HAZARD ANALYSIS USING RESPONSE SURFACE TECHNOLOGY ON 2-BUTANOL OXIDATION TO 2-BUTANONE USING RC1 CALORIMATRY

A Thesis

by

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ABSTRACT

Process scale-up for highly exothermic reactions often comes with the risk of runaway reactions. In order to prevent thermal runaway reactions and its associated incidents, requirements on cooling equipment and operating regions on chemical process should be determined. To do so, a specific chemical reaction system was investigated. The purpose of research is to investigate in a specific exothermic reaction and determine the heat release amount based on the chosen parameters. Response surface methodology is utilized to determine the operating regions of synthesis reaction of 2-butanol to 2-butanone based minimize the heat release. Three Parameters used for experiments are operating temperature, 2-butanol concentration, and catalyst amount. The result of response surface methodology indicates that the optimum operating ranges for this synthesis reaction were at relatively low and high 2-butanol concentrations, as well as moderate temperatures and catalyst amounts. Additionally, 2-butanol concentration played a more significant role in heat release compared to operating temperature and catalyst amount. 2-butanol concentration of 0.5 mol/L combined with either a titanium silicalite-1 of approximately 8 g (2.4 wt %) or 15 g (4.8 wt %) would result higher amount of total heat release. Furthermore, qualitative risk matrix is constructed by calculating the total heat released as “severity” and Process and Hazard Control Index (PHCI) as “likelihood”. The purpose of qualitative risk matrix is to rank the risks of hazards associated with the oxidation reaction of 2-butanone. Hazard or event with high risk level would be marked as red, indicating that additional layers of protection such as cooling utilities should be installed if performing under such conditions. Region highlighted in yellow indicates that hazards for operation are controllable and less protections are required. Region highlighted in green indicate that hazards for operation are low and acceptable. This experiment provides useful data for determining the parameters that will generate sufficient low heat release amount and which can be used for cooling equipment designs in industry that perform scale-up synthesis reactions.

DEDICATION

To my mother, Tiffany Zhou and my father, Jian Zhou, who have always believed in me and supported me throughout my education. To my love, Xinqiu Huang, who has always encouraged me through her humor in my persuasion of master’s degree.

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Contributors

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NOMENCLATURE

ΔT	Excess Temperature [°C]
T_{sat}	Saturation Temperature [°C]
Psig	Gauge Pressure [atm]
Q	Heat Release Amount [kJ]
T	Temperature [K]
T_j	Surrounding Temperature [°C]
T_r	Reactor Temperature [°C]
T_w	Wall Temperature [K]
U	Overall Heat Transfer Coefficient [$W/(m^2*K)$]
OSHA	Occupational Safety and Health Administration
CSB	Chemical Safety and Hazard Investigation Board
MCMT	Methylcyclopentadienyl manganese tricarbonyl
TRI:	Thermal Risk Index
QSPR	Quantitative Structure-Property Relationship
RSM	Response Surface Methodology
RC1	Reaction Calorimeter 1
FTIR	Fourier-Transform Infrared Spectroscopy
Barg	Bar (Gauge Pressure)
Wt %	Percentage by Weight
PHCI	Process and Hazard Control Index

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CHAPTER I

INTRODUCTION*

1.1 Motivation

Effective process safety management programs involve good design principles, engineering, and operating practices. As a result of this, OSHA Standard “29 CFR 1910.110” requires written management systems and written procedures [1]. From these, effective process safety management programs result in prevention and control of hazards, which translates to reduction in risk and thus sustained value [2]. One of the major hazards in chemical industrial facilities is that of process scale-up, in which a reaction is conducted at the laboratory scale which is then increased to the industrial scale to produce some desired product. Process scale-up often attributes to thermal runaway incidents where excess heat produced by exothermic reaction exceeds the capacity of cooling systems, leading to runaway explosions that results personal and capital losses. Therefore, there is a huge motivation on determining the parameters that will generate sufficient low heat release amount which can be used for cooling equipment designs in industry that perform scale-up synthesis reactions.

1.2 Incidents Overview

A large number of process scale-up incidents have occurred at industrial facilities over the years. The case studies regarding process scale-up incidents in T2 Laboratories will be presented to show how incidents regarding thermal runaways occurs at chemical facilities.

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1.2.1 T2 Laboratory Runaway Explosion

On December 17, 2007, in Jacksonville, Florida, T2 Laboratories, Inc. (T2) was destroyed by a massive explosion which caused a following fire. This incident injured 32 people, including four employees and 28 people who were working in nearby businesses. On the day of explosion, T2 was producing methylcyclopentadienyl manganese tricarbonyl (MCMT) with three sequential steps in a single reactor. The design of reactor is shown in Figure 1. Overpressure protection for the reactor was provided by a 4-inch19 vent pipe that made two 90-degree pipe bends before connecting to a 4-inch rupture disk. The rapture disk is set to 400 psig. The reactor pressure was controlled by a pressure control valve installed in a 1-inch vent pipe

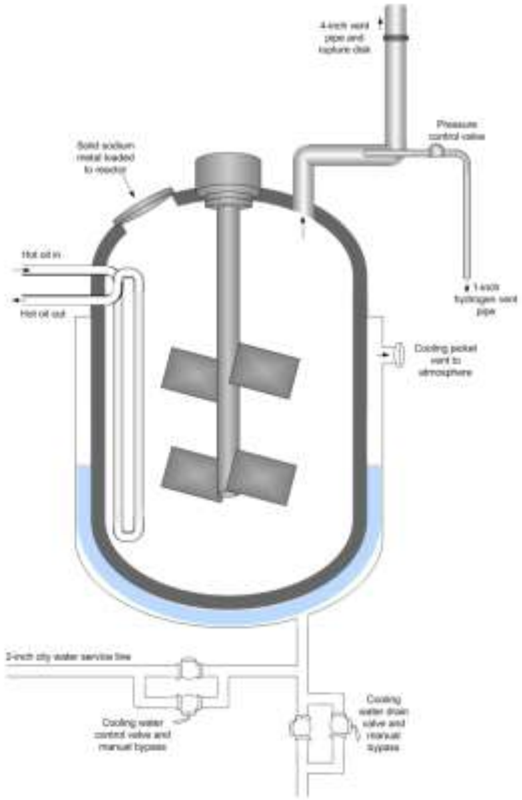

Figure 1: Reactor cross-section (reprinted from [3]. Chemical Safety and Hazard Investigation Board, 2009)

that branch off the 4-inch vent pipe below the rupture disk. Both heating and cooling are required to the MCMT process. A heating system circulated hot oil around the inside of the reactor and lower reactor was covered by cooling jacket. A control valve was connected to the pipe from the city water system to inject water into the cooling jacket. Steam from the boiling water was vented to the atmosphere via an open pipe linked to the jacket's top. The incident occurred at the first step of the reaction, also known as the metalation process, where a mixture of methylcyclopentadiene (MCPD) dimer20 and diethylene glycol dimethyl ether (diglyme) was introduced into the reactor by the process operator. The solid metal was manually loaded by the outside operator, who then will close the valve after job was finished. The mixture was heated with a hot coil. The reactor pressure is set to 50 psig (3.45 bar) and hot coil temperature at 360^{o}F (182.2^{o}C). Once the temperature reaches 210°F (98.9^{o}C), the operator will start the agitator. The metalation process is increased by mixing and higher temperature. When the temperature reaches 300°F (148.9^{o}C), the operator will turn off the hot oil, but the reaction temperature continues to raise due to heat generated by the metalation reaction. The cooling system is initiated when the temperature reaches 360°F (182.2^{o}C), as an operator will inject water into cooling jacket. However, no emergency plan was developed when cooling system lost its power. Furthermore, backup source of cooling system is not available in case of initial cooling system failure. After the incident, the CSB launched an investigation on December 19, 2007. To establish the most likely failure scenario, the CSB tested the T2 batch recipe and found out that the runaway reaction was most likely caused by a lack of appropriate cooling during the operation, which resulted in an uncontrollable pressure and temperature rise in the reactor. The reactor was blown apart by the pressure, and the contents ignited, resulting in an explosion equivalent to 1,400 pounds of TNT [3].

1.2.2 Similar Incidents in History

Additionally, following Hurricane Harvey, the refrigeration system for trailers containing 350000 lbs. of organic peroxides at the Arkema chemical facility in Crosby, Texas lost power due to the flooding. Because of this, the peroxides in the nine trailers caught fire between August 31 and September 2, 2017, resulting in 21 injuries [4]. Furthermore, at the MFG Chemical facility in Dalton, Georgia, a reactor overheated on April 12, 2004. This resulted in 4000 gal. of triallyl cyanurate exploding which caused 154 injuries [5].

Many of this process incidents are attribute to thermal runaway, which generated by an exothermic reaction exceeds the ability of the cooling system to remove the heat. This is especially significant for highly exothermic reactions, which describes many of the synthesis and decomposition reactions commonly found in industrial processes. As providing the capacity of heat removal necessary for reactions with uninhibited rates can result in a capital cost that exceeds the value of the maximized output, the reaction rates must often be limited using lower temperatures, concentrations, or controlled dosing of reactants to minimize costs [6-10]. Thermal runaway typically occurs as a result of two factors, which are that there is a lack of understanding of the reactive chemistry hazards and/or that there is ineffective process design and hazard review. In prior work, a thermal risk index (TRI) was developed to represent the thermal hazard of a particular compound relative to di-tert-butyl peroxide in order to establish a preliminary thermal risk assessment for reaction hazards [11]. The reactive chemistry hazards can be divided into two distinct types, intended and unintended chemical combinations. Intended combinations result from a facility intentionally combining chemicals in order to generate a desired product. Unintended combinations, on the other hand, can result either from inadvertent mixing of chemicals or from chemical security vulnerabilities in which an individual works to cause harm by mixing highly reactive chemicals.

1.3 Cooling Methods Overview

In response to the process incidents regrading thermal runaway, cooling systems are widely used in the industry to remove the excess heat generated from thermal runaway. Some of the common cooling methods applied to the industry include evaporative cooling, forced air cooling, and pool boiling.

