Project Number: MQP-WMC-2520

Heat Transfer in Reactor Scale-Up

A Major Qualifying Project Report:
Submitted to the Faculty
Of the

WORCESTER POLYTECHNIC INSTITUTE

In partial fulfillment of the requirements for the

Bachelor of Science Degree

by:

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Kellie Dickerson

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Erika Kirichenko

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Melinda Lei

April 30, 2015

Approved:

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Professor William Clark, Major Advisor

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Robert Prytko, Sunovion Pharmaceuticals Inc. Co-Advisor

Abstract

Minor temperature rises in lab scale reactions are sometimes not relayed to engineers in charge of scale-up, potentially causing runaway reactions. This project investigated differences in heat transfer between round bottom flasks and industrial sized equipment through research, laboratory experiments, and computer modeling. A non-linear relationship between reactor size and cooling capability was established, and the feasibility of accurate computer modeling was determined.

Acknowledgements

Our MQP team would like to take the time to thank the people and organizations who have helped us in determining the direction of our project, the set-up of experiments, and the analysis of our results. Credit for the success of this project is due to the considerable time and attention put in by the following people:

- Our faculty advisor, Professor William Clark, for the great amount of support and guidance he has provided us with throughout the course of our project, from presenting us with necessary materials and tools, to always being open to discuss our ideas and direction throughout every step of the project.
- Sunovion Pharmaceuticals Inc. for sponsoring this project and for their continued collaboration with WPI in sponsoring MQPs.
- Robert Prytko of Sunovion Pharmaceuticals Inc., for identifying this project for our team. His feedback and direction throughout the year were very helpful in ensuring the success of the project.
- Tom Partington and Douglas White from the Goddard Lab Machine Shop, who helped us find and customize tools which were essential to complete our MQP.
- Worcester Polytechnic Institute for supporting our MQP and providing the necessary laboratory space to complete the project.

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Introduction

Typically, any large scale chemical process originates from a small-scale set-up in a laboratory. In order to convert a process to full-scale production, the reaction is often tested in stages, in reactors of increasing size. Nonetheless, occasionally, it is still possible to upgrade directly from the laboratory equipment to a full scale pilot plant if proper precautions and factors are considered (Starkie, Rowe, 1992). However, because only limited amounts of reactants are initially used, little is known about the true nature of the reaction; such as its side reactions, potential delays and other temperature effects, up until the pilot plant reactor size is reached (RSC, 2014). It's important to note that there are two main factors that change during scale-up: rates of heat production and removal (RSC, 2014). Scientific papers often cite that round bottom flasks have a higher heat removal rate per unit area. The hazards associated with changes in these two rates as the reactor size is increased are not only limited to the release of excess heat, but sometimes include overpressurization and the discharge of harmful, toxic vapors. Due to an extensive history of runaway exothermic reactions in the chemical engineering industry, which often occur due to inadequate scale-up procedures relating to heat transfer, a closer look should be taken at heat transfer relationships among various sized reactors.

In the pharmaceutical industry, round bottom flasks are commonly used; however, there is not much research available on the scale-up of round bottom flasks. This project focuses on studying the heat transfer characteristics when scaling up a round bottom flask with the following goal and key project objectives in mind:

Goal

To determine the heat transfer characteristics and parameters that affect the heat transfer coefficient of various lab scale reactors up to 10,000 L industrial sized reactors.

Key Project Objectives

1. Identify factors that affect heat dispersion from a reaction when scaling up from a round bottom flask.
2. Create a feasible heat transfer model backed up by experimental data to demonstrate the behavior of heat of reactions in increasing reactor size.
3. Deliver a teaching tool to make chemical engineers, chemists, and others in the field aware of the safety concerns during scale-up involving heat transfer.

Laboratory experiments were completed with these objectives in mind, and were compared to two different computer programs, COMSOL Multiphysics and DynoChem, to determine their effectiveness at modeling round bottom flask scale-up. In the laboratory, heat transfer coefficients of various round bottom flasks were determined and it was proven that more cooling is needed with increasing reactor size in order to keep a reaction at a consistent temperature. The round bottom flasks were then modeled in the two computer programs and several conclusions concerning heat transfer trend data were found.

Through this research, trends modeling the scale-up of round bottom flasks were produced which were comparable to literature data. The findings of this MQP report will help chemists, engineers, and students better understand safety concerns during scale-up and could aid in predicting heat transfer characteristics in increasing round bottom flask and full-scale reactor size.

Background

From the laws of thermodynamics, it is known that energy cannot be created nor destroyed but energy can be transferred through interactions. There are two ways in which energy can be transferred: work and heat. Specifically this project focuses on energy transferred as heat. Heat transfer is thermal energy transferred due to a temperature difference gradient. There are three modes in which heat can be transferred.

Modes of Heat Transfer

Heat is transferred by one or more of the following modes: conduction, convection, and radiation.

In conduction, heat moves through either a solid or a liquid due to a temperature gradient across the solid or liquid. This mode of heat transfer is modeled by the expression called Fourier's Law, where the rate of heat transfer per unit area, q, is equal to $-k * \frac{dT}{dx}$, where $\mathrm{k}\ (\frac{\mathrm{W}}{\mathrm{m}} * \mathrm{K})$ represents the material-specific thermal conductivity.

Convective heat transfer occurs between a moving fluid and a surface body at different temperatures. In this mode of heat transfer, the hotter portions of the fluid move through the rest of the body, which circulates and mixes hot and cold portions of the fluid. Convection tends to transfer heat faster than conduction (Berger, 2001). Newton's Law of Cooling expresses the rate of convective heat transfer as $q \text{ in units } of\ \frac{W}{m^2}$ equal to $h * (T_s - T_\infty)$, where h $(\frac{W}{m^2} * K)$ is the convective heat transfer coefficient, dependent on boundary layer conditions and surface geometry.

Radiation is the simplest mode of heat transfer that does not require solids or fluids to achieve the energy transfer; instead, heat travels by electromagnetic waves. For the purposes of this experiment, only convection and conduction were taken into the account, due to negligible effects of radiation (Incropera, DeWitt, 2011).

Overall Heat Transfer Coefficient

An overall heat transfer coefficient, U, can be used to take into account the total thermal resistance of the system. The overall heat transfer coefficient has the same units as the convective heat transfer coefficient h. The overall heat transfer coefficient is used for composite systems and takes into account the heat transfer inside the medium, through the walls of the system, and the heat transfer on the outside of the system. The overall heat transfer coefficient U is given by the equation:

$$\frac{1}{UA} = \frac{1}{h_i A} + \frac{t_w}{kA} + \frac{1}{h_o A} \qquad Eq.(1)$$

Where h_i is the inside heat transfer coefficient, t_w is the wall thickness, k is the thermal conductivity, and h_o is the outside heat transfer coefficient (Incropera, DeWitt, 2011). As the overall heat transfer coefficient includes the inside and outside heat transfer coefficients, any factors that affect the inside and outside heat transfer coefficients will also affect the overall heat transfer coefficient. The inside heat transfer coefficient h_i is affected by the stirring of the fluid and will increase with better mixing. The outside heat transfer coefficient is affected by the cooling jacket flowrate and will also increase with higher flowrates (Welty, Rorrer, Foster, 2013). Thermal conductivity is a property of the material of the reactor and wall thickness varies from reactor to reactor.

Figure 1 below shows a typical reactor used in industry. As you can see in the figure, the reactor contains an internal stirrer as well as a baffle. A baffle is commonly used to disrupt the vortex from the stirring and help promote better mixing. It is common for reactors to be glass lined with a cooling jacket. Reasons of how the stirring, cooling jacket rate, and wall thickness affect the heat transfer coefficient are discussed below.

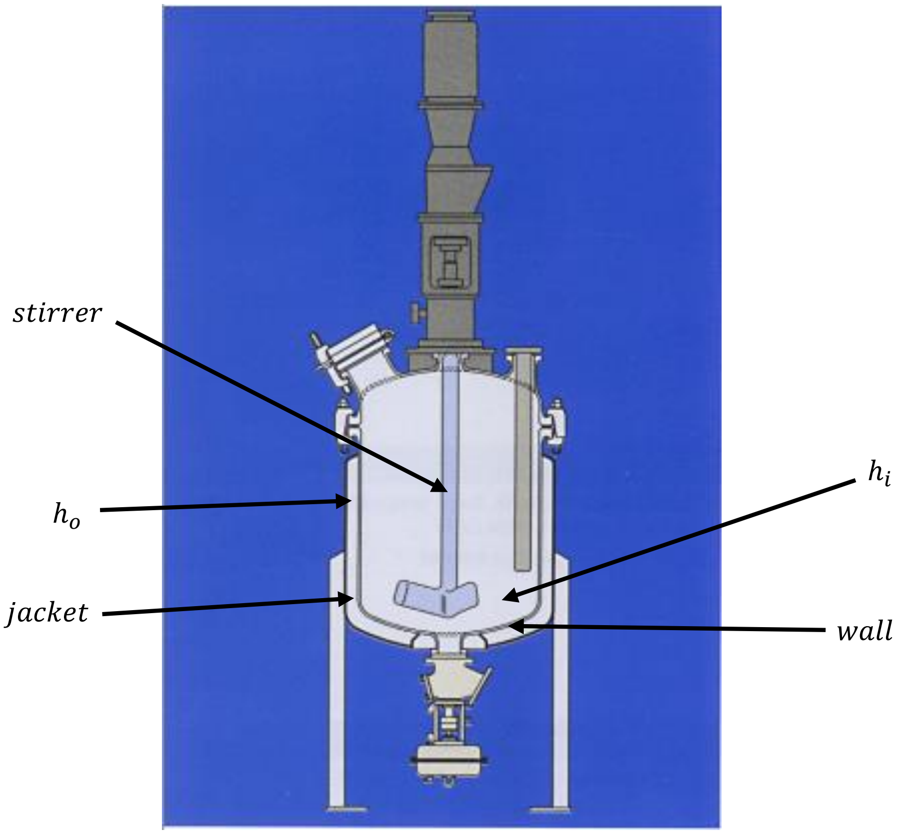


Figure 1: AE1000 Glass Lined Reactor
(Adapted from http://www.rcprocess.se/bdh_filearea/Pfaudler/TI_AE.pdf)

Factors that Affect Heat Transfer in a Reactor

The main goal and challenge of reactor scale-up lies in replicating laboratory results in significantly larger, industrial-sized reactors. Despite the fact that scale-up is essential to the creation of any production process, no systematic methodology exists for this procedure, which can be attributed to a number of factors. First, the kinetic behavior is particular to any one reaction, in addition to fluid dynamics and other transport phenomena (Donati, Paludetto, 1997). Additionally, it is normally not feasible to directly compare laboratory equipment to industrial size reactors; therefore, little research can be made using even the largest apparatuses available in the lab. Also, for either small or large scale, many varieties of equipment exist. For example, reactor types vary from batch, fixed-bed, to distillation columns and plug-flow reactors. Therefore, most of the industrial scale-up techniques tend to be shaped by relevant scale-up experience and its successes and mistakes (Donati, Paludetto, 1997).

