
The multi-pulse experiment	1	1	2.90×10^7	47.10
Ethyl acetate in excess	2	0	3.20×10^7	47.00

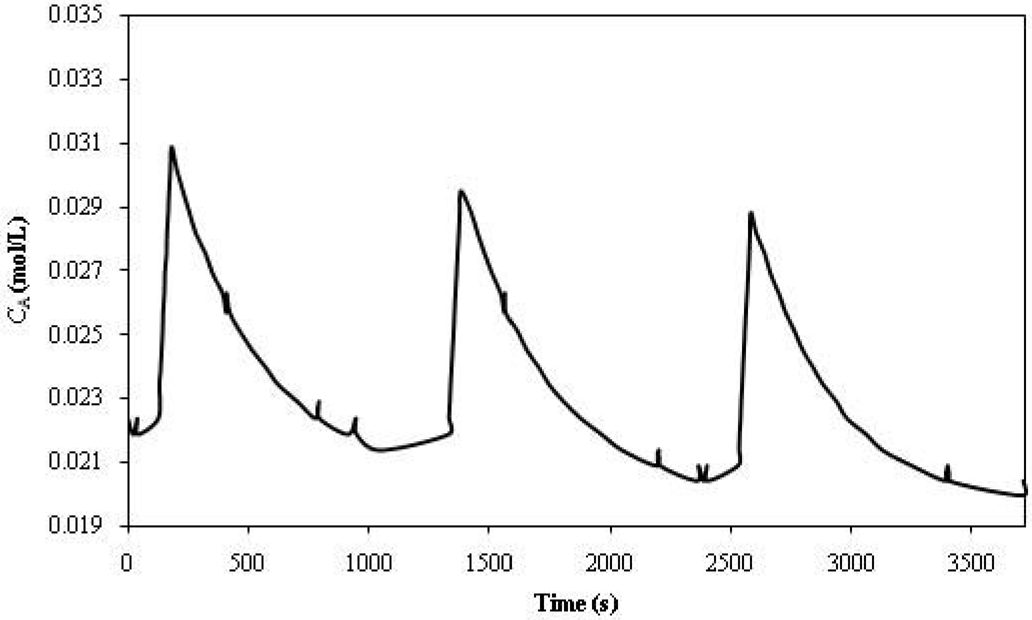


Figure 14 The time-evolved concentration from the mixing tank for the case of ethyl acetate in excess.

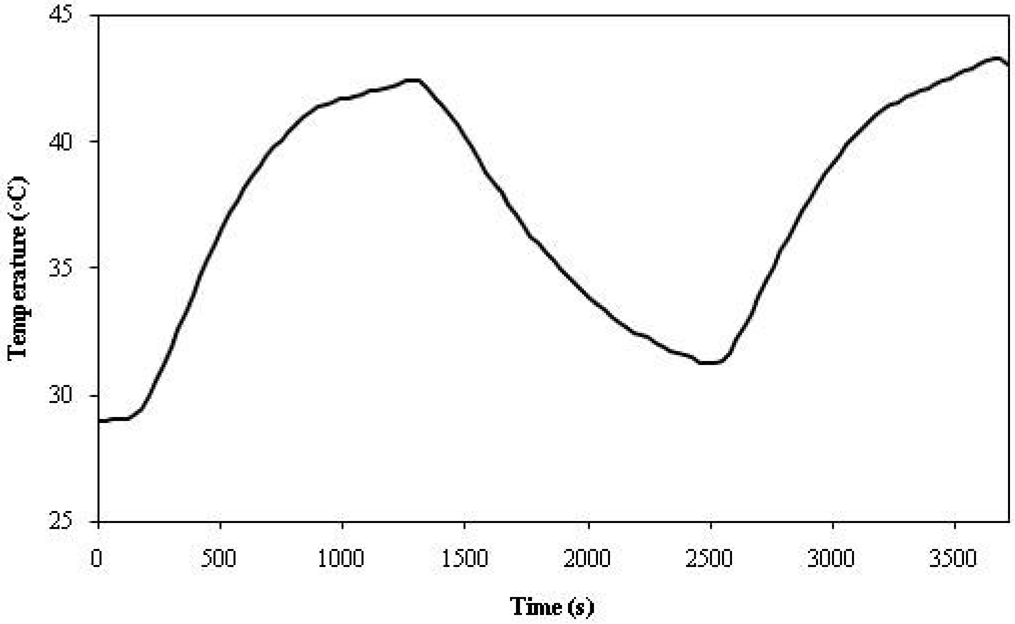


Figure 15 The temperature variation with time of TS-CM CSTR for the case of ethyl acetate in excess.