The primary principle of evaporative cooling is heat and mass transfer, which employs the evaporation of water to cool the air by transferring a huge quantity of heat from air to water, resulting in a decrease in air temperature. Evaporative cooling has several advantages including simple operation, low maintenance cost, and relatively low air pollution [12]. Evaporative cooling can be categorized into Direct evaporative cooling and Indirect evaporative cooling [13]. Direct evaporative cooling occurs when air is directly contacted with cooling water, which will cool the air by changing the sensible heat to latent heat. On the other hand, Indirect Cooling System operates on the same principle as the Direct Cooling System. The difference is that water is not directly contacted with air. The air on the dry side that is cooled and the air/water on the wet side served as coolant are separated by heat transfer surface. Compared to the Direct evaporative cooling, Indirect evaporative cooling cools the air without adding much humidity, which becomes suitable in areas where additional humidity is not desired.

Forced air cooling is a physical cooling method that employs the use of a fan to blast or ventilate in order to increase air flow rate for the purpose of cooling. It is widely used in the high-power electronic device field because its heat transfer capacity is several times greater than that of natural air cooling. However, due to its complex system, heavy noise, low reliability, expensive maintenance costs, and extra power dissipation, it is rarely applied to LED thermal design and is only applied to electronic devices whose outer surface heat flux density does not exceed 10 W/cm^2 [14].

The pool boiling process is one of the most effective heat transfer mechanisms for transferring enormous amount of heat with small change in temperature between the heat surface and the fluid. It is widely used in cooling nuclear reactors, heat exchangers and high-power electronics. The heat transfer mechanism is illustrated in Figure 1, and it can be summarized by four regions: (I) natural convection, (II) nucleate boiling, (III) transition boiling, (IV) film boiling [15]. The pool boiling curve is a plot of heat flux verses excess temperature, which is defined as the difference between wall temperature and the saturation temperature.

$$\Delta T = T_{\mathrm{w}} - T_{\mathrm{sat}}$$

Equation 1

In the natural convection region, the excess temperature is less than 5 °C, indicating there is no bubble formation. Natural convection takes place where heat is transferred from solid surface to bulk liquid. In the nucleate boiling region, the curve is divided into two regions: curve AB represent liquid entrainment and curve BC represent critical heat flux. In the liquid entrainment region, bubble started form at the surface of the wall. These bubbles start moving upwards and carrying some water with them. The heat transfer coefficient increases as a result of disturbance caused by liquid entrainment. As the bubble generation process occurs, the primary heat transfer mechanism is still convection in the “isolated bubble” regime. As the excess temperature increase across point B, vapor bubble starts to form at a faster rate and continuous columns of bubble is formed. The bubbles in the column then move upwards and break up in the surface, releasing the vapor content. Before of this, the heat flux increases and eventually obtain the maximum value known as the critical heat flux.

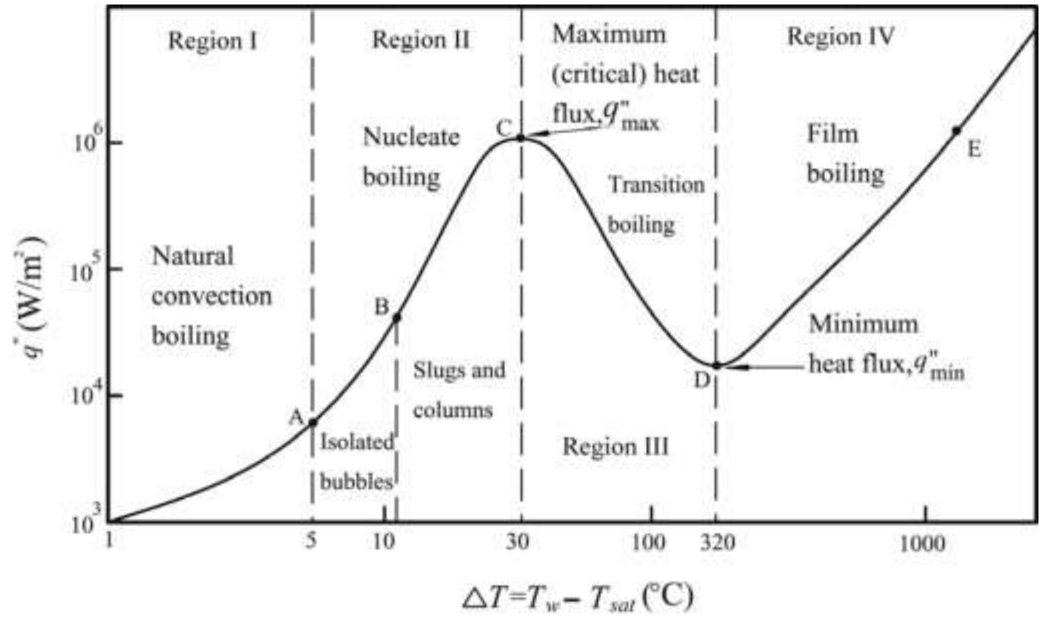

Figure 2: Pool boiling curve for saturated water (Reprinted from [15]. Faghri.A. & Zhang.Y, 2010)

In the transition boiling phase, excess temperature increases beyond the critical heat flux, a large part of heated surface of wall is covered with the vapor film. The thermal conductivity of the vapor film is lower than water, which acts as an insulator that block the heat transfer from wall to water. In the film boiling phase, increase of excess temperature leads to complete coverage of wall surface by vapor film. In this case, the radiant heat transfer between wall surface and water through vapor film takes place instead of convection. If heating continuous beyond point E, the wall surface could melt in a potential failure [15]. The pool boiling curve showed that pool boiling method can remove enormous amount of heat and maintain little temperature difference at the same time. As a result, pool boiling can reduce the size of heat exchanger by improving the equipment performance in refrigeration and air-conditioning industries [16].

Cooling systems are important applications in response to the thermal runaway because they serve to be an important layer of protection to chemical incidents. Without proper installation and maintenance, chemical incidents for process scale-up are more likely to occur.

1.4 2-butanol Oxidation Reaction

An organic solvent of relatively low toxicity is 2-butanone, which is found in many applications. These include being used in industrial and commercial products as a solvent for paints, adhesives, and cleaning agents. Furthermore, it can be used as a dewaxing agent and in the manufacture of smokeless powder and colorless synthetic resins [17]. One method of generation of 2-butanol involves the oxidation of 2-butanone using hydrogen peroxide in the presence of a catalyst. This catalyst can consist of a number of compounds, with titanium silicalite-1 (TiO2/SiO2) being a commonly used catalyst [18]. Typical operating temperatures and pressures of 2-butanone generation process include temperatures of 50 ˚C and pressures of approximately 1 bar [19]. Oxidation of 2-butanol is also studied at high temperature with range of 1200-1650 K using jet-stirred reactor (JSR) [20]. However, such high temperature range was not chosen in this experiment because of the temperature capacity of RC1 is 392 K. The oxidation rate of methanol is significantly lower than those of secondary alcohols, making it a commonly used solvent for this reaction [18]. The heat of reaction for the primary 2-butanol to 2-butanone reaction is 273.3 kJ/mol, indicating that this is a significantly exothermic process [21]. Hydrogen peroxide as the oxidant provides the benefit of being a relatively “green” oxidant, as it produces only the side product of water rather than other harmful products [22]. Furthermore, it is an effective oxidant for a variety of organic oxidation reactions [23-25].

One of the drawbacks of using hydrogen peroxide, however, is that its decomposition is highly exothermic, with the heat released from self-decomposition being 98.2 kJ/mol [21]. As such, its use in industrial processes must be controlled carefully to ensure that thermal runaway as a result of process scale-up does not occur, as referenced above. In past work, thermal hazards associated with the epoxidation of 2,4-pentadien-1-ol using hydrogen peroxide in combination with tungsten catalyst were investigated. From this, it was determined that a runaway situation was readily achieved when the heat output exceeded the cooling capacity of the system [26]. Similar to hydrogen peroxide, inorganic peroxide initiators can decompose and release large amounts of heat, with prior research showing that the effects of water on them must be taken into account during their production, transportation, and storage so as to prevent fires or explosions. This is due to the fact that an increase in water content reduces the onset temperature of the inorganic peroxide initiators [27]. In order to predict the self-accelerating decomposition temperature and other fire and explosion-related properties of organic peroxides, quantitative structure-property relationship (QSPR) models have been developed for these peroxides [28-29]. Furthermore, methods for assessing and ranking thermal hazards using these QSPR models have been proposed [30].

1.5 Problem Statement

The interaction effects of multiple parameters on the heat release for the synthesis of 2-butanone from 2-butanol has not been investigated. In this work, the effects of catalyst amount, reactant (2-butanol) amount, and reaction temperature on the heat release amounts during the synthesis of 2-butanone from 2-butanol are investigated, with the results presented here. The aim of this work is to identify operating regions in which the yield of 2-butanone is maximized while minimizing heat release and hydrogen peroxide side decomposition. In order to identify the interactions between these parameters on the output variable (heat release), response surface methodology (RSM) was used. The purpose of RSM is to optimize a response of interest which is influenced by several variables [31-39]. This is described in detail on section 3.

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CHAPTER II

MATERIALS AND METHODS*

2.1 Chemicals

For this work, Titanium Silicalite-1 (ACS Materials, 20–50 μm, MSTS1001), 2-Butanol (99%, Alfa Aesar, A18658AP), Methanol (99.8%, Fisher Chemical, A412-500), and Hydrogen Peroxide (35%, Millipore Sigma, 7722841) were used as supplied.