Despite the subjectivity of reactor scale-up, the two standard parameters that tend to change every time are the rate of heat production and the rate of heat removal. These rates and the factors that affect them are further discussed in the sections below.

Rate of Heat Production

There are several major contributors to the changing rate of heat production during scale up, such as concentration of reactants and catalysts, reactor size and starting temperature (RSC, 2014).

While chemists tend to only consider the stoichiometry given for a particular chemical reaction, where a certain number of moles of each reagent produce a set number of moles of a reactant, the chemistry is not so simple on a larger scale. For example, mixing affects the stoichiometry of a reaction over time in a stirred tank reactor (Laird, 2010). Additionally, rates of addition, reaction, and removal affect overall production and the physical conditions within the reactor. Primarily, with the decrease in heat transfer area per unit volume, longer reagent addition times are required to prevent runaway reactions. However, this often affects the yield and quality of the product (Laird, 2010). Therefore, factors that contribute the most to changing the rate of heat production are reactant concentration and the starting temperature of the reaction.

Reactant Concentration

The approach to choosing the right reactant concentration often depends on the type of reactor in question. For example, for a CSTR, small reagent concentration would allow for higher conversion. It also raises the potential for exothermic runaways. On the other hand, in a batch reactor, feeding all of the reactants right at the start results in higher conversion. Meanwhile, this move would also produce large amounts of heat that may be dangerous for the process (Luyben, 2007). Since a batch reactor follows a dynamic temperature profile over the course of the chemical process carried out in a given reactor, the initial reactant concentration, along with the starting temperature discussed below, is of great importance. Properly balancing between starting temperature and reactant concentrations, as well as varying concentrations and temperature throughout the process, such as using a fed-batch reactor approach for a highly exothermic process, can help lower risk factors during reactor design.

Starting Temperature

The rate of a chemical reaction is temperature-dependent and fixed. However, it can in turn be influenced by changes in heat and mass transfer, which are reactor-dependent; for example, although a CSTR maintains a constant temperature during production, a batch reactor’s temperature is often adjusted during the different stages of a process. Occasionally in industry, high starting temperatures are desired for greater yield or faster production rates; however, a careful balance must be reached between cost and safety. For example, if a reversible, exothermic reaction is carried out in a batch reactor, it may require an initial boost in temperature, followed by a gradual decrease once enough reactants have converted to products in order to prevent the equilibrium from shifting back to reactants (Luyben 2007). This initial spike in temperature should be large enough to jump-start production without compromising safety. To eliminate risk for scaled-up processes, advanced calorimetric equipment is necessary in the initial testing phases; those may involve running the reaction under adiabatic condition to better understand how much heat a reaction is capable of producing, and more accurately estimate appropriate reactor conditions down the line. Moving from one scale-up stage to the next, close attention must be kept to the temperature increases in the reactor each time.

For most simple exothermic reactions, the collision speed of high energy particles increases with temperature, creating a boost in the reaction rate. The Arrhenius equation can be used to better gauge this relationship between the two rates:

$$k = A * e^{-\frac{E_a}{R*T}} \qquad Eq.(2)$$

Where k is the rate constant, A is a constant, E_a is the activation energy, R is the gas constant and T is the temperature of the reaction. Due to the nature of the Arrhenius relationship, heat production is more influenced by even the smallest changes to its variables compared to heat removal. Therefore, careful kinetic analysis and testing must be performed to make confident predictions for starting temperatures in larger reactors.

Rate of Heat Removal

The major factors that affect the rate of heat removal are the size/geometry of the reactor, cooling, and stirring (RSC, 2014).

Reactor Size and Geometry

Increasing the size of the reactor, even while keeping consistent geometry, alters both the rate of heat production as well as the rate of heat removal. The heat removal is mostly affected by the surface area to volume ratio of a reactor. Assuming consistent geometry, heat removal decreases with increasing size. This relationship can be described by Equation 3 (Starkie, Rowe, 1992).

$$\frac{A}{V} = \frac{1}{V^{\frac{1}{3}}} \qquad Eq.(3)$$

This relationship implies that during scale-up, the temperature difference between the reactor and its cooling jacket becomes significantly larger, and can be estimated by Equation 4 below (Starkie, Rowe, 1992).

$$\left(T_r - T_j\right)_2 = \left(T_r - T_j\right)_1 * \left(\frac{V_2}{V_1}\right)^{\frac{1}{3}} \qquad Eq.(4)$$

As the size of the reactor goes up, the heat transfer surface area per unit volume decreases, with very significant consequences for large-sized reactors. It is important to note that due to this relationship, the heat removal rates do not increase as fast as heat production rates during scale-up. In fact, since larger reactor’s cooling capacity varies linearly with the temperature difference between the reactants and their surroundings (such as a jacket), the reaction eventually reaches a point when the heat generation is equivalent/greater than heat removal (Starkie, Rowe, 1992). The vessel must not pass this point, since it signifies the beginning of an exothermic runaway. This can further cause an overpressurization of the system due to the gaseous nature of the desired product, gaseous by-products of the side-reactions, or the evaporation of the lowest-boiling point components of the mixture within the reactor (AIChE, 1995). Meanwhile, the vessel's heat absorbance becomes insignificant, since the heat capacity of the vessel surface area exposed to the mixture becomes nearly negligible compared to the heat capacity of the contents of the vessel (Stoessel, 2008). This aspect, too, decreases the amount/rate of heat removed from the mixture. Therefore, to better simulate a large reactor on a laboratory scale, both the heat losses to the surroundings as well as the container have to be minimized in order to prevent the slowing down of the reaction that would not otherwise occur on a large scale.

Cooling

By the Tr-Tj relationship presented above, a temperature difference of 2 °C in a 100 mL flask can translate to as large as a 40 °C temperature difference requirement between the jacket and the reactor in order to achieve the same rate of cooling. This phenomenon poses serious safety hazards in case of improper process scale up, especially when it comes to the use of certain materials that do not allow for a large reactor-jacket temperature difference, such as glass. Therefore, the rate of the coolant flowing through the jacket has to be optimized. As has been noted in the sections describing the importance of choosing an appropriate starting temperature and reactant concentrations, the use of proper process controls is absolutely crucial. Whether the scaled-up reactor is a CSTR that must maintain constant conditions, and therefore, follows a linear model for selecting variables for tuning controllers, or a batch reactor with a constantly changing temperature and reactant concentration profile, the necessary controllers are chosen for the next size up at every step of the scale-up process (Luyben, 2007). For example, the operating conditions and controllers for a pilot reactor are chosen based on the laboratory experiment and kinetic analysis of the reaction in question. If done in incremental steps, this approach to scale-up ensures proper cooling and minimizes risk in danger-prone, larger reactors.

Stirring

Proper stirring scale-up ensures that the vessels, although different in size, are geometrically similar and operate under turbulent conditions. In order to appropriately scale-up stirring, engineers typically use one of two main approaches: constant flow per unit volume or constant power per unit volume. The appropriate approach relies on the type of the reactions that will be carried out in these vessels, such as liquid-liquid, gas-liquid, solid suspension among many others. For example, if only liquids are mixed in reactor, the stirrer tip speed should be equal. However, a distribution of solids would instead require a closer look at maintaining the same energy input during stirring, which means the speed of mixing may not necessarily stay constant from one size to another (Brechtelsbauer, 2012).

Steps to Reactor Scale Up

Traditionally, scale-up is completed in three phases: lab reaction development, pre-scale-up, and scale-up. In the lab reaction development phase, various lab experiments are tested to obtain the desired product. After proper data analysis from the lab trials, reaction kinetics calculations, and computer or mathematical modeling are completed, parameters for the pilot unit are chosen (Hoffmann, 2012). When the scale-up process moves on to the pilot plant scale, engineers want to ensure that the larger equipment will produce the same results as the initial lab experiments. At this stage, necessary process controls are also tested for later use at industrial scale. In the pharmaceutical industry, pilot plants typically range from 80 to 5,000 L. Depending on the process, the scale-up may require more than a single pilot stage. Typically, batch reactors are safe to upgrade to commercial stage from a pilot reactor. However, fixed or fluidized bed reactors require a scale-up process with a few more steps (Zeton, 2012).

As the scale-up testing proceeds from one step to another, it is important that each one passes risk assessment and generates controls and automation necessary for the following step in the process. It is also crucial that the vessels used for scale-up testing are similar in geometry, since it has a profound effect on the heat transfer behavior of a reactor. Depending on the trend in heat transfer behavior, a runaway reaction may be possible which would suggest failure of scale-up or re-evaluation of the process at the lab scale. Mass transfer rates and mixing rates must also be evaluated during the scale-up process to ensure that the cells are capable of handling the shear stress from the increased mixing. A cost analysis should also be performed at the pilot plant scale to ensure that the process is economically feasible before moving forward to plant scale. It is desirable to have the lowest achievable cost at the plant scale or the process will not be considered for scale-up.

Often times, lab experiments at the pilot plant size are costly, timely, and sometimes unsafe but data on large scale performance is necessary for proper scale-up. Process modeling with computer software is an alternative to lab experiments that allows for the prediction of the experiment while still obtaining the necessary information.

Scale-Up Safety Concerns

There are many safety concerns when scaling up a process. If safety is not taken into account, a runaway reaction could occur, which could potentially injure or kill employees and result in a loss of time and money. These accidents are usually caused by lack of data or understanding of the scale up and the many factors that affect scaling up to different sized reactors (CCPS, 2013).
Research has shown that exothermic runaway reactions usually occur due to similar problems. The main causes of runaway reactions include improper technique in the addition of chemicals to a reactor, a misunderstanding about reaction steps and exothermic reactions, insufficient cooling, mixing problems, equipment malfunction, contamination, and human error (HSE, 2008). Many of the top causes of runaway reactions are preventable through education on factors affecting scale-up and how it is not a linear process. Following are two recent examples of the many runaway reactions that have resulted in catastrophic explosions in the United States.

In 2007, T2 Laboratories in Jacksonville, Florida was destroyed due to a runaway reaction in a batch reactor. The laboratory was making a batch of MCMT when there was insufficient cooling on the reactor resulting in a runaway reaction due to a sudden increase of temperature and pressure inside of the reactor. The reactor exploded and killed four people. Twenty eight people outside of the company were injured and debris from the incident was later found one mile away (CSB, 2009).

In 2006, a runaway reaction occurred at Synthron LLC plant in Morganton, North Carolina. The plant was using a 1,500 gallon reactor to make paint additives. The company received an order that was 12 percent larger than usual and scaled up the process. This scale up resulted in a runaway reaction due to a large increase in energy and pressure and not enough cooling capabilities. Vapor was released from the reactor, which ignited and initiated the explosion. The plant was destroyed, one person was killed, and fourteen people were injured (CSB, 2007).