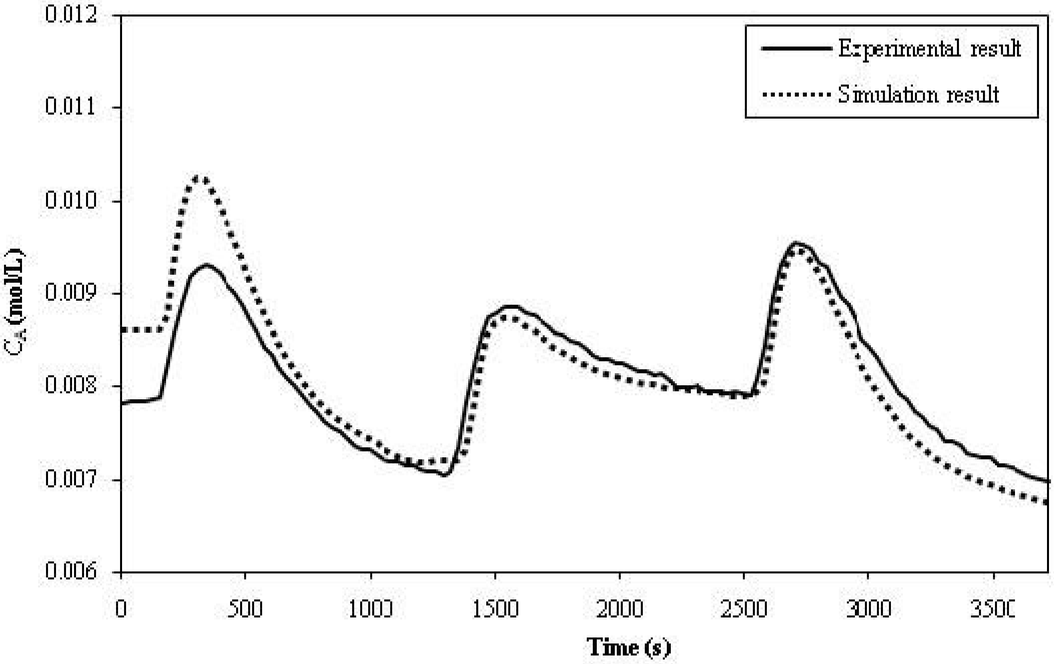


Figure 16 The concentration profile of TS-CM CSTR versus time for the case of ethyl acetate in excess.

CONCLUSION AND RECOMMENDATION

Conclusion

In the past, old-fashioned studies on reaction kinetics require a lot of time and resources by systematically varying reactant concentration and reaction temperature in a series of steady-state experiments. An alternative approach for kinetics studies by performing transient experiments, which requires less time and resources, is presented in this work. This alternative approach including the temperature scanning (TS) and composition modulation (CM) techniques is established by periodical forcing both of them simultaneously to a CSTR initially operating at steady state. The proposed technique can be used to predict the kinetics parameters for liquid-phase reactions via the transient experiment and computer simulation by using the presumed reaction kinetics model *i.e.* power law model and the Arrhenius equation. To verify the developed technique with the model reaction in TS-CM CSTR, the alkaline hydrolysis of ethyl acetate was chosen as the model reaction for demonstration of the new technique in this work. The parameters obtained from the minimum SSE based on the time-evolution of output concentration are similar to those obtained from steady-state experiments. Therefore, this technique can be an important tool for studies on reaction kinetics.

Recommendation

1. Due to the limitation of the power-law model, there may be errors if the model is used for concentration and temperature that are beyond the scope of experimentation. The kinetic parameters should be re-evaluated for those applications.
2. Further studies on transient kinetics (TS-CM CSTR) may be conducted for systems with heterogeneous catalyst. The mechanistic model can also be applied instead of the power-law model.
3. Optimization may be applied for the determination of reaction parameters in order to decrease the number of trials simulating dynamic response of the system.