2.2 Introduction to RC1 calorimeter

The Mettler Toledo RC1 Calorimeter setup is shown in Fig. 2. Image (a) shows a photograph of the RC1 setup while image (b) shows a diagram of the major components of the calorimeter. The calorimeter consists of a 1 L glass reactor which is resistant to a pressure of up to 10 barg. As can be seen in image (b), the temperature sensor allows the temperature of the vessel contents to be maintained at a specified value as a result of a silicone oil heating/cooling jacket. The reactor contains heat flux sensors within it for heat flow measurement. Additionally, the reactor contains a pressure gauge (analog AISI316, digital HC-22) and rupture disk (set to 10 barg) to perform reactions at controlled pressures. Batch or semi batch dosing can be attained with a ProMinent solenoid metering pump, which contains an interlock that halts the dosing if the temperature or pressure exceeds 150 ◦C or 6 barg, respectively. To measure the product composition, a ReactIR 15 spectrometer that is composed of a mercury cadmium detector and

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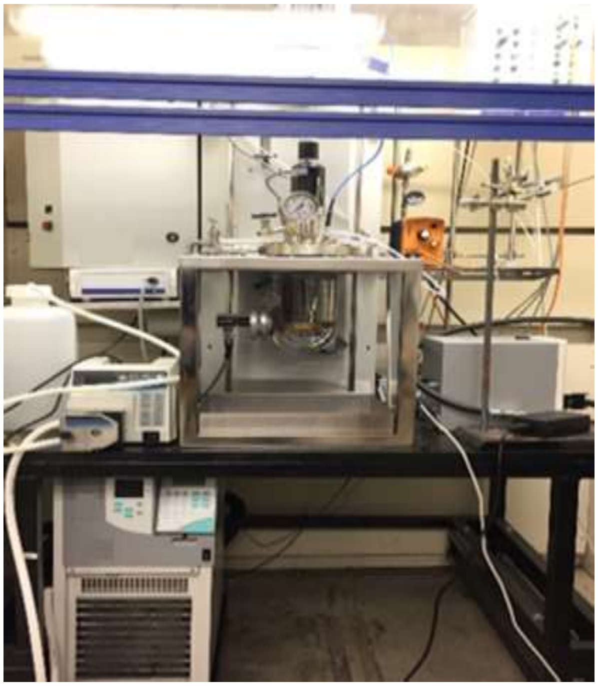
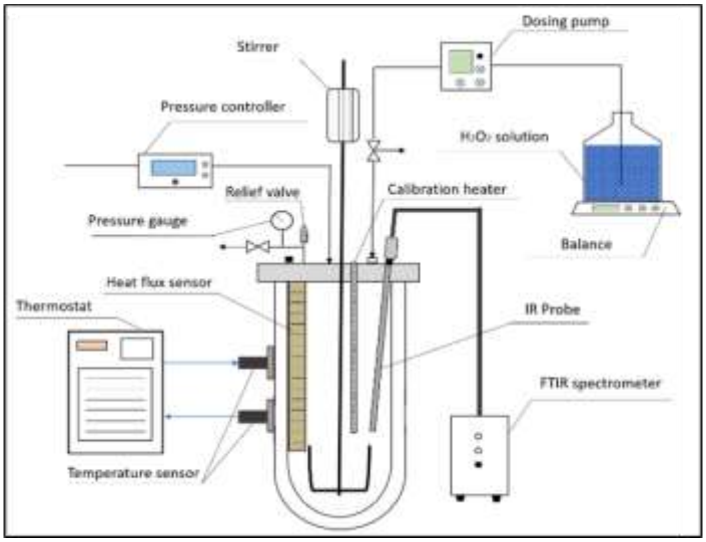


(a)



(b)

Figure 3: RC1 Laboratory Setup (a) Photograph (b) Diagram (Reprinted from [56]. Parker, T., Mao,Y., Wang, Q., 2022)

diamond composite in situ FTIR sensor probe can be used. In order to maintain the vessel contents as well-mixed, a stirring rod is used within the vessel which rotates at a specified speed and is positioned in such a manner as to not contact the probes and sensors within the vessel. The temperature within the vessel is maintained in real-time using a high performance RTCal box which is connected to a Julabo temperature-controlled chiller. The iControl software is connected to the RC1 which allows data analysis in real-time.

2.3 Introduction to Risk Matrix

Risk assessment and risk matrices are powerful risk management tools that aid in the decision-making process in organizations [40]. Risk management is the process of analyzing hazards and implementing control measures to either eliminate or decrease them (as far as is reasonably practicable). The goal of risk management is to decrease risk to a point where society can tolerate while ensuring control, monitoring, and public disclosure [41]. There are no common accepted definitions of risk, however, all risk concepts have one thing in common: the distinction between reality and possibility [42]. In this paper, risk in defined as the product between “severity” and “likelihood” as shown in Equation 2 below.

$$Risk = Severity \times likelihood$$

Equation 2: Definition of Risk

The structure of risk matrix will be built based on the definition of risk. Risk matrices are simple tools that prioritize the risk of event to make decisions on whether certain risk can be tolerated. Risk matrices have two main applications. When considering the usefulness of risk matrices, it's important to consider the application or goal of the risk matrix. One application is deciding whether or not to accept risk, while the other is prioritizing which risks should be addressed first [43]. There are three types of risk matrices that are used in risk prioritizing: qualitative risk matrix, quantitative risk matrix and SEMI-quantitative matrix.

The qualitative risk matrix is essentially a task and/or hazard analysis with some relative judgments made to categorize the risks. When the 3x3 matrix is employed, the frequency and impact of each accident scenario are calculated using simple relative scales such as low, medium, and high. The risk of each scenario will be a product of consequences and frequency, indicating that the qualitative risk matrix in this case would have nine distinct regions. Because some parts are directly comparable and others are not, the intermediate regions are more difficult to interpret [44]. The quantitative risk matrix utilizes relative or absolute numeric scales instead of relative judgement used in quantitative risk matrix. By using a quantitative risk matrix, each incident scenario will have relative risk value associated with it, making all scenarios able to be ranked and compared [45]. Finally, SEMI-quantitative risk matrix has one quantitative variable, usually the frequency, and the other scale is qualitative variable [46].

In this case, the goal of risk matrix would be to help facilities to decide whether or not to accept risk. To do so, a qualitative risk matrix would be developed with three levels of risk acceptance would be distinguished on the risk matrix: hazard or event with unacceptable risk would be marked as red, hazard or event where risk should be reduced as low as possible would be marked as yellow, and hazard or event with generally acceptable risk would be marked as green. Furthermore, the “severity” sector on the risk matrix in this experiment is defined as the total heat generated measured in kJ/kg, and the “probability” sector on the risk matrix in this experiment is calculated with the Process and Hazard Control Index (PHCI). The methodology of PHCI will be discussed in section 3.

2.4 Experimental Procedure

For these experiments, titanium silicalite-1, 2-butanol, and methanol were added to the vessel initially. The amounts of titanium silicalite-1 and 2-butanol were varied for the different experiments to determine their effects on the heat release amounts. Sufficient methanol was added to the vessel for each experiment so that the total contents had a volume of 0.4 L. This was to ensure that there was sufficient volume of contents to ensure that the reaction mixture would be well-mixed throughout the experiments. Methanol was chosen as the solvent, as its oxidation rate is much lower than that of secondary alcohols [18]. Additionally, the stirrer speed was set at 150 rpm, as it was demonstrated in prior literature that this speed sufficiently mixed the contents [47]. These reactants were then heated to the desired reaction temperature, with the pressure held constant as atmospheric pressure. Once the temperature was sufficiently stabilized at the proper value, room temperature hydrogen peroxide was added to the mixture over the course of a 10-min period. For this, 20.4 mL of hydrogen peroxide was added in total, with 5.1 mL being added in 2.5-min increments. The reaction parameters were continually monitored during this process using the iControl software. Once the heat release of the reaction mixture was complete, the vessel contents were then cooled back to ambient temperature. The complete reaction is shown in Fig. 3, including the decomposition of hydrogen peroxide.

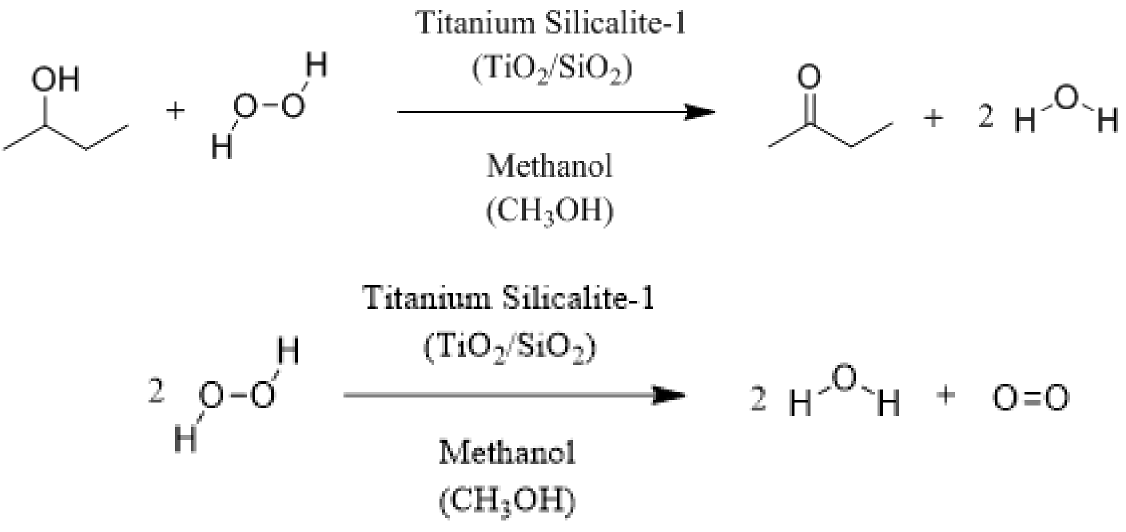


Figure 4: 2-Butanone Synthesis Reaction with Hydrogen Peroxide Side Reaction (Reprinted from [56]. Parker, T., Mao,Y., Wang, Q., 2022)