These two examples are part of the reason this project is being completed. This project aims to improve upon current knowledge of reactor scale-up process safety. This project focuses on small-scale laboratory testing strictly concerning heat production and removal, followed by extrapolations and use of computer software to model larger reactors unavailable to conduct safely in the laboratory.

Computer Models of Reactor Heat Transfer

Two computer modeling programs were used in this project: COMSOL Multiphysics, and DynoChem. COMSOL is a modeling and simulation software equipped with physics for heat transfer, equations, and solvers necessary for simulating various engineering problems in chemical, mechanical, electrical and other engineering fields. There are various examples on COMSOL's website of models and how to build them which are useful references depending on the application of the project (COMSOL, 2015). Sunovion Pharmaceuticals Inc. does not currently use COMSOL Multiphysics. DynoChem is a scale up software developed by Scale-Up Systems which can be used by pharmaceutical companies. Scale-Up System encourages companies to have their facilities' reactors identified in DynoChem so that they can run theoretical tests on their reactors. It helps with safety because a process can be modeled and determined safe for scale-up before the actual experiment is performed in the laboratory. DynoChem's website is equipped with teaching tutorials and are useful for people who are new to the program. (DynoChem, 2015). One employee at Sunovion currently uses this software, but not for the purposes related to this project.

Worcester Polytechnic Institute (WPI) currently holds a license for (Classkit) COMSOL Multiphysics 4.3b, which was the package used in this MQP. However, COMSOL offers other modules which would be better suited for this project but WPI does not currently own those modules. The Mixer Module download allows a user to model stirred reactors and to optimize their product through mixing variation. It is advertised as a useful tool for pharmaceutical industries on its website. Another module that would aid in this project is the Chemical Reaction Engineering Module. This allows a user to model chemical reactions and heat transfer that occurs as a result of those reactions. The description claims that it can model mixers and other unit operations. These two modules would make this project more precise because both mixing and reactions need to be "simulated" in the Classkit version of COMSOL Multiphysics. Due to the lack of access to those modules, factors need to be inputted to mimic the effects of stirring and a reaction. This leads to many places where error could occur.

Each computer program served a different purpose in the heat transfer scale-up investigation. COMSOL was used in combination with the water experiments, and the data was manipulated to ensure that the COMSOL temperature profile over time data can be superimposed onto similar experimental data. By modeling the flasks used to carry out the experiments as closely as possible in COMSOL, the scale-up factor in COMSOL was calculated.

In turn, DynoChem was used to model large, industrial-sized reactors that would not otherwise be available for our experimental purposes. Typically used industrial sized reactors are built into DynoChem allowing models to be easily built. The capabilities of DynoChem were explored and it was determined that DynoChem is capable of modeling reactions in reactors and predicting cooling times, reactor temperatures, and jacket temperatures among others.

Methodology

Round Bottom Flask Water Experiments

The experimental portion of this project was split into a series of different experiments. First, the effect of increasing volume, and in turn, volume to surface area ratio was considered by performing a series of simple heat transfer experiments to study temperature drop over time. For this set up, several sizes of round bottom flasks (RBF) were utilized: 50 mL, 100 mL, 250 mL, 500 mL, and 1,000 mL. Each flask was placed in an ice bath and kept at a nearly constant temperature of 0 °C to mimic a cooling jacket in a reactor. After adding a specified volume of water to the flask, the liquid was cooled down to 0 °C, and an equal amount of hot water was added to the flask. Temperatures of the water, the inside surface of the RBF, the outside surface of the RBF, and the ice bath were monitored using temperature probes that were connected to a data acquisition computer software program. The probes were hooked up to the interior and exterior walls of the flasks to measure the temperature difference across the wall. At this point, the amount of time it took for the water to cool down to 0 degrees was recorded along with a temperature profile over time for each flask experiment. Using the recorded data, the overall heat transfer coefficient was calculated, and these values were compared to all given volumes. Examples of this experimental setup can be seen below in Figures 1 and 2.

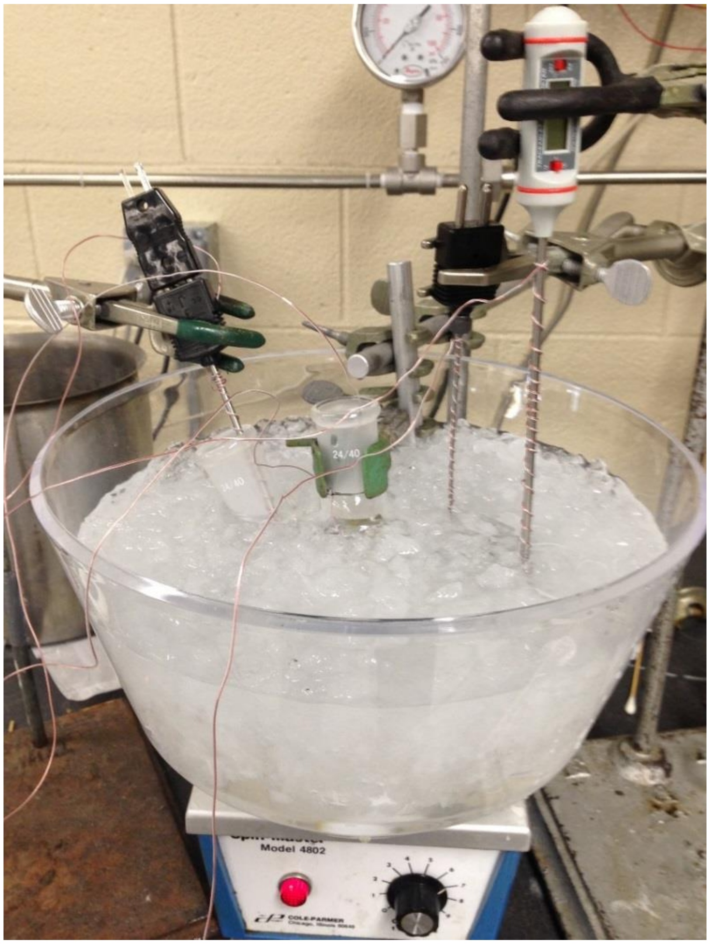


Figure 2: Round Bottom Flask Experiment with Five Temperature Probes Hooked up to Computer Software

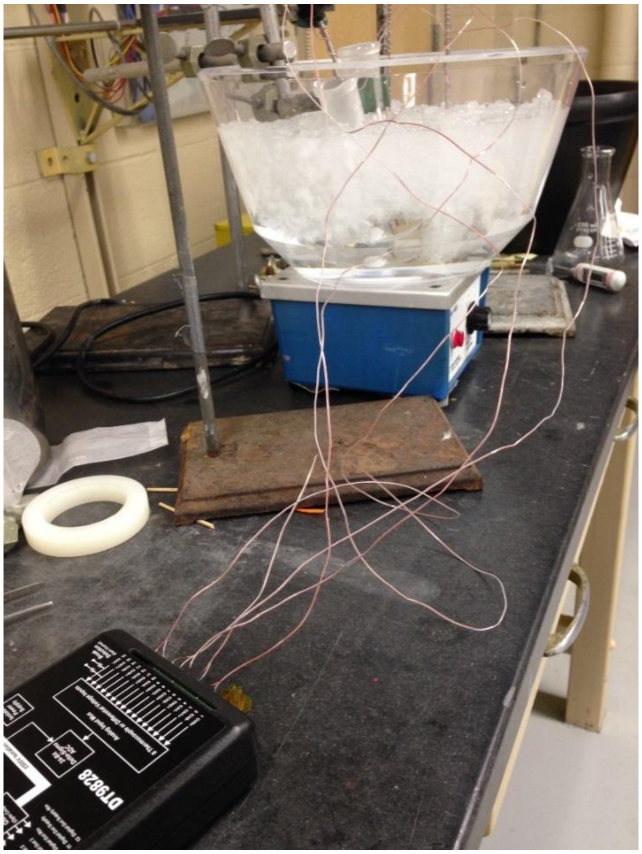


Figure 3: Side View of Figure 1

Iodide-Catalyzed Hydrogen Peroxide Decomposition Reaction Experiments

In order to better represent the heat of reaction, a well-studied exothermic reaction was chosen. The exothermic reaction involved the decomposition of hydrogen peroxide into water and oxygen gas with an iodide catalyst. The reaction proceeds as follows:

$$2\ H_2O_2\ (aq) \xrightarrow{I^-} 2H_2O(l) + O_2(g) \qquad Eq.(5)$$

This reaction is commonly used in classrooms to calculate activation energy and the heat of reaction has been determined to be around -98,000 J/mol. Multiple studies on the hydrogen peroxide decomposition reaction have been published into the *Journal of Chemical Education*. The reactions performed in the lab were conducted following methods in "Efficient Method for the Determination of the Activation Energy of the Iodide-Catalyzed Decomposition of Hydrogen Peroxide (Sweeney, Lee, Abid, and DeMeo, 2014)." In this study, 4 mL of 0.10 M potassium iodide was added to 30 mL of 12% hydrogen peroxide in a Styrofoam cup calorimeter.

The initial calorimeter experiment was performed to attempt to recreate the temperature vs. time profile found in the study and to demonstrate how great of a temperature increase the reaction produces if heat is not purposely removed from the container. The reaction was run in an 8 ounce Styrofoam cup calorimeter, shown in the figure below:

Figure 4: Styrofoam Cup Calorimeter Set Up

Due to unavailability of 12% hydrogen peroxide necessary for the experiment, 30% solution was diluted to the required percentage. Next, 30 mL of the 12% solution were added to a calorimeter made of two 8 ounce Styrofoam cups. To begin the experiment, 4 mL of 0.1 M potassium iodide were poured into the cup. The calorimeter was covered for the entirety of the run, and the temperature profiles of the container's inner and outer walls, as well as the mixture itself, were recorded using type J, bare wire thermocouples. The data was recorded every second from the time potassium iodide was added, to the moment the reaction had reached completion.

After running the experiment under near-adiabatic conditions in a calorimeter, similar experiments were performed in the flasks used for heat transfer coefficient calculations in previous trials. This time, flasks sizes 100 mL and 1 L were used to observe how the temperature profile is affected by the size of the flask. For both flasks, 50% of the volume was filled with the 12% hydrogen peroxide solution, and appropriate, scaled-up amounts of potassium iodide were added to start the reaction. The temperature profiles were once again recorded for the solution, inner, and outer walls of the round bottom flasks. The calculations and results of the experiments described can be found in the Appendix, as well as in the Results and Discussion sections.

Overall Heat Transfer Coefficient Calculations

In order to account for all major forms of heat transfer in this experiment, the overall equation used has several parts. First, the heat in and out of the container can be represented by the following equation:

$$\frac{dQ}{dt} = U * A * (T_1 - T) \qquad Eq. (6)$$

Where U is the overall heat transfer coefficient, A is heat transfer area, T_1 is the temperature of the ice bath, and T is the inside temperature of the water at any point in time.