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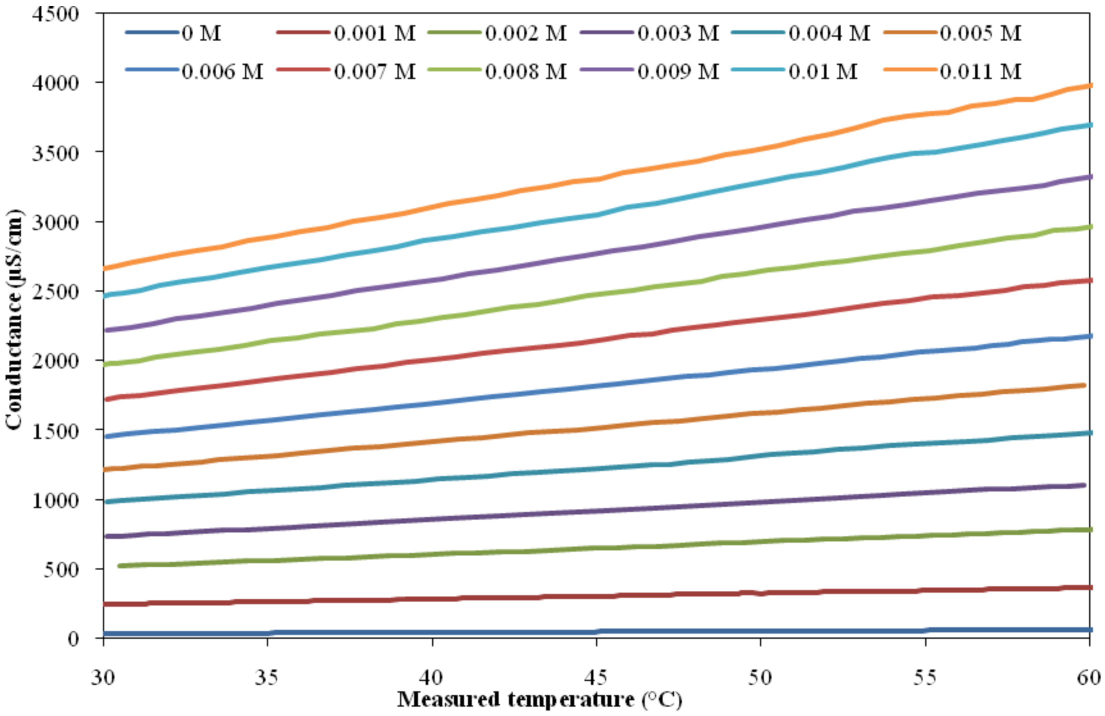
APPENDICES