2.5 Response Surface Methodologies

For this work, the influences of reaction temperature, 2-butanol concentration, and catalyst amount on the heats of reaction were investigated, with response surface methodology utilized. In prior work, it was found that titanium silicalite-1 is an effective catalyst for the oxidation of 2-butanol to 2-butanone, and that temperature and initial reactant concentrations have significant impacts on the reaction heat release amounts as well [18]. For each variable, three values were utilized, as described. Catalyst amounts of 7.90 g, 11.85 g, and 15.80 g, 2-butanol volumes of 19.89 mL, 37.39 mL, and 54.95 mL, and temperatures of 30 ◦C, 45 ◦C, and 60 ◦C were used, respectively. In addition, the concentration of hydrogen peroxide was kept constant at 0.49 mol/L, with 2-butanol volumes corresponding to concentrations of 0.28 mol/L, 0.53 mol/L, and 0.78 mol/L, respectively. For this reaction system, the 2-butanol reacts with the hydrogen peroxide in a 1:1 M ratio, as shown in Fig. 2. Thus, for the case in which the 2-butanol volume of 19.89 mL was used, the 2-butanol was the limiting reactant. On the other hand, when

2-butanol volumes of 37.39 mL and 54.95 mL were used, the hydrogen peroxide was the limiting reactant. Provided that the limiting reactant was consumed entirely in the production of 2-butanone, this would result in excess reactant of 8.74 mL of hydrogen peroxide for an initial 2-butanol volume of 19.89 mL, 2.84 mL of 2-butanol for an initial 2-butanol volume of 37.39 mL, and 20.43 mL of 2-butanol for an initial 2-butanol volume of 54.95 mL. The temperature values were chosen based on the results of previous findings regarding effective 2-butanol synthesis at 45 ◦C [18]. The catalyst amounts were chosen based on a median amount of 11.85 g corresponding to 2.5 wt % of the catalyst, which had previously been shown to result in effective synthesis of 2-butanone
from 2-butanol. The volumes of 2-butanol were chosen based on the median value of 37.39 mL corresponding to a concentration of 0.534 mol/L, which had been shown to result in effective conversion of 60–70% [18]. A sufficient amount of methanol was added to the vessel for each of the experiments to result in a total reactant volume of 0.4 L, as this allowed a sufficient amount of liquid within the RC1 vessel to be thoroughly mixed throughout the process.

CHAPTER III

THEORY*

3.1 Application of Response Surface Methodology

Response surface methodology involves the exploration of relationships between explanatory variables (reaction conditions) and the response variable (heat release amount) by using statistical models [48]. This methodology is utilized in a number of process safety applications, which can include identifying optimal conditions to minimize electrostatic hazards inside scrubber columns as well as those to minimize pressure generated inside a reactor [9]. To do so, a sequence of experiments was designed to obtain an optimal response. This was to determine which of the explanatory variables most affected the response variable. This project involves a full factorial design for two parameters and three levels. A 9-run array was desirable to reduce the number of experimental tests without losing system characteristics [49]. Therefore, a total of 9 experimental tests were required, with the varied parameters for each of those 9 experimental tests shown in Fig. 3. To reduce the number of experiments to 9 while effectively capturing the system characteristics, response surface methodology was utilized to model curvature of the data and identify factors that contribute most to the response.

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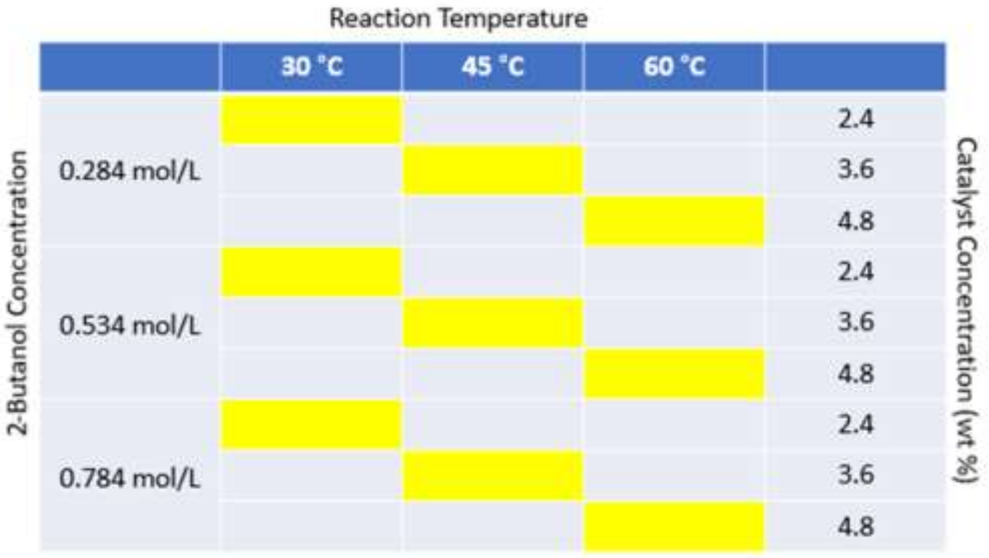

Reaction Temperature

2-Butanol Concentration	30 °C	45 °C	60 °C	Catalyst Concentration (wt %)
0.284 mol/L	🟨			2.4
		🟨		3.6
			🟨	4.8
0.534 mol/L	🟨			2.4
		🟨		3.6
			🟨	4.8
0.784 mol/L	🟨			2.4
		🟨		3.6
			🟨	4.8

Figure 5: Reaction Conditions for Experiments (Reprinted from [56]. Parker, T., Mao,Y., Wang, Q., 2022)

For this, Minitab software was used, and the method of least squares (Bezerra et al., 2008) was used to generate surface maps and contour plots illustrating the contributions of each variable, including the initial 2-butanol concentration, catalyst amount, and reaction temperature, to the overall heat release amounts. By doing so, the optimum operating regions for carrying out this synthesis with limited cooling capacity were identified.

3.2 Reaction Calorimeter Fundamentals

A reaction calorimeter is a device used by scientists in the chemical and pharmaceutical industries to determine how much energy is released or absorbed during a chemical or physical reaction. It usually consists of variable-size stirred tank reactor in which the temperature of the reaction mass and other essential process perimeters are monitored and controlled. The information obtained by the reaction calorimeter describes the heat release over time, which provides useful data when considering transferring from lab scale to plant scale. The heat released by the oxidation reaction of 2-butanol is determined by heat flow calorimetry method, which measures the heat of the chemical reaction while the process temperature remains at set value. In this case, Mettler Toledo RC1 Calorimeter will be used and operated under isothermal (constant reaction temperature) mode to obtain the heat released data. The heat flow principle measures the temperature difference ΔT which is the difference between the reaction mass temperature T_r and the surrounding temperature T_j.

$$\Delta T = T_r - T_j$$

Equation 3

In this case, ΔT serves as an indication for the reaction progress, as 2-butanol is converted to 2-butanone due to oxidation, the reaction temperature increase as heat is released to the surrounding. To remove the heat produced by the oxidation reaction and to maintain the desired temperature, the temperature of the surrounding, T_j, needs to be adjusted forcing the energy released to be transferred across the reactor wall. Using ΔT as a driving force, heat transfer can be calculated using the following equation:

$$q = UA\,\Delta \mathrm{T}$$

Equation 4

For this, q is the amount of heat transfer, U is the heat transfer coefficient, and A is the heat transfer area. Because the heat transfer coefficient and heat transfer area are changing throughout the reaction, the conversion factor UA needs to be determined. To do this, Mettler Toledo RC1 Calorimeter uses a small electrical heater to introduce certain amount of heat into the system. The response of the system is measured and the conversion factor, UA, along with the overall heat transfer coefficient, U, are determined. The heat flow will then be calculated and it enables the total heat released to be determined by integrating heat flow over certain period of time.

3.3 Process and Hazard Control Index Fundamentals

Process and Hazard Control Index (PHCI) is a tool that is used to quantify the probability of an incident. It is also an index that is used to calculate numerous optional process and hazard control measures that are necessary or present in the system. The application of PHCI in risk matrix assessment is often combined with Inherent Danger (DI). Inherent danger is used to evaluate severity of the incidents, and the severity of such incident is often calculated into the worst case [50].

The framework of PHCI calculation is illustrated in Figure 6. To quantify this index, process safety experts need to choose scales that can be mutually agreed on. For any control arrangement, the index ranges from 1 to 10 and is quantified depending on the importance of this control arrangement in ensuring safe operation. As shown in Figure 7, the importance of control is divided into nine groups [51].