Next, assuming ideal convection inside the container, the change in the amount of heat contained by the fluid per unit time can be described by the Equation 7.

$$\frac{dQ}{dt} = \rho * C_p * V * \frac{dT}{dt} \qquad Eq.(7)$$

The combination of Equation 6 and 7 creates the following relation:

$$U * A * (T_1 - T) = \rho * C_p * V * \frac{dT}{dt} \qquad Eq.(8)$$

Separating the variables and integrating over time and temperature provides us with the overall heat transfer equation:

$$\frac{T_1 - T}{T_1 - T_i} = e^{\frac{-U*A*t}{\rho*C_p*V}} \qquad Eq.(9)$$

Variable values used:

Flask dimensions (100 mL): O.D. by Height: 65 mm by 120 mm;

Radius: 0.0325 m

Flask dimensions (250 mL): O.D. by Height: 82 mm by 134 mm;

Radius: 0.0410 m

Flask dimensions (500 mL): O.D. by Height: 103 mm by 174 mm;

Radius: 0.0515 m

Flask dimensions (1000 mL): O.D. by Height: O.D. by Height: 132 mm by 213 mm;

Radius: 0.066 m

A =Surface Area (half-sphere): $A = 2\pi r^2$

V =Volume (half-sphere) = $= \frac{2}{3}\pi r^3$

Density and specific heat values are taken at 10 °C, since it's approximately the half-way point between the lowest and the highest values of the temperatures used in the equation.

$$C_p = 4185.5 \frac{J}{kg * K}$$

$$\rho = 999.8 \frac{kg}{m^3}$$

T_1 = Temperature of the ice; 0 °C

T_i = Initial temperature of the water; taken as the highest temperature achieved after mixing equal amounts of cold and hot water

T = Final temperature of the water when the timer was stopped

t = Time taken to cool the water from T_i to T in seconds

U = Overall heat transfer coefficient in $\frac{W}{m^2 * K}$

This concept can be graphically represented by plotting the time versus the natural log of $\frac{T_1 - T}{T_1 - T_i}$. The slope of the straight portion of the graph is then equivalent to $\frac{-U * A * t}{\rho * C_p * V}$, from where U can be calculated based on the respective surface area and volume of each flask.

COMSOL modeling

Geometry

The COMSOL testing was completed using a COMSOL Multiphysics 4.3b axisymmetric model. The physics used were two “Heat Transfer in Solids” modules which were time-dependent. To set-up the geometry, the following calculations were made, the example being for a 100 mL flask.

$$volume = 100\ mL = 1e^{-4}\ m^3$$

$$\frac{4}{3}\pi r^3 = 1e^{-4}\ m^3$$

$$r_{inside} = 0.02879\ m$$

$$Glass\ thickness = 0.0027\ m$$

$$r_{outside} = 0.02879m + 0.0027m = 0.03149\ m$$

$$d_{outside} = 0.03149m \times 2 = 0.06298\ m$$

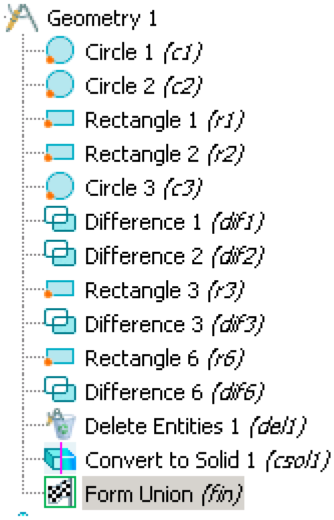


Figure 5: COMSOL Geometries Used to Construct Round Bottom Flask Model

First, the outside (Circle 1) and inside wall (Circle 2) of the spherical portion of the round bottom flask were constructed.

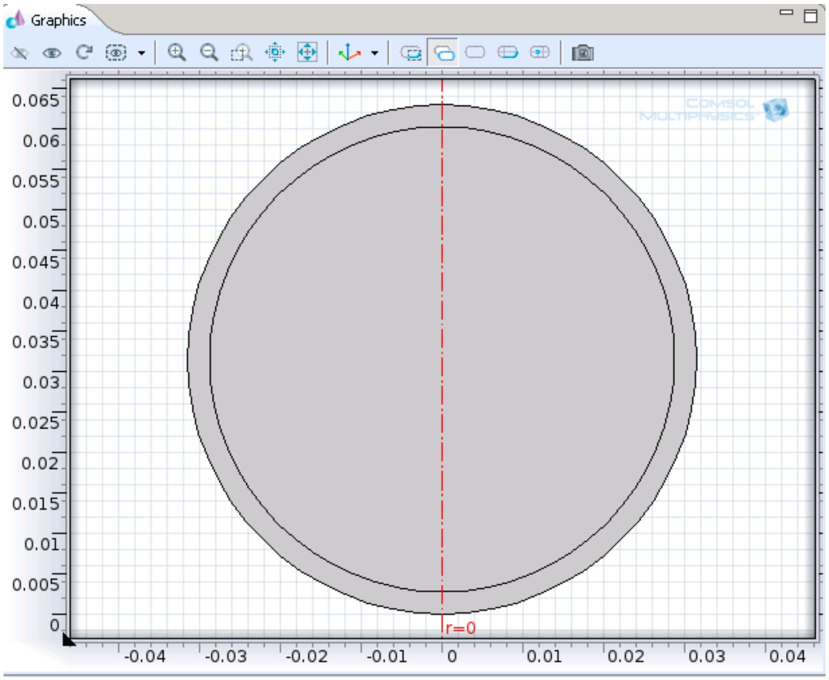


Figure 6: COMSOL Construction of Spherical Portion of Round Bottom Flask

The outside wall of the neck (Rectangle 1) was constructed next. Rectangle 2 was created to make the flask only half full of water. To achieve this, Circle 3 was drawn with the same dimensions as Circle 2.

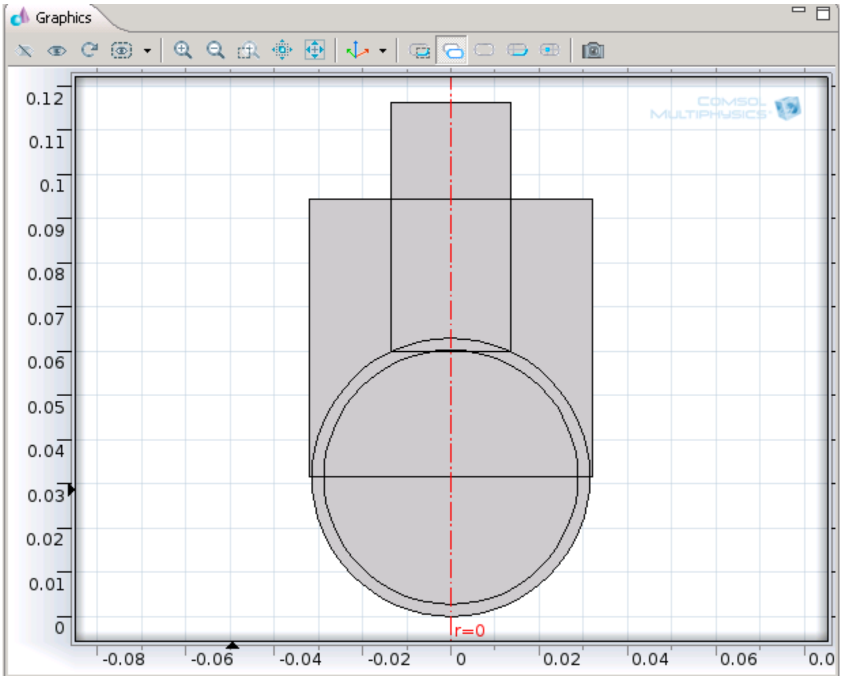


Figure 7: COMSOL Construction of Round Bottom Flask Neck and Water Part 1

Next, Difference 1 was executed, subtracting Circle 3 from Circle 1. This creates the air space in the top half of the round bottom flask. Next, Difference 2 was completed by subtracting Circle 2 from Rectangle 2 which creates the water portion in the bottom half of the flask.

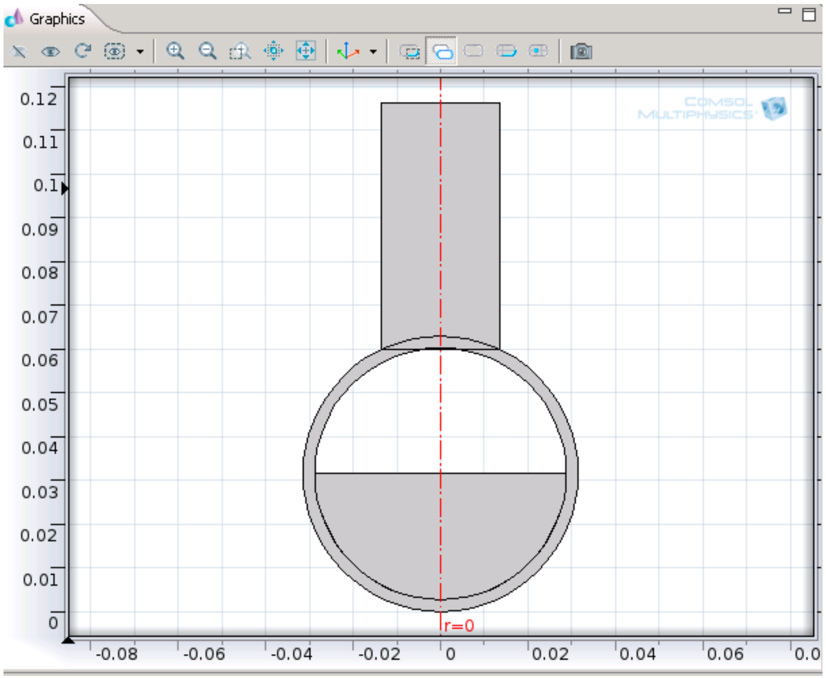


Figure 8: COMSOL Construction of Round Bottom Flask Neck and Water Part 2

Rectangle 3 was made, which creates the inner wall of the neck.

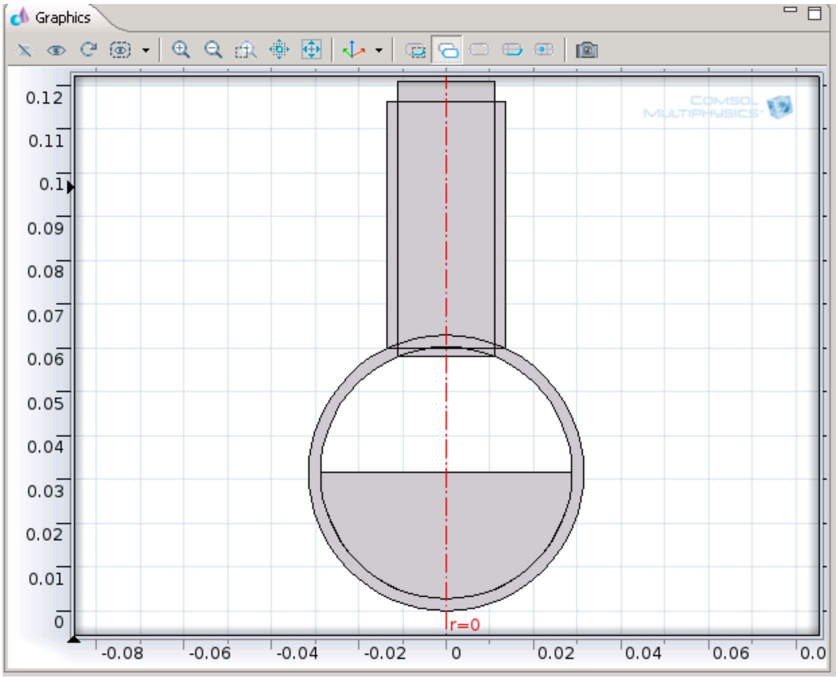


Figure 9: COMSOL Construction of Round Bottom Flask Neck Wall

Difference 3 was performed by subtracting Rectangle 3 from both Rectangle 1 and Difference 1. After, Rectangle 6 was drawn which covers the left half of the geometry.