Appendix A

The calibration line of Conductance of NaOH solution

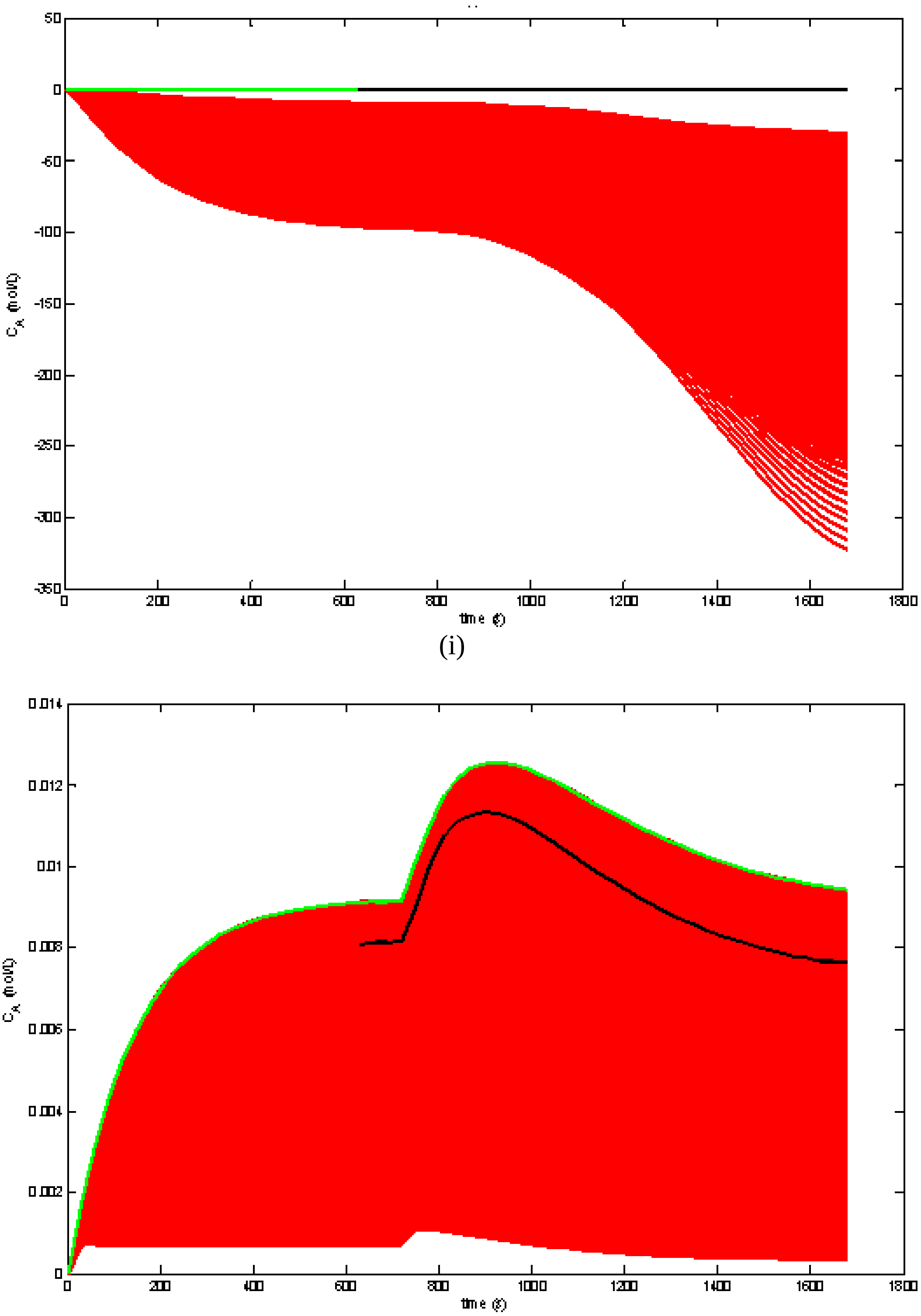


Appendix Figure A1 The calibration line of conductance of NaOH solution at various concentration.

Appendix B

The simulation results at various kinetic parameters

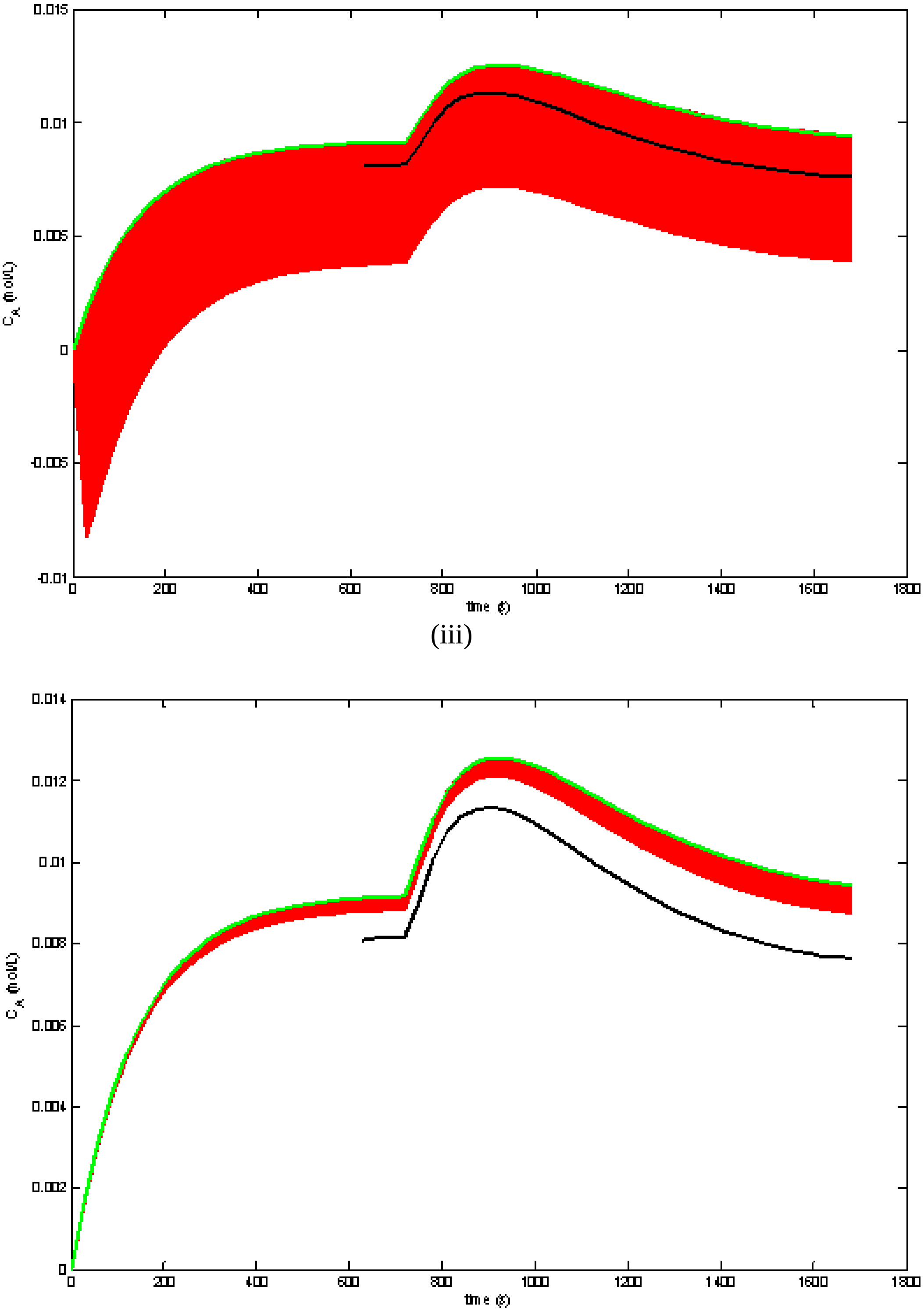
From two experiments, i.e. the response of single-pulse and multi-pulse experiments, all of the simulated results from all parts are illustrated in Figures B1 and B2. The black line represents the experimental result, the red lines represent the simulation results, and the green line represents the last simulation result or the simulated result of current kinetics parameter set. Array of reaction parameters are divided into four parts: (i) γ = 0-1 and β = 0-1; (ii) γ = 1-2.2 and β = 0-1; (iii) γ = 1-2.2 and β = 0-1; and (iv) γ = 1-2.2 and β = 1-2.2.