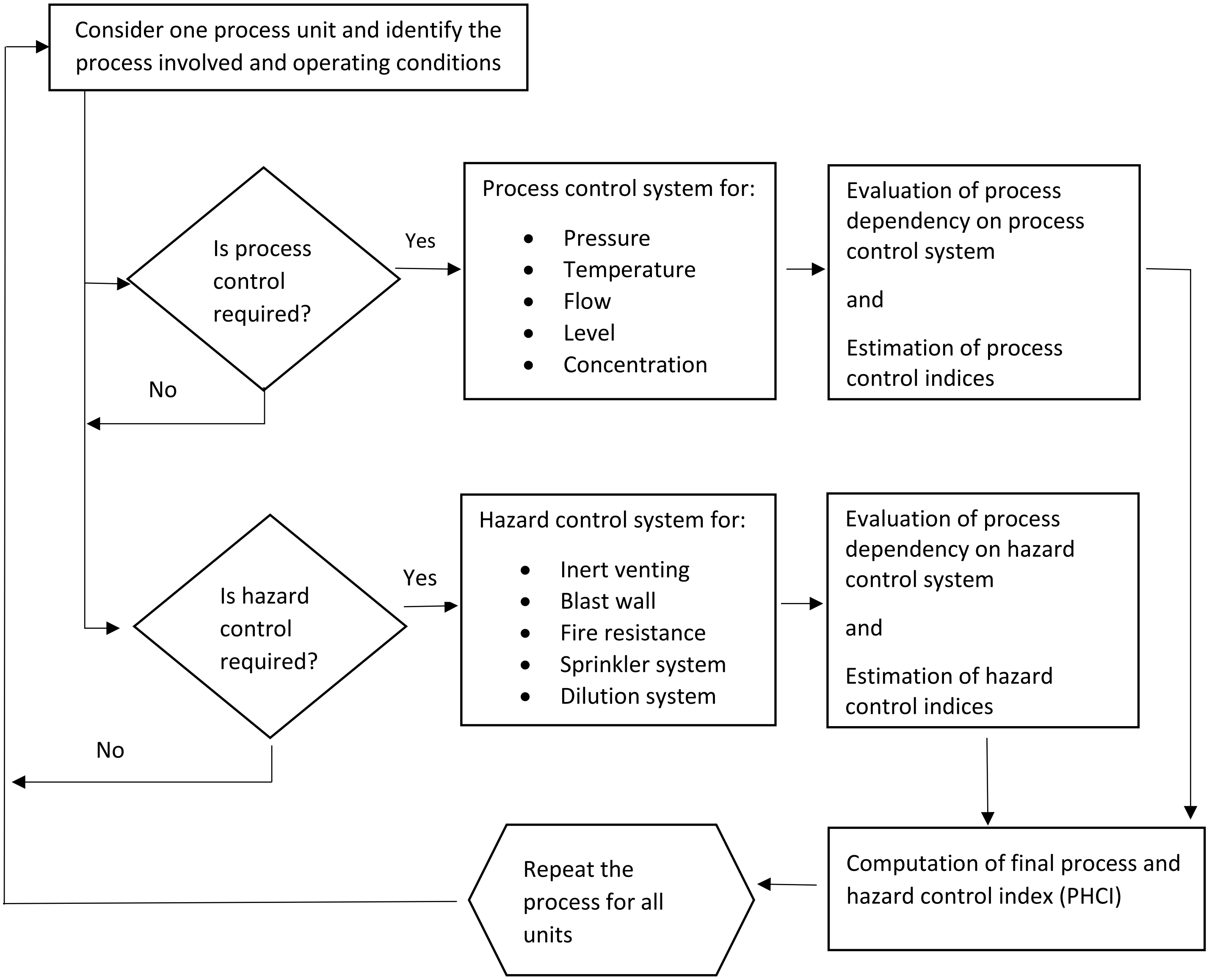

Figure 6: Concept of Process and Hazard Control Index (PHCI) Calculation (Reprinted from [51]. Khan, F. I., & Amyotte, P. R.,2014)

Description	Extent of Requirement
Essential	10
Very Important	9
Important	8
Not greatly important but required	7
Required	6
Required in moderate	5
Good if available	4
Requirement does not affect process	3
Not required	1-2

Figure 7: Guideline to decide extent of requirement of control arrangement (Reprinted from [51]. Khan, F. I., & Amyotte, P. R.,2014)

From the requirement of control arrangement shown in Figure 7, an index can be derived form Figure 8. The process is then repeated for ten control systems shown in Figure 6 and PHCI can be calculated using Equation 5 [50].

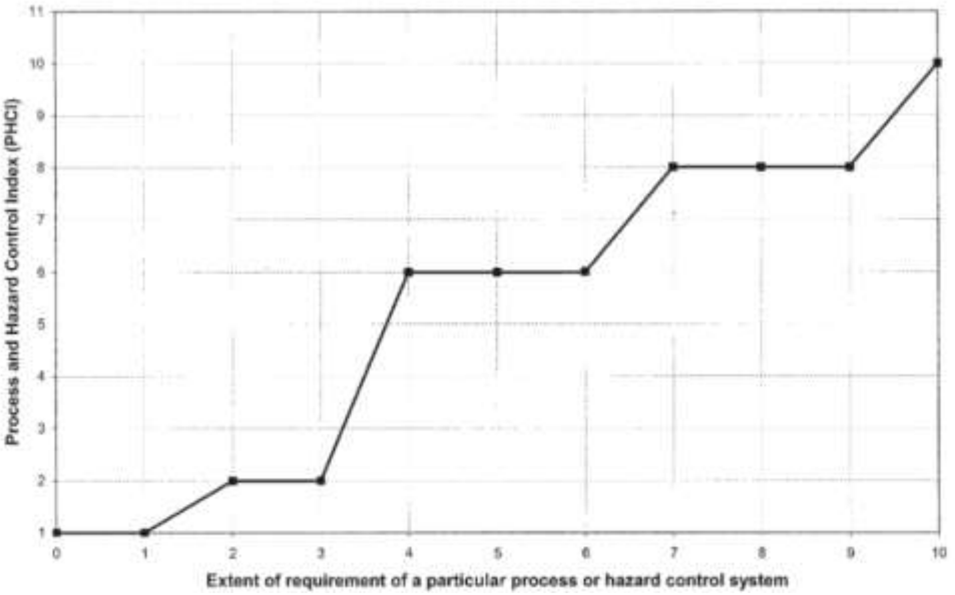

Figure 8: Monograph for process and hazard control index (PHCI) (Reprinted from [51]. Khan, F. I., & Amyotte, P. R.,2014)

$$PHCI = PHCI_P + PHCI_t + PHCI_f + PHCI_l + PHCI_C + PHCI_{iv} + PHCI_b + PHCI_{fr} + PHCI_s + PHCI_d$$

Equation 5: Process and Hazard Control Index (PHCI) calculation

For this, p stands for pressure, t stands for temperature, f stands for flow, l stands for level, c stands for concentration, iv stands for inert venting, b stands for blast wall, fr stands for fire resistance wall, s stands for sprinkler system, and d stands for forced dilution.

It is important to recognize that the ten control systems in Figure 6 are divided into two categories: process control and hazard control, which indicate that not all control systems will be used to calculate the PHCI.

CHAPTER IV

RESULTS AND DISCUSSION*

4.1 Heat Release Peaks

For each of the 9 experiments conducted, a graph showing the heat release rates and vessel temperature in real-time were generated using the iControl software. These graphs are provided in the Supporting Information for this work (Figs. A.1-A.9). An example of one of these graphs for the experiment conducted with a 2-butanol concentration of 0.534 mol/L, catalyst concentration of 2.4 wt %, and temperature of 28 ◦C is shown in Fig. 9.

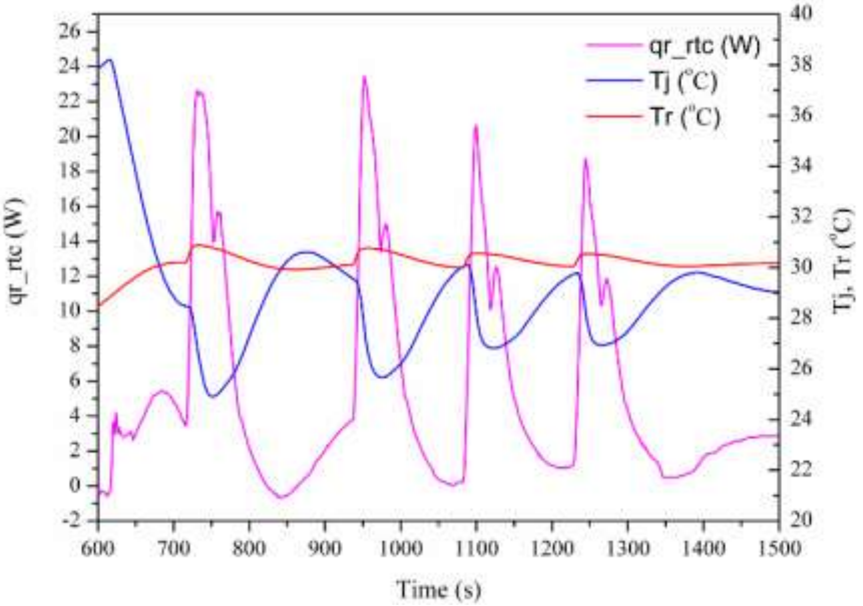

Figure 9: Example iControl Temperature and Heat Release Graph (Reprinted from [56]. Parker, T., Mao,Y., Wang, Q., 2022)

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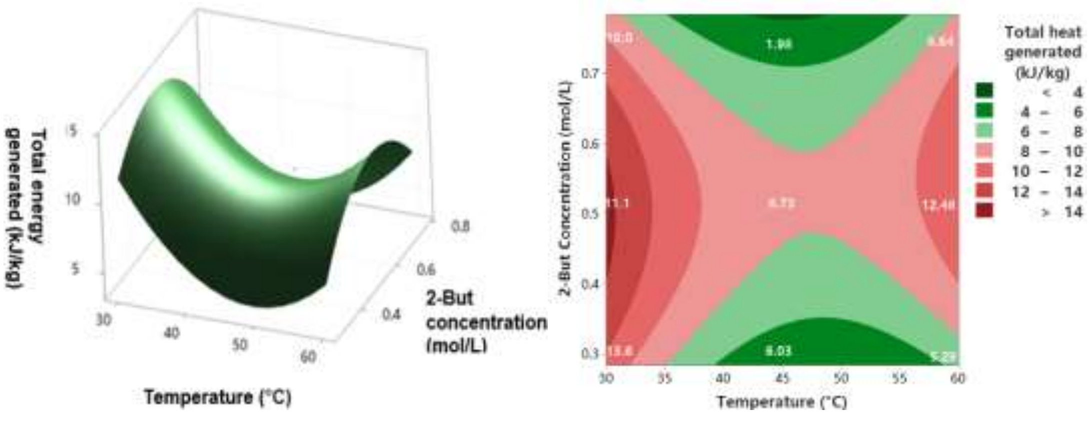
Integrating and summing the 4 heat release peaks for each of the experiments provided the total heat release amount (kJ) for each of the experiments. The integrals for each peak were obtained over the interval from the time the hydrogen peroxide was added until the change in heat release rate (dq/dt) was 0 W, as shown in Fig. 4. This was normalized to the scale-independent parameter of kJ/kg reaction mass and served as the response variable for each of the surface maps and contour plots. As heat release peaks resulted from the addition of hydrogen peroxide every time and were of similar heights for cases in which the 2-butanol concentration was 0.534 mol/L or 0.784 mol/L, this indicates that there was unreacted 2-butanol that remained in the vessel. This is because the hydrogen peroxide was the excess in the reaction only in cases in which the 2-butanol concentration was 0.284 mol/L, as discussed in section 2.4. These data were likely influenced by external factors including the evaporation of methanol (with a vapor pressure of 13.0 kPa). Fig. 10 shows the surface map and contour plot for the effects of vessel temperature and initial 2-butanol concentration on the heat release amounts. For these, the catalyst concentrations at each data point correspond to the reaction conditions in Fig. 5.