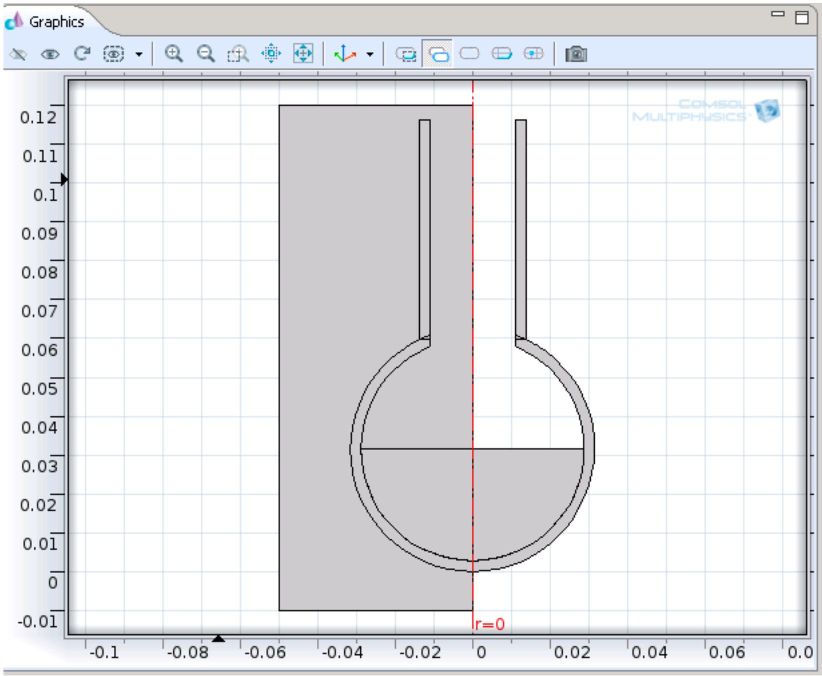


Figure 10: COMSOL Construction of Axisymmetric Round Bottom Flask

Difference 6 was completed, which subtracted Rectangle 6 from both Difference 2 and Difference 3. Also, three entities were deleted where the neck meets the round portion of the round bottom flask. The object was converted to a solid and the union was formed.

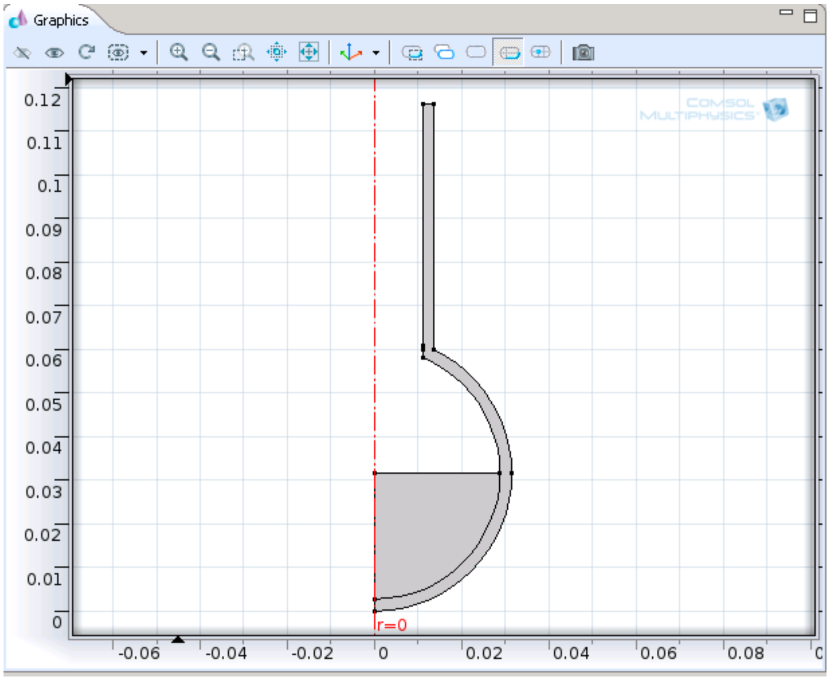


Figure 11: Complete Axisymmetric COMSOL model of Round Bottom Flask

**Note: For larger flask sizes, the relative repair tolerance for some differences needed to be adjusted in order for the model to work.

Materials

Liquid water was selected for the material inside the flask. Silica glass was selected as the material for the wall of the round bottom flask. The thermal conductivity, k, of the silica glass was changed from 1.38 $\left(\frac{W}{m^2K}\right)$ to 2.38 $\left(\frac{W}{m^2K}\right)$. (The thermal conductivity of the water can also be adjusted to mimic stirring, but was not done in this study).

Physics

Heat Transfer in Solids

This physics focused on the water inside of the round bottom flask. Heat flux was added to the physics and the boundary between the water and the inside wall of the flask was selected. For the heat flux, "general inward heat flux" was selected and q_o was set equal to $706(T_2 - T)$, modeling heat transfer from the water to the wall where T was the temperature of the water and T_2 was the temperature of the inside glass wall. The value "706" was selected as the heat transfer coefficient. The initial value of the temperature was set to 287.45 K, based off the highest temperature recorded of the inside wall of the flask in the lab experiments conducted in Goddard Lab.

Heat Transfer in Solids 2

This physics focused on the glass wall. Two heat fluxes were added. The first heat flux was for the boundary between the water and the inside wall of the flask. For the heat flux, "general inward heat flux" was selected and q_o was set equal to $100(T - T_2)$, modeling heat transfer from the wall to the water, where T was the temperature of the water, and T_2 was the temperature of the inside glass wall. The value "100" was selected as the heat transfer coefficient. The second heat flux was for the outside wall of the flask that would touch the ice bath (three boundaries needed to be selected to complete this). For the heat flux, "inward heat flux" was selected and an h value of 650 $\frac{W}{m^2K}$ and a T_{ext} of 272.15 K was chosen because in the lab experiment, the ice bath was recorded at -1 degrees Celsius. The initial value for T_2 was also set to 272.15 K.

Mesh

A "fine" mesh was built.

Solve

A time-dependent solver was used with a Times range(0,1,1000). This means that COMSOL solves the problem from time=0 seconds to time=1000 seconds while evaluating every second.

Results

A cut point 2D was made, selecting the inside wall of the flask, about halfway down through the water portion. A point graph was made using the cut point 2D and a temperature vs time plot was graphed. A point evaluation was made for the cut point 2D and a table was added to represent the point graph. The “evaluate” button on the point evaluation needed to be clicked every time the study was computed (the table does not automatically update to reflect the graph). The table was studied to determine the second that the temperature of the inside wall of the flask reached zero and was compared to the experimental lab data to ensure the two times matched.

The values used in the heat fluxes were determined by comparing the graph of temperature vs time that COMSOL generated to the same graph from the lab experiment. The goal was to get the COMSOL graph to model the experimental graph as closely as possible, with focus on ensuring both graphs used the same amount of time to cool to 0 °Celsius. Therefore, the values used in the heat fluxes as well as the thermal conductivity of the glass were adjusted until a comparable graph to the experiment was achieved.

DynoChem Modeling

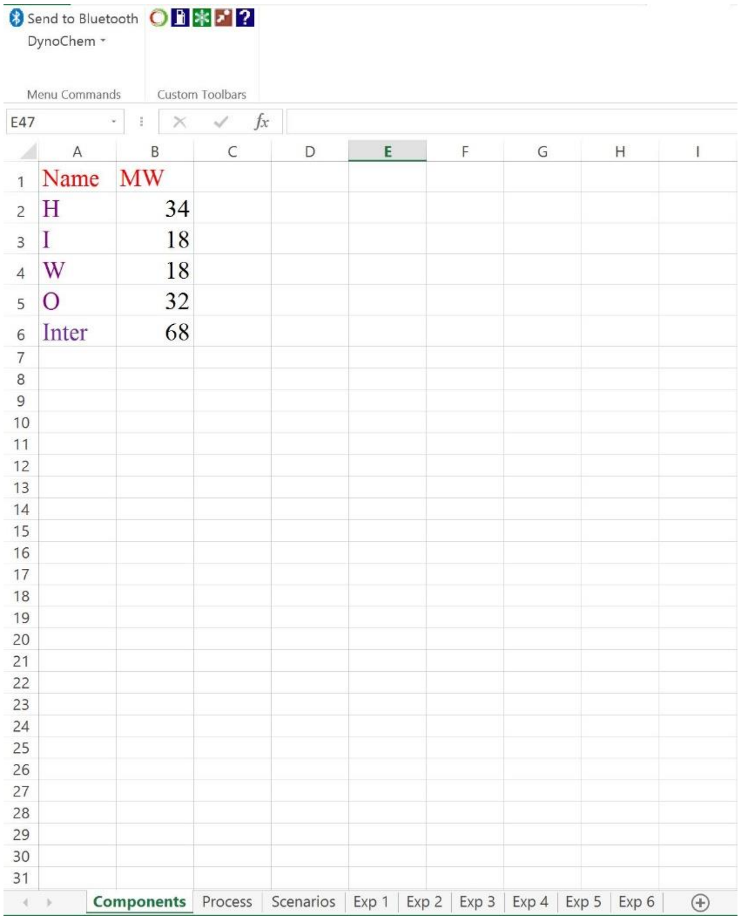
The hydrogen peroxide decomposition reaction was modeled in DynoChem for the Styrofoam cup calorimeter, 100 mL and 1,000 mL round bottom flasks. The reaction was also scaled up and modeled in 100 L, 1000 L, and 10,000 L reactors. DynoChem is an Excel based software program where inputs are read through Excel. For DynoChem to run, there must be a Components tab, a Process tab, a Scenarios tab, and a tab for each of the different experiments. More than one experiment can be inputted into Excel and run by DynoChem simultaneously.