(i)

(ii)

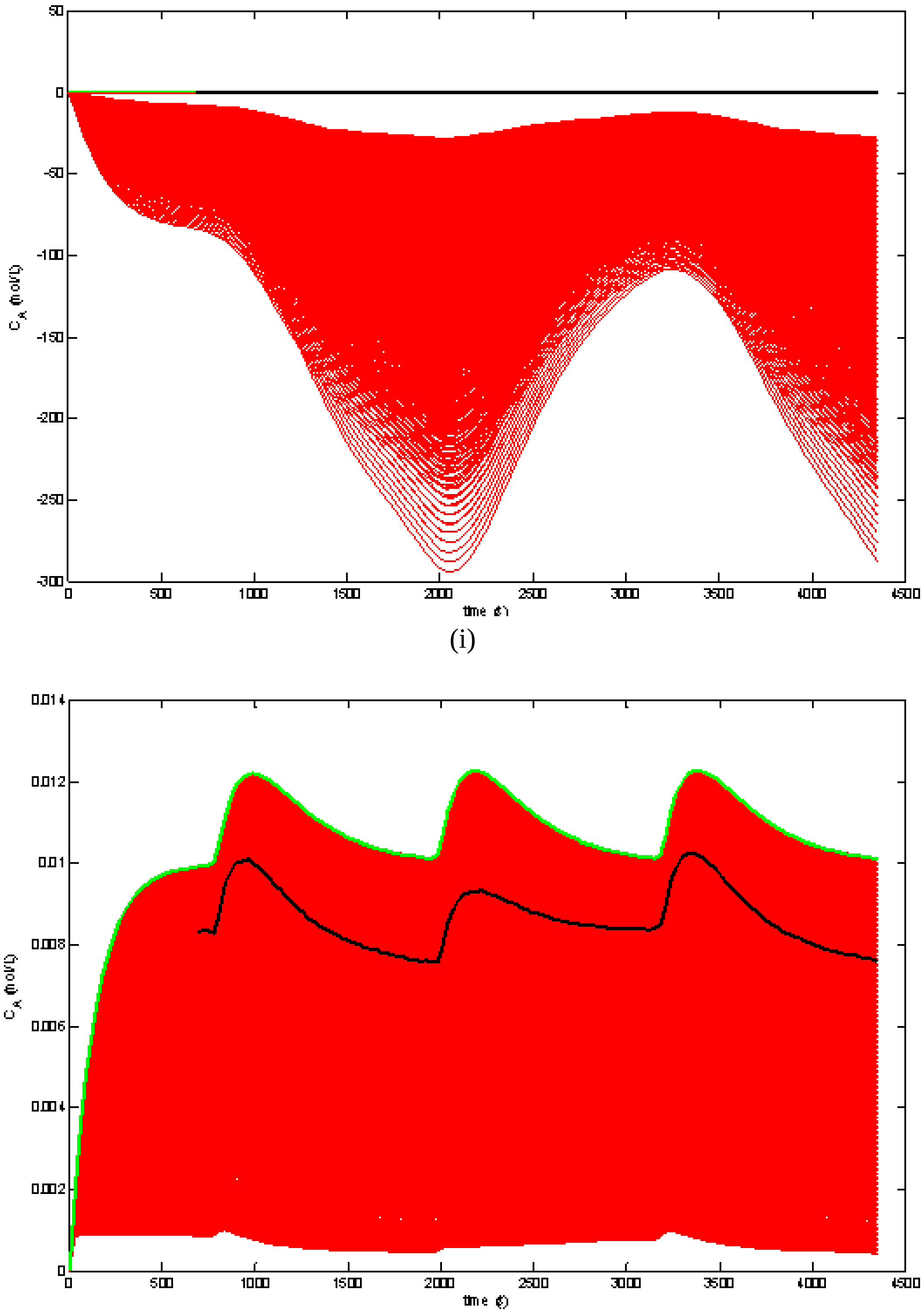
Appendix Figure B1 The simulated results of C_{NaOH} comparing with the experimental result from single-pulse experiment: (i) γ = 0-1 and β = 0-1; (ii) γ = 1-2.2 and β = 0-1; (iii) γ = 1-2.2 and β = 0-1; and (iv) γ = 1-2.2 and β = 1-2.2.