(a) (b)

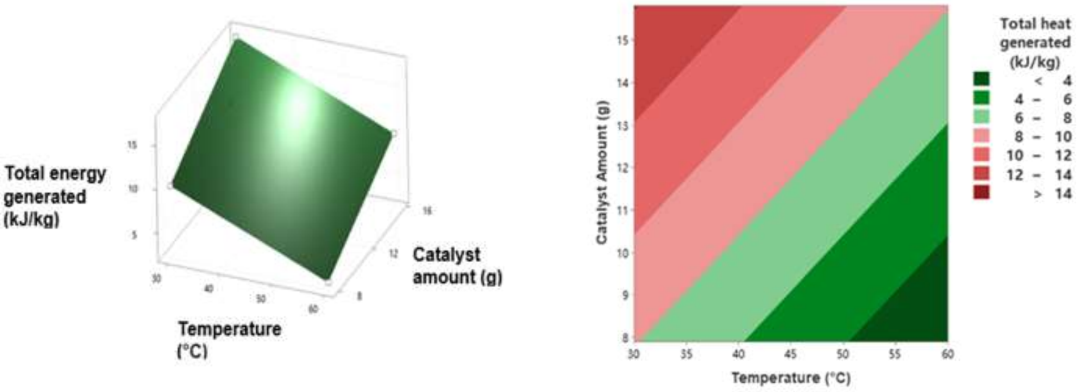
Figure 10: Effects of Temperature and Initial 2-Butanol Concentration on Heat Release based on RSM Method (a) Surface Map (b) Contour Plot. (Reprinted from [56]. Parker, T., Mao,Y., Wang, Q., 2022)

4.2 Surface map and contour plot

As can be seen from the contour plot in Fig. 5 (a), the highest amount of heat release (kJ/kg reaction mass) occurred at a temperature of 30 ˚C with a 2-butanol concentration of approximately 0.5 mol/L. Furthermore, the lowest total heat release amount occurred at 2-butanol concentrations of approximately 0.3 and 0.78 mol/L at a temperature of 45 ˚C. Possible explanations for the lowest heat release occurring at moderate temperatures include that the side reaction of hydrogen peroxide decomposition may be prominent at the lower temperature due to the slower primary reaction of butanol to butanone. Thus, a higher heat release at low temperatures occurs. Furthermore, the primary reaction of butanol to butanone occurs faster at higher temperatures, leading to higher heat release at high temperatures. The p-value is a statistical measure that describes the probability of obtaining results at least as extreme as the observed results of a statistical hypothesis test. For this, a lower p-value corresponds to a pattern observed being more statistically significant. Furthermore, the R^2 value is a statistical measure of fit, with values close to 100% representing that variation of a dependent variable is nearly entirely explained by the independent variable(s). The p-value for this regression model is 0.099. Furthermore, the regression model has an R^2 of 89.93%, indicating that the data fits relatively closely with the regressed model. The quality of the fit for this model indicates that the effects of reaction temperature in combination with the initial concentration of 2-butanol play a very significant role in the heat generation from the reaction.

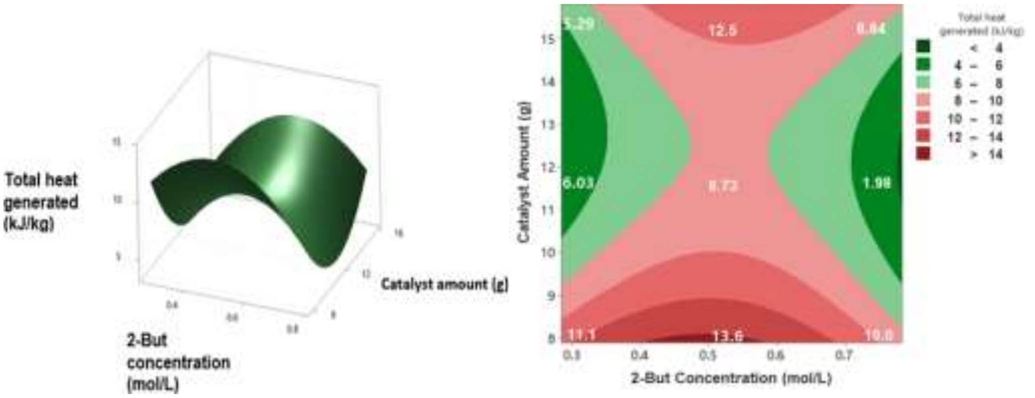
Fig. 11 shows the surface map and contour plot for the effects of vessel temperature and catalyst concentration on the total heat release amounts. The contour plot in Fig. 11(a) indicates that lower temperatures of approximately 30 ◦C and high catalyst amounts of approximately 15 g

(4.8 wt %) resulted in higher total heat release amounts (kJ/kg reaction mass), while higher temperatures of approximately 60 ◦C and low catalyst amounts of approximately 8 g (2.4 wt %) resulted in lower heat release amounts. Fig. 8 shows the surface map and contour plot for the effects of catalyst amount and initial 2-butanol concentration on the total heat release amounts. The p-value for this regression model is 0.115. Furthermore, this regression model has a R2 of 51.31%. This indicates that these data do not fit closely with the regressed model. The quality of the fit for this model indicates that the effects of reaction temperature in combination with the catalyst amount play a less significant role in the heat generation from the reaction.



(a) (b)

Figure 11: Temperature and Catalyst Amount Effects (a) Surface Map (b) Contour Plot (Reprinted from [56]. Parker, T., Mao,Y., Wang, Q., 2022)



(a) (b)

Figure 12: 2-Butanol Concentration and Catalyst Amount Effects (a) Surface Map (b) Contour Plot (Reprinted from [56]. Parker, T., Mao,Y., Wang, Q., 2022)

The contour plot in Fig. 12 (a) indicates that a 2-butanol concentration of approximately 0.5 mol/L combined with either a low amount of catalyst of approximately 8 g (2.4 wt %) or high amount of approximately 15 g (4.8 wt %) resulted in higher total heat release amounts (kJ/kg reaction mass), while low 2-butanol concentrations of approximately 0.3 mol/L or high concentrations of approximately 0.78 mol/L combined with moderate catalyst amounts of approximately 12 g resulted in the lowest total heat release amount. The p-value for this regression model is 0.098. Furthermore, this regression model has a R^2 of 90.03%, indicating that the data fits relatively closely with the regressed model. The quality of the fit for this model indicates that the effects of the initial concentration of 2-butanol in combination with the catalyst amount play a very significant role in the heat generation from the reaction. Potential reasons that moderate temperatures and catalyst amounts result in the lowest heat release amounts include that for lower temperatures, more of the hydrogen peroxide will decompose and thus more heat is released. Furthermore, for higher temperatures, a higher 2-butanone conversion is achieved, resulting in an increase in the quantity of heat released. The physicochemical significance of this is that all reactions occurring simultaneously can influence the heat released, rather than simply the synthesis reaction. For higher catalyst amounts, the 2-butanone synthesis reaction proceeds more quickly and thus the heat release cannot be moderated readily. Moreover, for lower catalyst amounts, more of the hydrogen peroxide will decompose.

From the plots in Figs. 10-12, it is demonstrated that 2-butanol concentration is a more dominant driving force for the total heat release compared with the reaction temperature and catalyst amounts. However, all three parameters investigated play a significant role in the amount of heat release and thus must be carefully controlled based on available cooling capacity of the industrial facility, which can be affected by the phi factor [52]. For a system with a high phi factor, a large amount of heat is lost to the test cell (reaction vessel), which reduces the final temperature of the vessel contents. However, for a system with a low phi factor, nearly all of the thermal energy is retained by the vessel contents. As a result, this is closer to the conditions encountered when scaling-up the reaction for industrial use and thus results in more useful data for scale-up simulation. The contour plots in this work represent the total heat release amounts of the reactions in different layers, with each layer having a different color indicating the magnitude of heat release. Layers with low total heat release amounts are labeled in dark green and layers with high total heat release amounts are labeled in dark red. From a process safety perspective, a higher rate of heat release requires higher cooling capacity from industrial facilities to prevent severe incidents from occurring. Moreover, reaction systems with large amounts of total heat release can be operated with lower cooling capacity provided that the heat release rate is controlled. This can include methods such as carefully controlling the addition of reactants or using a large heat sink. In addition to concerns regarding heat release and thermal runaway, the flammability of the reaction system can present hazards. For example, the flash point of methanol is 9 ◦C. In this work, all of the experiments were carried out above this temperature (30 ◦C, 45 ◦C, and 60 ◦C) and O2 gas was generated as a result of the hydrogen peroxide decomposition. Although these experiments were carried out with the vessel open to the atmosphere, under certain conditions, the methanol could undergo combustion when combined with heat and O2 gas. Thus, the flammability of a reaction system must be taken into account when scaling it up for industrial use. In order for an industrial facility to properly identify and address potential risks associated with cooling system failures for this reaction system, a risk matrix could be developed. For this, performing the reaction using parameters associated with higher heat release amounts as described above would have the potential to cause more significant damage if the cooling system were to fail. Thus, a higher severity ranking for a potential incident would be assigned to the reaction system, resulting in an increased risk rating for the system. Because of this, knowledge of the effects of operating parameters on the heat release amount of the reaction system is of utmost importance in order to determine the risk associated with the reaction and safeguards that must be implemented.

4.3 Risk Matrix Assessment

To construct a risk matrix that will accurately represent the degree of hazard in each of the nine experiments, “severity” and “likelihood” must be redefined based on the experimental results and parameters. In this case, the “severity” is defined as total heat generated which is calculated by integrating and summing the 4 heat release peaks for each of the nine experiments. Table 1 shows total heat generated based on the different parameters in this experiment. Furthermore, total heat generated calculated in Table 1 will be divided and ranked into three-point scale: negligible (1), marginal (2) and critical (3). The total heat generated corresponding to each category is shown in Table 2.