DynoChem requires reactions to be broken down into their elementary steps if the reactants are not 1:1 in stoichiometric ratios. Due to this, the hydrogen peroxide reaction was broken down into the following two elementary steps:

$$(1) \qquad H_2O_2 + H_2O_2 \rightarrow Inter$$

$$(2) \qquad Inter + I^- \rightarrow 2H_2O + O_2 + I^-$$

To model the hydrogen peroxide reaction, the five components from the elementary steps were entered into the Components tab of Excel with their respective molecular weights. The molecular weight of iodide was taken to be the same as water as the concentration of potassium iodide used was dilute. The molecular weight of the intermediate component Inter was taken to be twice that of hydrogen peroxide. A screenshot of the Components tab is shown below as Figure 12.



Name	MW
H	34
I	18
W	18
O	32
Inter	68

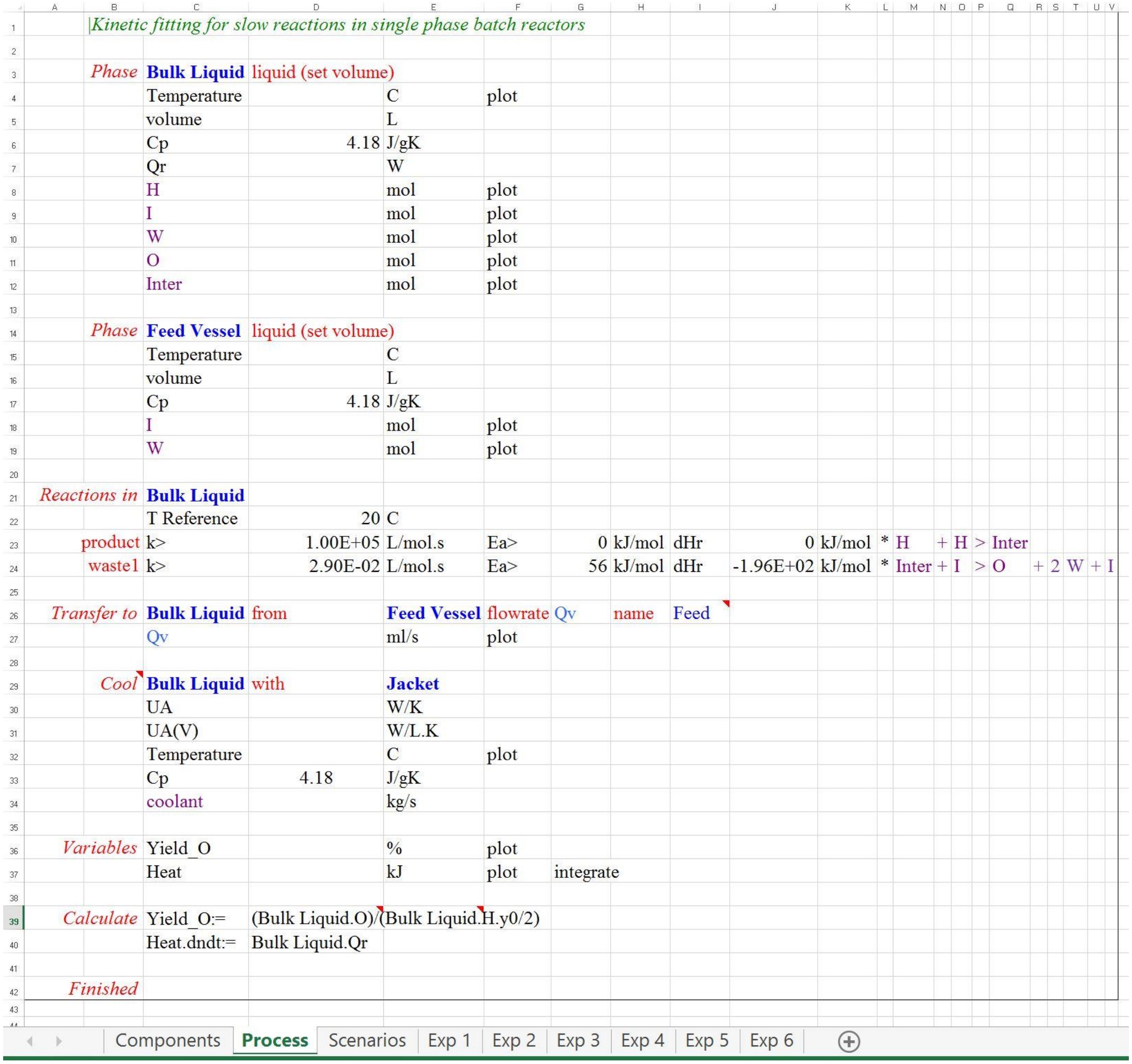
Figure 12: Components Tab of DynoChem

Next, information on the two phases (hydrogen peroxide and potassium iodide) such as temperature, volume, components, and heat capacity were added to the Process tab. The elementary reactions were also added to the Process tab as well as parameters listed in Table 1.

Table 1: Parameter Inputs for DynoChem

Parameter	Input Value
Activation Energy	56,000 J/mol
Heat of Reaction	-98,000 J/mol
Rate constant k @ 20 °C	0.029 L/mol*s

User-defined variables and equations to calculate the variables can be added to the Process tab as well as plot commands to tell DynoChem what to plot in the simulation. From Figure 13 of a screenshot of the Process tab, it can be observed that values are not entered for some parameters, components, and properties. Values for parameters, components, and properties can be entered into the Process tab but if these values change for the different experiments to be run in DynoChem then they can be entered in the Scenario tab instead.

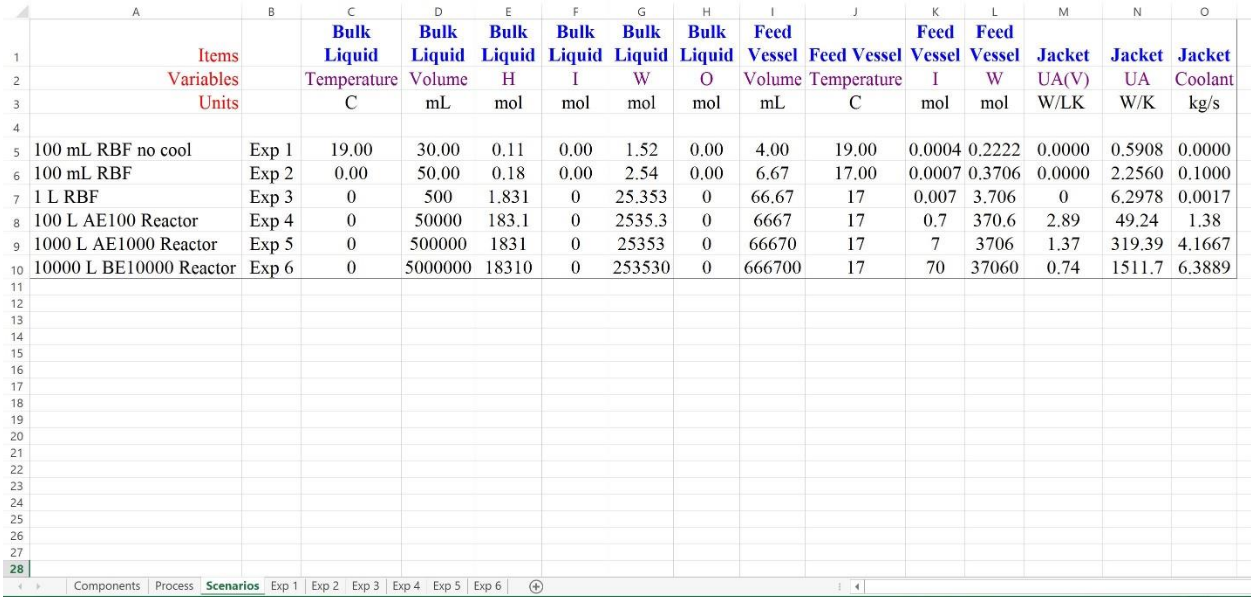


	A	B	C	D	E	F	G	H	I	J	K	L	M	N	O	P	Q	R	S	T	U	V
1		*Kinetic fitting for slow reactions in single phase batch reactors*																				
2																						
3		*Phase*	**Bulk Liquid**	liquid (set volume)																		
4			Temperature		C	plot																
5			volume		L																	
6			Cp	4.18	J/gK																	
7			Qr		W																	
8			H		mol	plot																
9			I		mol	plot																
10			W		mol	plot																
11			O		mol	plot																
12			Inter		mol	plot																
13																						
14		*Phase*	**Feed Vessel**	liquid (set volume)																		
15			Temperature		C																	
16			volume		L																	
17			Cp	4.18	J/gK																	
18			I		mol	plot																
19			W		mol	plot																
20																						
21		*Reactions in*	**Bulk Liquid**																			
22			T Reference	20	C																	
23		product	k>	1.00E+05	L/mol.s	Ea>	0	kJ/mol	dHr	0	kJ/mol	*	H	+	H	>	Inter					
24		waste1	k>	2.90E-02	L/mol.s	Ea>	56	kJ/mol	dHr	-1.96E+02	kJ/mol	*	Inter	+	I	>	O	+	2	W	+	I
25																						
26		*Transfer to*	**Bulk Liquid**	from	**Feed Vessel**	flowrate	Qv	name	Feed													
27			Qv		ml/s	plot																
28																						
29		*Cool*	**Bulk Liquid**	with	**Jacket**																	
30			UA		W/K																	
31			UA(V)		W/L.K																	
32			Temperature		C	plot																
33			Cp	4.18	J/gK																	
34			coolant		kg/s																	
35																						
36		*Variables*	Yield_O		%	plot																
37			Heat		kJ	plot	integrate															
38																						
39		*Calculate*	Yield_O:=	(Bulk Liquid.O)/(Bulk Liquid.H.y0/2)																		
40			Heat.dndt:=	Bulk Liquid.Qr																		
41																						
42		*Finished*																				
43																						

Figure 13: Process Tab of DynoChem

The Scenarios tab defines the different experiments to be simulated in DynoChem. Every row is defined as a separate experiment and a total of six experiments were added to the Scenarios tab. The six experiments included the Styrofoam cup calorimeter, 100 mL, 1000 mL, 100 L, 1000 L, and 10,000 L reactor sizes. The corresponding temperatures, volumes, components, and other properties were inputted for each of the experiments as seen in Figure 14. Experimentally calculated overall heat transfer coefficients for the Styrofoam cup calorimeter, 100 mL, and 1000 mL round bottom flasks were used in the model. Overall heat transfer coefficients for the 100 L, 1000 L, and 10,000 L reactors were predicted using the “Estimate_UA” DynoChem module available from their online resources. The coefficients were predicted using reactor types AE100, AE1000, and BE10000 which were built into DynoChem. Experimental temperature vs. time data for the Styrofoam cup calorimeter, 100 mL, and 1000 mL round bottom flasks were also entered into the

“Estimate_UA” module and a fitted UA was predicted by DynoChem. Fitted UA values were similar to values calculated experimentally from equations. Table 2 lists the overall heat transfer coefficients used for each of the experiments.