(iii)

(iv)

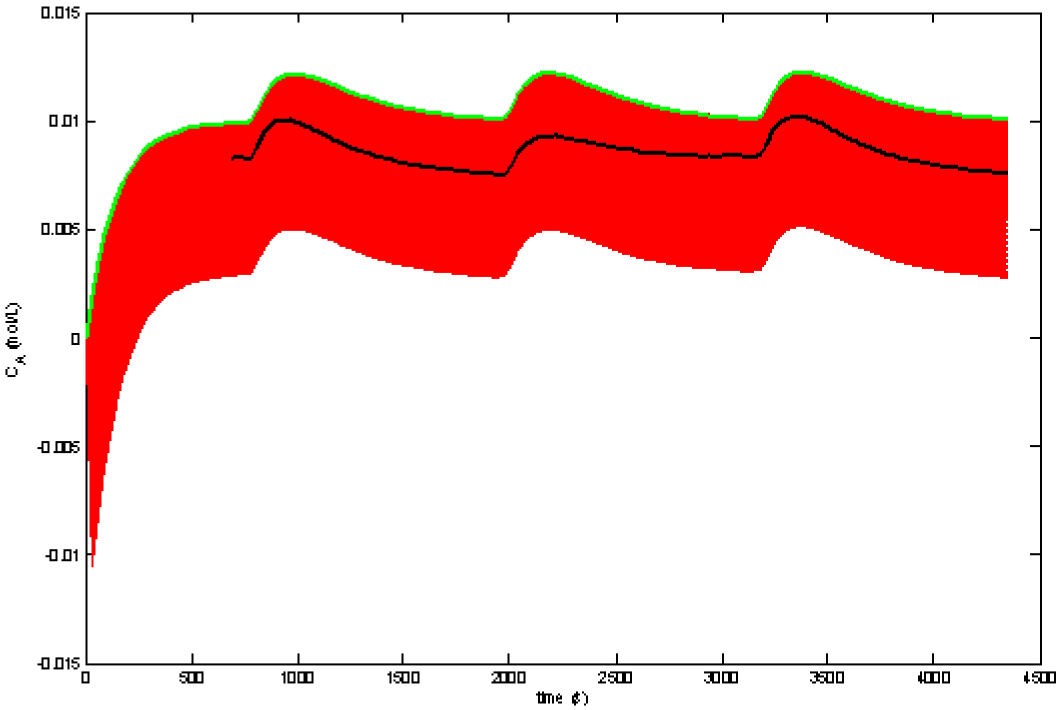
Appendix Figure B1 (Continued) The simulated results of C_{NaOH} comparing with the experimental result from single-pulse experiment: (i) γ = 0-1 and β = 0-1; (ii) γ = 1-2.2 and β = 0-1; (iii) γ = 1-2.2 and β = 0-1; and (iv) γ = 1-2.2 and β = 1-2.2.



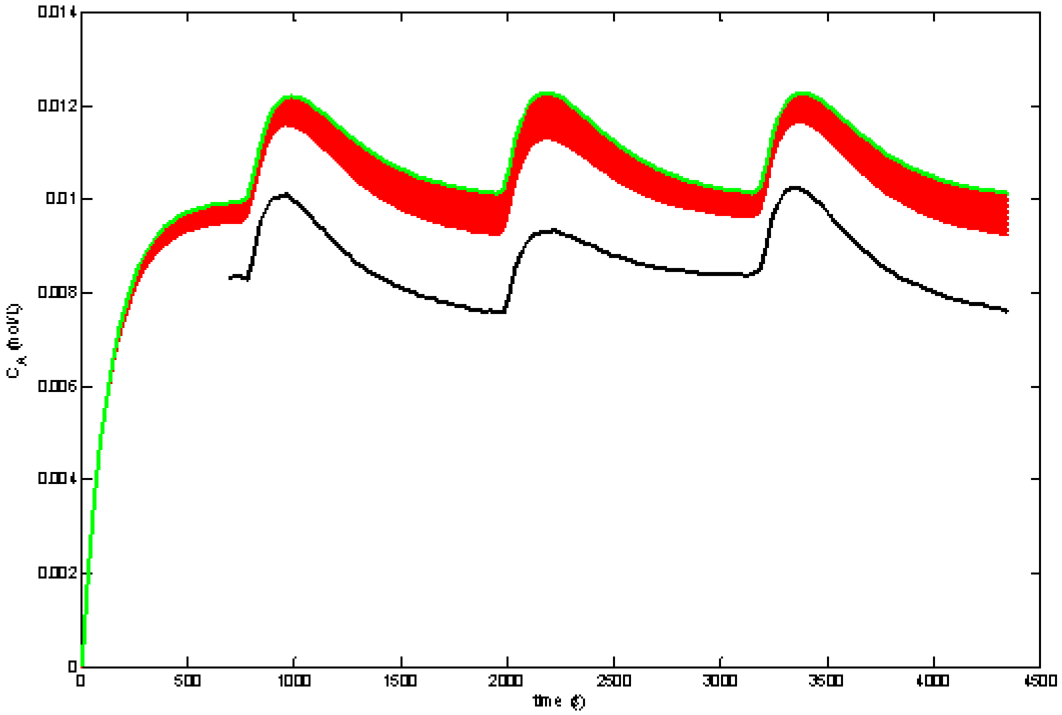
(i)