Run	Temperature (°C)	2-butanol concentration (mol/L)	Catalyst concentration (wt%)	Total heat generated (kJ)
1	30	0.284	2.4	3.62
2	45	0.284	3.6	1.98
3	60	0.284	4.8	1.75
4	30	0.534	2.4	4.44
5	45	0.534	3.6	2.87
6	60	0.534	4.8	4.13
7	30	0.784	2.4	3.28
8	45	0.784	3.6	0.65
9	60	0.784	4.8	2.86

Table 1: Heat generated data calculated by different temperature, catalyst, and 2-butanol concentration

Negligible (1)	Marginal (2)	Critical (3)
0-2 kJ	2-4 kJ	4-6 kJ

Table 2: Three-point division for total heat released

A negligible (1) heat generated indicate that the operational conditions will result no or less than minor injury in case of personal error, procedural deficiency or design deficiency. A marginal heat (2) generated indicate that the operation conditions will result in minor injury in case of human error, procedural deficiency or design deficiency. A critical (3) heat generated indicate that the operation conditions will result in sever injury in case of human error, procedural deficiency or design deficiency. Furthermore, the “likelihood” of is calculated using Process and Hazard Control Index (PHCI). In this case, not all control systems are used to calculate PHCI. Since the experiments done in laboratory did not require any of hazard control, indicating that control systems relating to hazard control is not considered. Furthermore, Therefore, calculation of PHCI can be reduced to equation 6.

$$PHCI = PHCI_P + PHCI_t + PHCI_f + +PHCI_C$$

Equation 6

For this, p stands for pressure, t stands for temperature, f stands for flow, c stands for concentration of 2-butanol and catalyst. For every control system, am extent of requirement score is determined based on Figure 7 and the corresponding PHCI is determined by Figure 8. In this experiment, since the pressure and flow are both held constant, an extent requirement score of 3 will be assigned to $PHCI_p$ and $PHCI_f$, corresponding to a PHCI of 2. Furthermore, for temperature, based on the result from surface map and contour plot, heat release is lower at moderate temperatures. Therefore, a extend requirement score of 6 will be assigned to reaction at low temperature (30°C) and high temperature (60°C), corresponding to a PHCI of 6. A score of extend requirement score of 5 will be assigned to moderate temperature (45°C), corresponding to a PHCI of 6. Furthermore, it is shown that 2-butanol concentration plays the most significant role in heat release amount. Thus, a higher extend requitement score will be given to 2-butanol concentration. From the surface map and contour plot, it is observed that 2-butanol concentration of approximately 0.5 mol/L combined with either a low amount of catalyst of approximately 8 g

(2.4 wt %) or high amount of approximately 15 g (4.8 wt %) resulted in higher total heat release amounts (kJ/kg reaction mass), while low 2-butanol concentrations of approximately 0.3 mol/L or high concentrations of approximately 0.78 mol/L combined with moderate catalyst amounts of approximately 12 g resulted in the lowest total heat release amount. The combination of moderate 2-butanol concentration with low and high amount of catalyst would receive a extend requirement score of 10, corresponding to PHCI of 10. The combination of low and high concentration of 2-butanol with moderate catalyst would receive a extend requirement score of 5, which indicate the control is good if available, corresponding to PHCI of 6. As a general principle, by observing the surface map and contour plot, higher heat release indicating the requirement of control becomes essential, resulting higher PHCI. Table 3 shows the PHCI calculated for all nine experiments.

Run	Temperature (°C)	2-butanol concentration (mol/L)	Catalyst concentration (wt%)	$PHCI_t$	PHCIc	PHCI
1	30	0.284	2.4	6	8	20
2	45	0.284	3.6	6	6	18
3	60	0.284	4.8	6	8	20
4	30	0.534	2.4	6	10	22
5	45	0.534	3.6	6	8	20
6	60	0.534	4.8	6	10	22
7	30	0.784	2.4	6	8	20
8	45	0.784	3.6	6	6	18
9	60	0.784	4.8	6	8	20

Table 3: Calculated PHCI based on requirement of control

Furthermore, calculated PHCI is divided and ranked into three-point scales: remote (1), occasional (2), and probable (3). The PHCI corresponding to each scale is shown in Table 4.

Remote (1)	Occasional (2)	Probable (3)
18	20	22

Table 4: Three-point division for PHCI

In this case, remote indicates that incidents are unlikely but possible to occur, occasional indicates incidents are likely to occur sometimes, and probable means incidents will likely to occur several times. Based on the “severity” and “likelihood”, qualitative risk matrix is constructed and shown in Figure 13. Based on the risk matrix, region highlighted in red indicates that the hazards for performing process scale-up under the given parameters are high, indicating that layers of protection such as additional cooling utilities and emergency response systems are required. Region highlighted in yellow indicates that hazards for operation are controllable and less protections are required. Region highlighted in green indicate that hazards for operation are low and acceptable.

	Negligible (1)	Marginal (2)	Critical (3)
Remote (1)	Low-1	Low-2	Low-3
Occasional (2)	Low-2	Medium-4	Medium-6
Probable (3)	Low-3	Medium-6	High-9

Figure 13: Risk Matrix Assessment

CHAPTER V

SUMMARY AND FUTURE WORK

The effects of catalyst amount, reaction temperature, and initial 2- butanol concentration on the heat release amounts during the conversion of 2-butanol to 2-butanone were investigated in this work. Based on the results of this, it was found that the optimum operating ranges for this synthesis were at relatively low and high 2-butanol concentrations, as well as moderate temperatures and catalyst amounts. Possible explanations for the optimum temperatures and catalyst amounts being moderate include that for lower temperatures, the reaction proceeds more quickly and the heat release cannot be moderated readily while for higher temperatures, the cooling capacity of the system is strained. Additionally, for higher catalyst amounts, the reaction proceeds more quickly and thus the heat release cannot be moderated readily while for lower catalyst amounts, more of the hydrogen peroxide will decompose. Furthermore, it was found that the 2-butanol played the most significant role in the heat release amount and thus must be carefully accounted for when determining the cooling requirements for the reaction vessel, particularly when scaled up for industrial processes. Response surface methodology was found to be a useful method for identifying optimum ranges of parameters under which 2-butanone synthesis from 2-butanol takes place to minimize cooling requirements for the reaction. Based on the data from nine experiments, a qualitative risk matrix is constructed where the severity is defined as total heat generated and likelihood is calculated using PHCI. Based on the result of the risk matrix, region highlighted as red indicating that the operating condition has a high risk and additional layers of protection are required.

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Possible extensions of this work would include thermal analysis of other oxidation reaction systems, including 2-pentanol to 2-pentanone and cyclohexanol to cyclohexanone. Furthermore, the effects of reactor pressure on the heat release rates and amounts as well as yields of 2-butanone could be investigated. Furthermore, Hazard and Operability Study (HAZOP) can be developed combined with the risk matrix to give a better picture of process hazard analysis in chemical plants. HAZOP is considered as a proper, organized, and critical evaluation used to assess the potential risks resulting from defective machinery and other property in terms of the effects on either new or existing processing facilities [53-54]. The methodology of HAZOP can be divided into four phases: definition, preparation, examination, and documentation [55]. Risk matrix can be used to estimate level of impact in the examination phase of HAZOP, which makes the recommendations based on the result of HAZOP more credible. In conclusion, HAZOP combined with risk matrix makes the investigation of potential hazards more comprehensive compared to performing either one technique alone.

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APPENDIX A

2-BUTANONE HEAT RELEASE AND FTIR DATA

Table A.1: Raw heat release data for Taguchi Orthogonal Array (OA) design for study of temperature, catalyst, and 2-butanol concentration impact on total heat generation

Run	Temperature (°C)	2-butanol concentration (mol/L)	Catalyst concentration (wt%)	Total heat generated (kJ)	Heat generated (kJ/kg reaction mass)
1	30	0.284	2.4	3.62	11.10
2	45	0.284	3.6	1.98	6.03
3	60	0.284	4.8	1.75	5.29
4	30	0.534	2.4	4.44	13.60
5	45	0.534	3.6	2.87	8.73
6	60	0.534	4.8	4.13	12.48
7	30	0.784	2.4	3.28	10.04
8	45	0.784	3.6	0.65	1.98
9	60	0.784	4.8	2.86	8.64

APPENDIX B

TEMPERATURE AND HEAT REALEASE CURVE FOR 9 EXPERIMENTS:

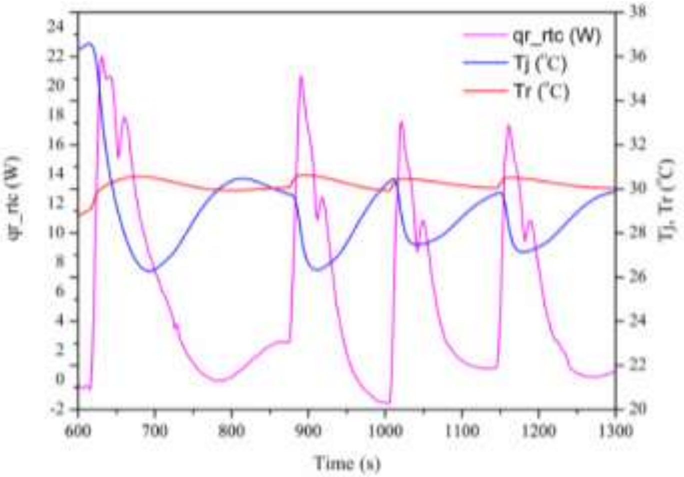

Fig. B.1: 30 °C, 2-Butanol Concentration: 0.28 mol/L, Catalyst Concentration: 2.4%