(ii)

Appendix Figure B2 The simulated results of C_{NaOH} comparing with the experimental result from multi-pulse experiment: (i) γ = 0-1 and β = 0-1; (ii) γ = 1-2.2 and β = 0-1; (iii) γ = 1-2.2 and β = 0-1; and (iv) γ = 1-2.2 and β = 1-2.2.



(iii)

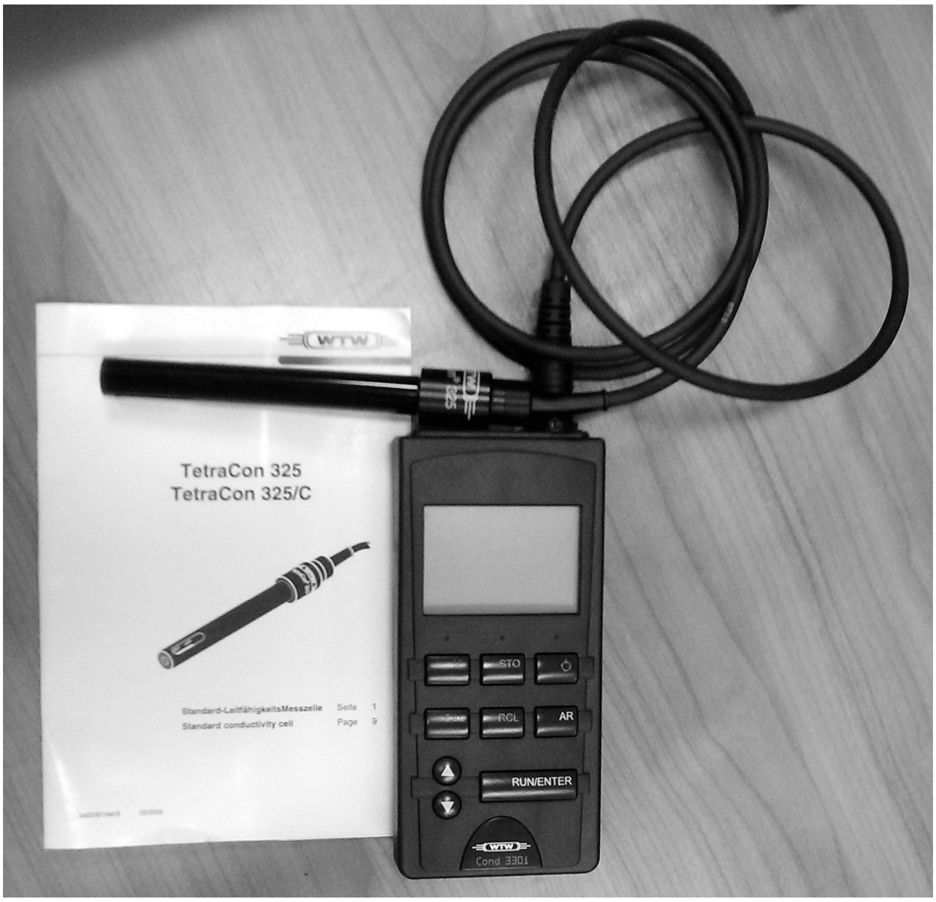


(iv)

Appendix Figure B2 (Continued) The simulated results of C_{NaOH} comparing with the experimental result from multi-pulse experiment: (i) γ = 0-1 and β = 0-1; (ii) γ = 1-2.2 and β = 0-1; (iii) γ = 1-2.2 and β = 0-1; and (iv) γ = 1-2.2 and β = 1-2.2.