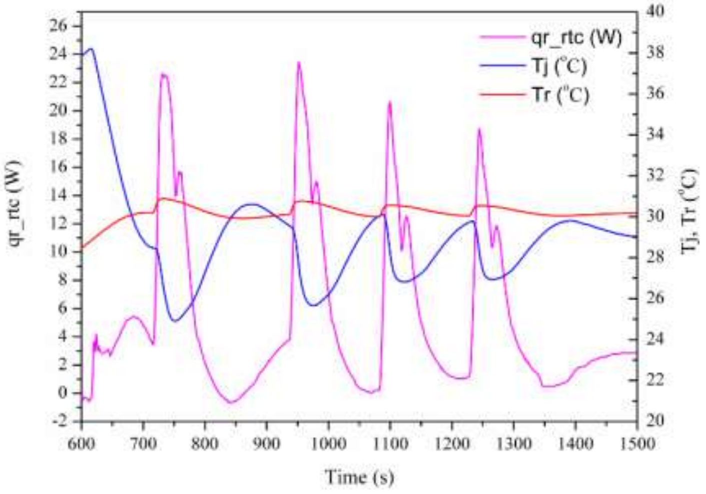

Fig. B.2: 30 °C, 2-Butanol Concentration: 0.53 mol/L, Catalyst Concentration: 2.4%

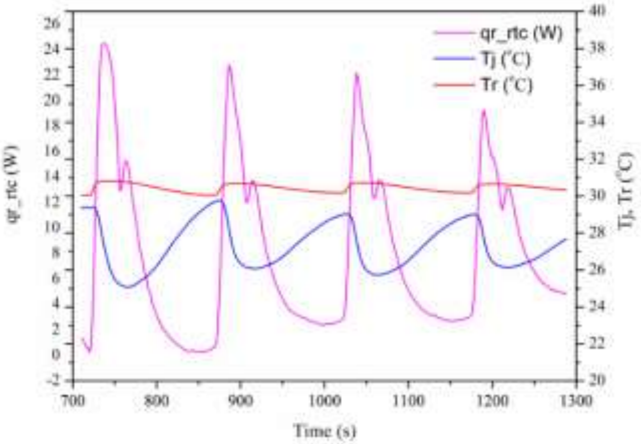

Fig. B.3: 30 °C, 2-Butanol Concentration: 0.78 mol/L, Catalyst Concentration: 2.4%

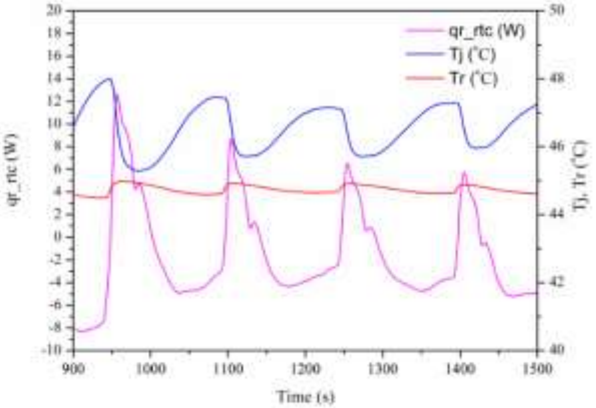

Fig. B.4: 45 °C, 2-Butanol Concentration: 0.28 mol/L, Catalyst Concentration: 3.6%

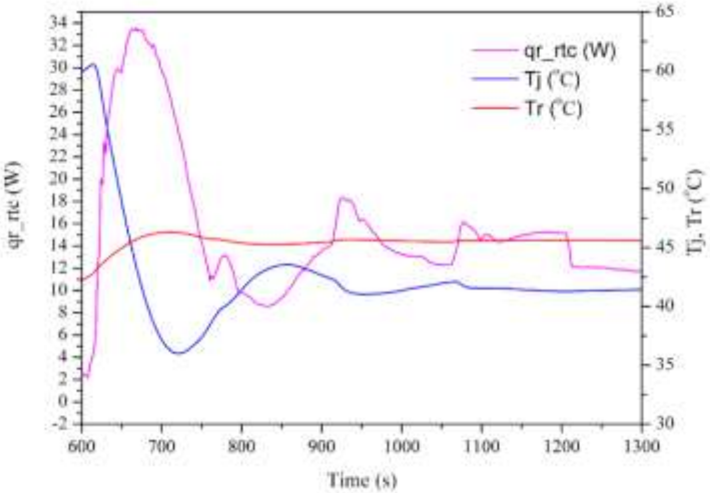

Fig. B.5: 45 °C, 2-Butanol Concentration: 0.53 mol/L, Catalyst Concentration: 3.6%

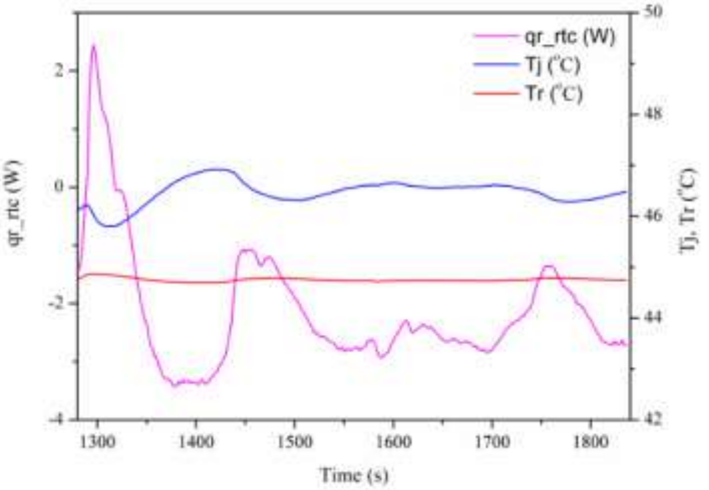

Fig. B.6: 45 °C, 2-Butanol Concentration: 0.78 mol/L, Catalyst Concentration: 3.6%

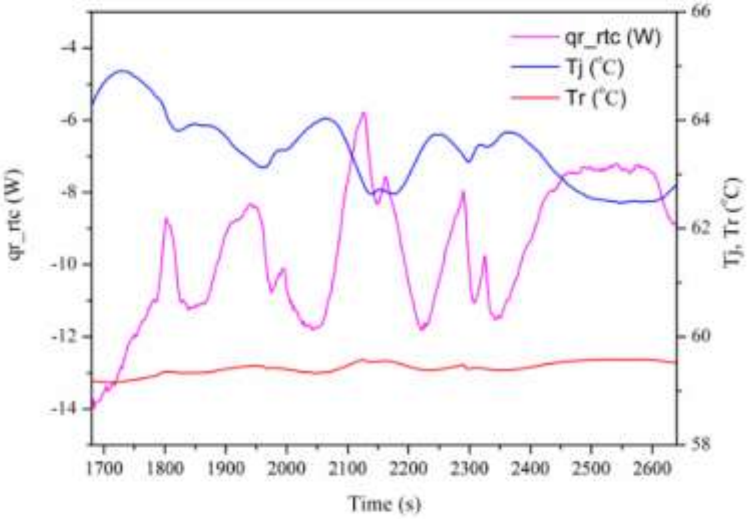

Fig. B.7: 60 °C, 2-Butanol Concentration: 0.28 mol/L, Catalyst Concentration: 4.8%

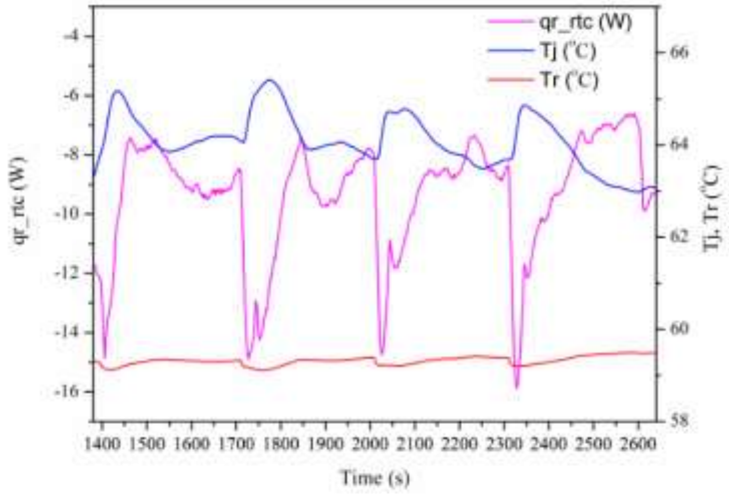

Fig. B.8: 60 °C, 2-Butanol Concentration: 0.53 mol/L, Catalyst Concentration: 4.8%

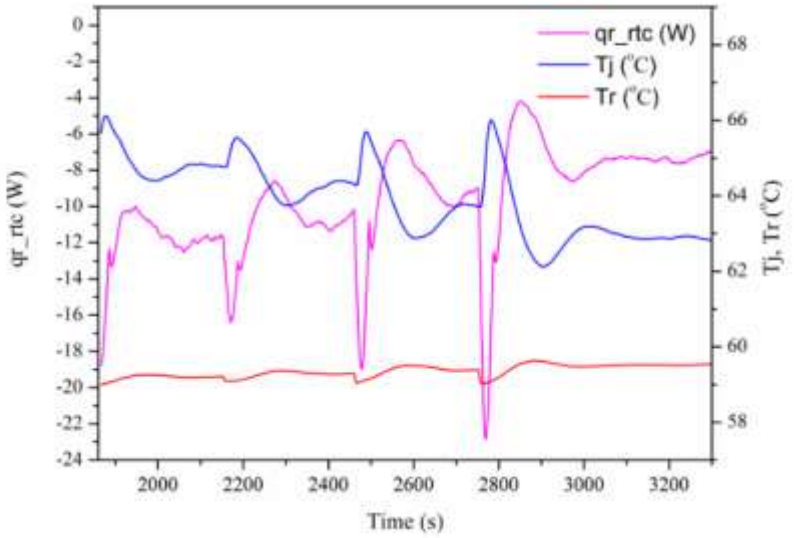

Fig. B.9: 60 °C, 2-Butanol Concentration: 0.78 mol/L, Catalyst Concentration: 4.8%