Appendix C

Photograph of experimental apparatus

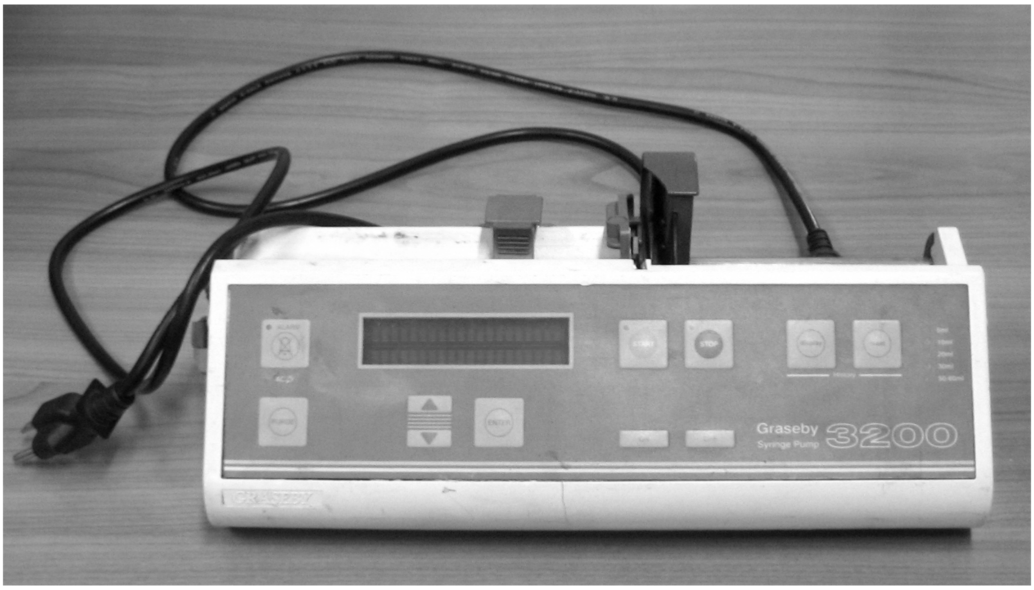


Appendix Figure C1 The conductivity measuring cell

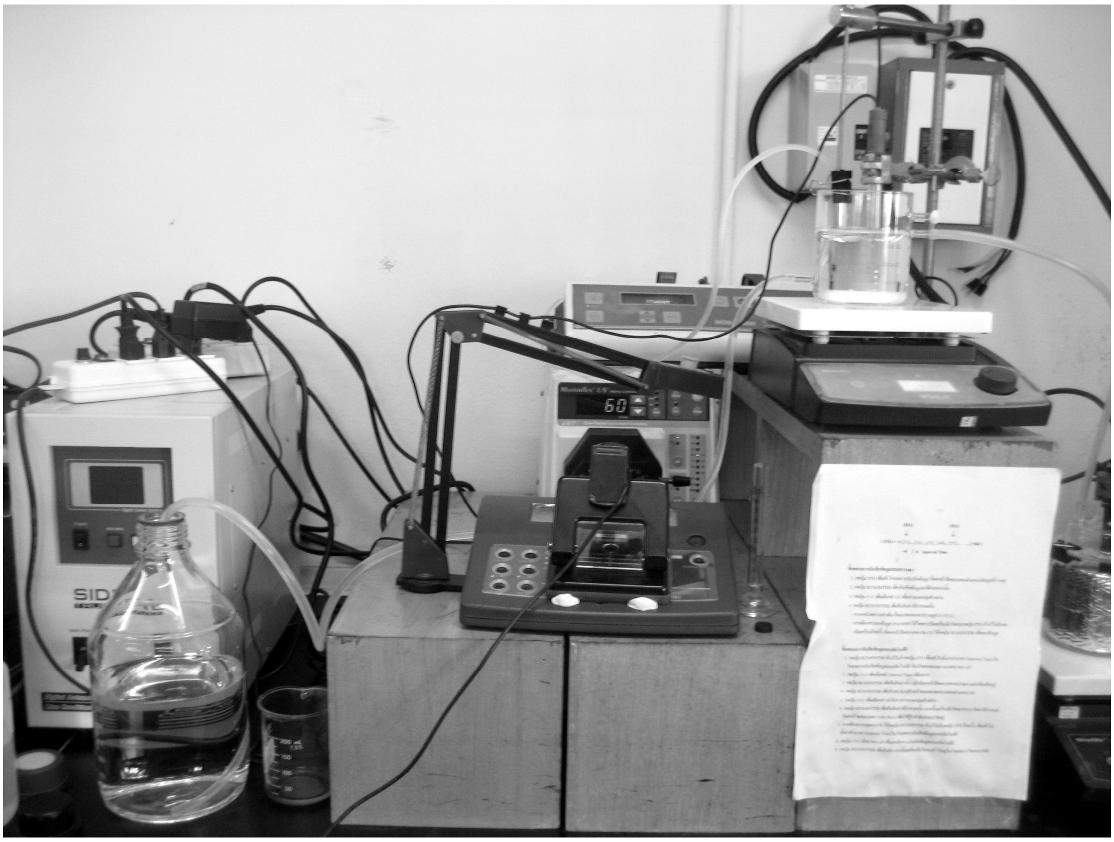
Appendix Figure C2 The pH meter

Appendix Figure C3 Peristalic pumps

Appendix Figure C4 Hotplate magnetic stirrer



Appendix Figure C5 Syringe pump



Appendix Figure C6 The mixing tank part of experimental set up (at left hand side of experimental set up)

Appendix Figure C7 The reactor part of experimental set up (at right hand side of experimental set up)

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