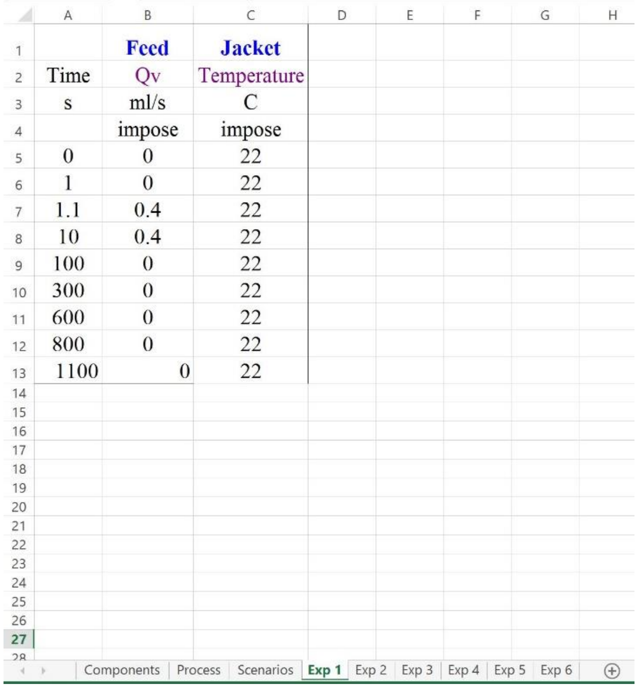
Items		Bulk Liquid	Bulk Liquid	Bulk Liquid	Bulk Liquid	Bulk Liquid	Bulk Liquid	Feed Vessel	Feed Vessel	Feed Vessel	Feed Vessel	Jacket	Jacket	Jacket
Variables		Temperature	Volume	H	I	W	O	Volume	Temperature	I	W	UA(V)	UA	Coolant
Units		C	mL	mol	mol	mol	mol	mL	C	mol	mol	W/LK	W/K	kg/s
100 mL RBF no cool	Exp 1	19.00	30.00	0.11	0.00	1.52	0.00	4.00	19.00	0.0004	0.2222	0.0000	0.5908	0.0000
100 mL RBF	Exp 2	0.00	50.00	0.18	0.00	2.54	0.00	6.67	17.00	0.0007	0.3706	0.0000	2.2560	0.1000
1 L RBF	Exp 3	0	500	1.831	0	25.353	0	66.67	17	0.007	3.706	0	6.2978	0.0017
100 L AE100 Reactor	Exp 4	0	50000	183.1	0	2535.3	0	6667	17	0.7	370.6	2.89	49.24	1.38
1000 L AE1000 Reactor	Exp 5	0	500000	1831	0	25353	0	66670	17	7	3706	1.37	319.39	4.1667
10000 L BE10000 Reactor	Exp 6	0	5000000	18310	0	253530	0	666700	17	70	37060	0.74	1511.7	6.3889

Figure 14: Scenarios Tab of DynoChem

Table 2: Heat Transfer Coefficients for DynoChem

Reactor Size	Reactor Type	UA(v) [W/K*L]	UA [W/K]
adiabatic - 34 mL	Styrofoam calorimeter	0	0.5908
100 mL	RBF	0	2.256
1 L	RBF	0	6.2978
100 L	AE100	2.89	49.24
1,000 L	AE1000	1.37	319.39
10,000 L	BE10000	0.74	1511.66

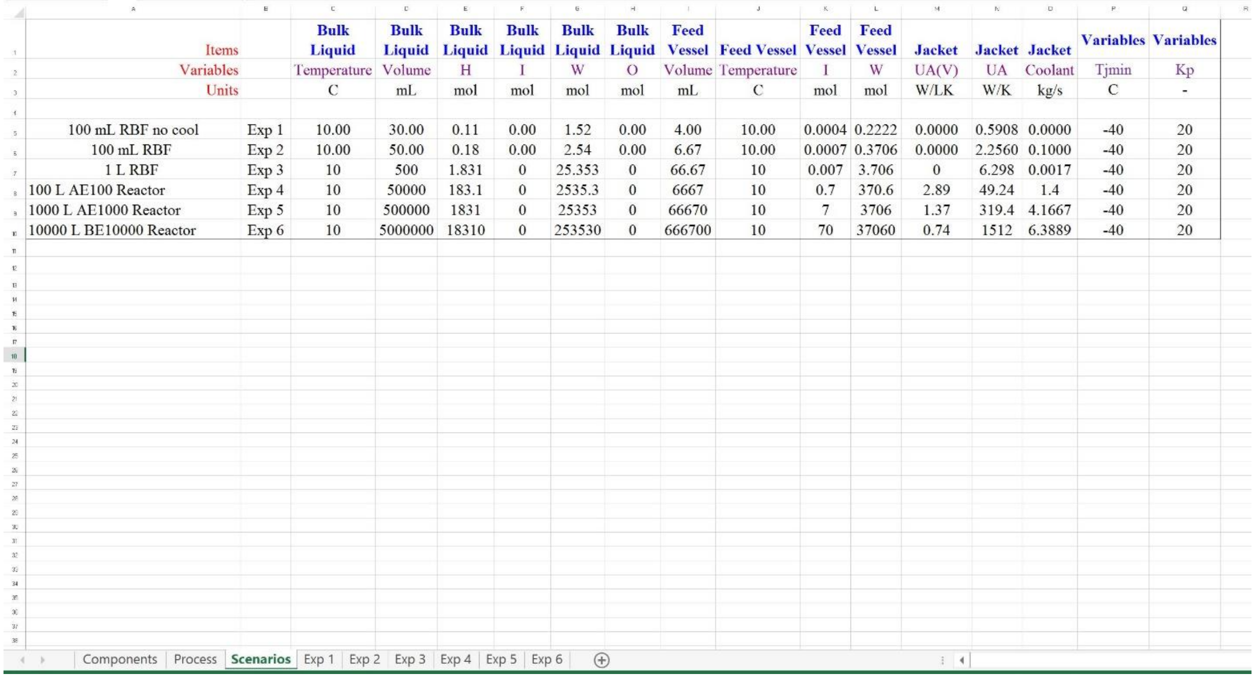
An additional tab for each of the six experiments were created after the Scenarios tab. In each of the individual experiments tab, the flowrate of the catalyst iodide and the time of the run was entered. An example of an individual experiment tab is provided below as Figure 15.



	Feed	Jacket
Time	Qv	Temperature
s	ml/s	C
	impose	impose
0	0	22
1	0	22
1.1	0.4	22
10	0.4	22
100	0	22
300	0	22
600	0	22
800	0	22
1100	0	22

Figure 15: Experiment Tab in DynoChem

The reactions were then run using DynoChem and graphs of the temperature over time were produced. The scenarios tab was also modified such that the reaction started at 10 °C with a variable jacket temperature to maintain the reactor at 10 °C as seen in Figure 16. A minimum jacket temperature of -40 °C was set and graphs of the reactor and jacket temperature over time were collected.



Items		Bulk Liquid	Bulk Liquid	Bulk Liquid	Bulk Liquid	Bulk Liquid	Bulk Liquid	Feed Vessel	Feed Vessel	Feed Vessel	Feed Vessel	Jacket	Jacket	Jacket	Variables	Variables
Variables		Temperature	Volume	H	I	W	O	Volume	Temperature	I	W	UA(V)	UA	Coolant	Tjmin	Kp
Units		C	mL	mol	mol	mol	mol	mL	C	mol	mol	W/LK	W/K	kg/s	C	-
100 mL RBF no cool	Exp 1	10.00	30.00	0.11	0.00	1.52	0.00	4.00	10.00	0.0004	0.2222	0.0000	0.5908	0.0000	-40	20
100 mL RBF	Exp 2	10.00	50.00	0.18	0.00	2.54	0.00	6.67	10.00	0.0007	0.3706	0.0000	2.2560	0.1000	-40	20
1 L RBF	Exp 3	10	500	1.831	0	25.353	0	66.67	10	0.007	3.706	0	6.298	0.0017	-40	20
100 L AE100 Reactor	Exp 4	10	50000	183.1	0	2535.3	0	6667	10	0.7	370.6	2.89	49.24	1.4	-40	20
1000 L AE1000 Reactor	Exp 5	10	500000	1831	0	25353	0	66670	10	7	3706	1.37	319.4	4.1667	-40	20
10000 L BE10000 Reactor	Exp 6	10	5000000	18310	0	253530	0	666700	10	70	37060	0.74	1512	6.3889	-40	20

Figure 16: Scenarios Tab of DynoChem for Controlling Reactor Temperature at 10 °C

Results and Discussion

Water Experiments: Calculated Values of the Overall Heat Transfer Coefficient

The following tables shows the values of overall heat transfer coefficients in round bottom flask sizes of 100 mL, 250 mL, 500 mL, and 1000 mL, as calculated through the water experiments.

Table 3: Experimental Heat Transfer Coefficients for 100 mL Round Bottom Flasks

100 mL Round Bottom Flask	
Trial	**U Value (W/m^2*K)**
1	363.19
2	354.11
3	345.03
Average:	**354.11**

Table 4: Experimental Heat Transfer Coefficients for 250 mL Round Bottom Flasks

250 mL Round Bottom Flask	
Trial	**U Value (W/m^2*K)**
1	272.63
2	266.83
3	272.63
Average:	**270.69**

Table 5: Experimental Heat Transfer Coefficients for 500 mL Round Bottom Flasks

500 mL Round Bottom Flask	
Trial	**U Value (W/m^2*K)**
1	237.00
2	244.17
3	244.17
Average:	**241.78**

Table 6: Experimental Heat Transfer Coefficients for 1000 mL Round Bottom Flasks

1000 mL Round Bottom Flask	
Trial	**U Value (W/m^2*K)**
1	230.10
2	230.10
3	230.10
Average:	**230.10**

The overall heat transfer coefficient values for larger flasks in sizes of 2 L, 5 L, 12 L and 22 L were extrapolated using the trends from experimental data:

Table 7: Extrapolated Heat Transfer Coefficients

Flask Size (L)	U Value (W/m^2*K)
2	192.80
5	162.14
12	137.42
22	122.54

The averages for each size flask produced the following overall trend of the overall heat transfer coefficient in relation to the size of the flask:

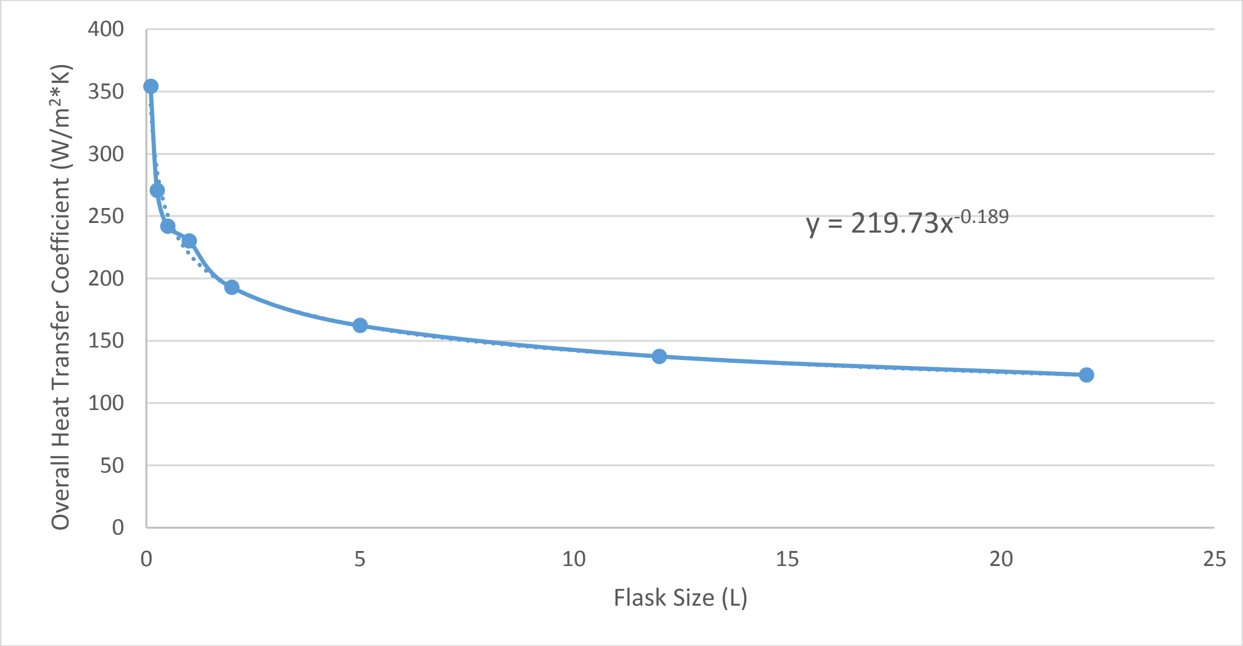


Figure 17: Overall Heat Transfer Coefficient Trend

The closest fitting trend equation is a power equation $y = 219.73x^{-0.189}$, which was used to predict heat transfer coefficients for larger flask sizes shown in the table and graph above.

For round bottom flasks alone, the heat transfer changed as the size of the flasks increased only slightly, for example, from 100 mL, to 250 mL or 1 L. This can be observed from the overall heat transfer coefficients calculated in the lab trials, where the hot water was added to the flasks at half-volume and cooled in an ice bath. The trials showed that with each flask of increasing size, this value decreases each time. This trend was also found to be non-linear in nature, which confirms the assumption that scale-up is not necessarily proportional. In additional to the increasing flask size, another explanation as to why the overall heat transfer coefficient decreases may be due to the stirring used in the experiments. The same stirring speed on the stir plate was used for each of the experiments which would cause worse mixing in the larger sized flasks. Mixing as discussed in the background influences the inside and outside heat transfer coefficient which would in turn affect the overall heat transfer coefficient. As mixing decreases, the inside and outside heat transfer coefficient decrease lowering the overall heat transfer coefficient.

Due to the heat transfer surface area-volume ratio's heavy influence on heat transfer scale up, the following graph was produced for comparison to the Flask Size vs Overall Heat Transfer Coefficient graph:

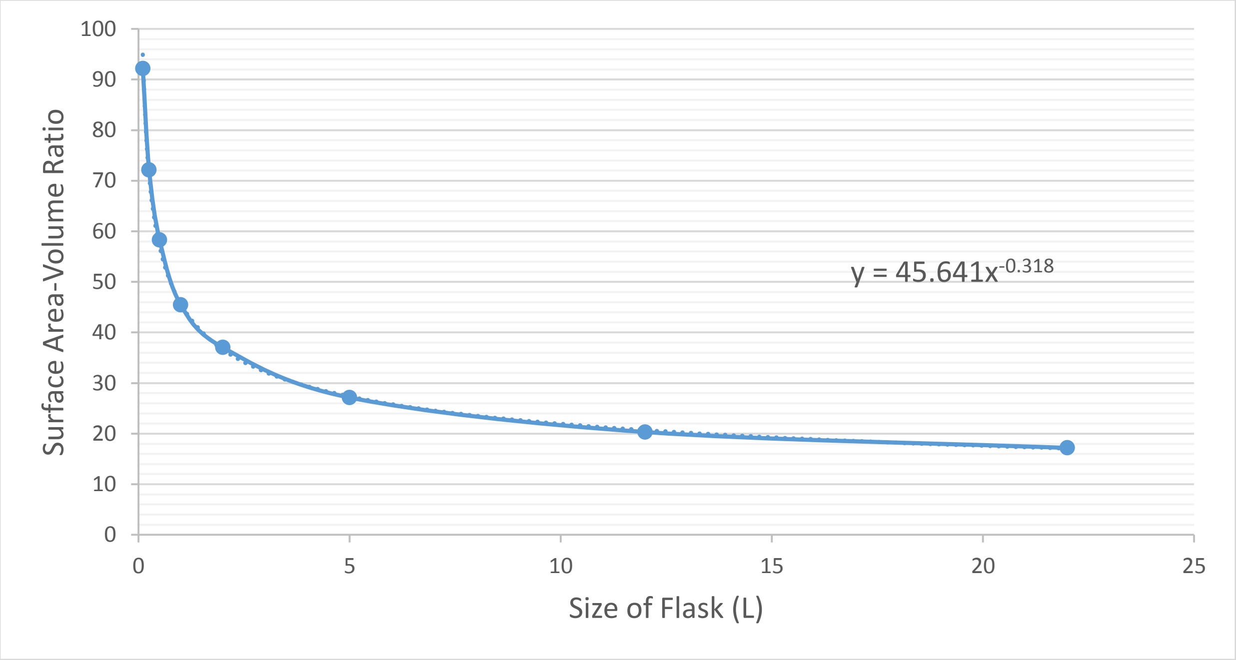


Figure 18: Flask Size vs. Surface Area-Volume Ratio

As seen above, the trends demonstrated in each of the two graphs are visually very similar. Both follow a power equation trend line, with a decrease in either the overall heat transfer coefficient, in case of the first relationship, or the surface to volume ratio with increasing flask volume. As has been noted from background research, heat transfer can be compared across vessels of similar geometry, but of different sizes. Experimental results demonstrate that under similar conditions, in vessels made of the same material, heat transfer becomes less efficient as the vessel size goes up, largely due to the decrease in the heat transfer surface area to volume ratio. However, factors such as proper stirrer scale-up may also influence the value of the heat transfer coefficient. Nonetheless, since a fair attempt to scale-up all variables with the capacity to influence heat transfer was taken, it is safe to conclude that at least some of the heat removal capability of the round bottom flask diminishes with increasing size.

In the water experiments, varying temperature drops among temperature probes at specific points in time were observed. The first vertical drop in Figures 19 – 22 below indicate the temperature drop from the middle of the flask to the inside wall of the flask. The second vertical drop is the temperature drop across the glass wall. The third vertical drop is from the outside flask wall to the ice bath close to the wall. The fourth vertical drop is across the rest of the ice bath. These graphs show how the inside and outside heat transfer coefficients and wall affect the overall heat transfer coefficient. This data could be used to find a correlation between the temperature drop and the stirring, and could possibly be used as another means in calculating heat transfer coefficients.

In the experiments, it was difficult to maintain consistent stirring inside the flask and inside the ice bath, which influenced the magnitude of the overall heat transfer coefficient for each run. For example, a large temperature drop from the inside of the flask to the wall could indicate insufficient stirring. As the flask size increased, the temperature drop increased. This makes sense because the same stir bar was used for three of the four flasks. Differences in stirring, stir bar size, stir plate, amount of ice, and other factors all contributed to differences in the overall heat transfer coefficient when the lab was repeated. Therefore, results from these experiments may not be repeatable due to all the possible variations in these factors.

The temperature probe numbers in the following graphs indicate the following: 0 is inside the flask, 1 is the inside wall, 2 is the outside wall, 3 is the ice bath near the flask wall, and 4 is the ice bath far from the flask wall. The numbers 1 through 5 of the temperature probes do not indicate distance from each other and the horizontal parts of the graph were drawn solely to aid in reading the graph.

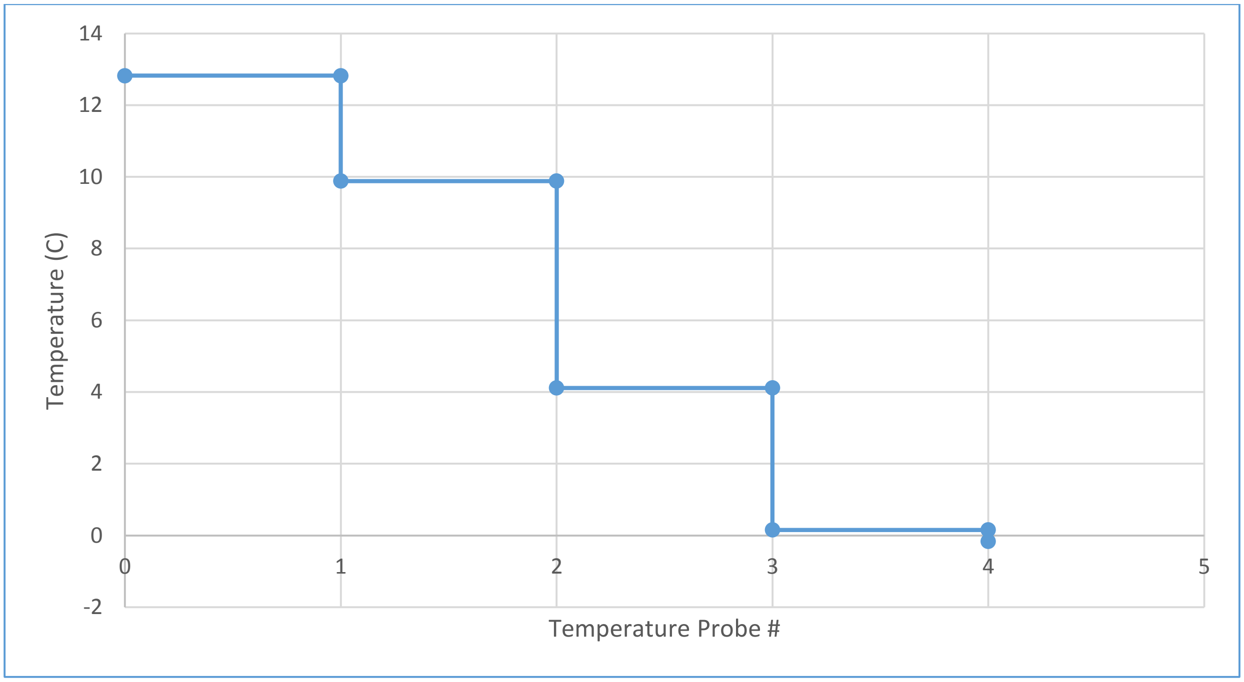


Figure 19: Differences in temperature at 50 seconds in a 100mL flask among the five temperature probes

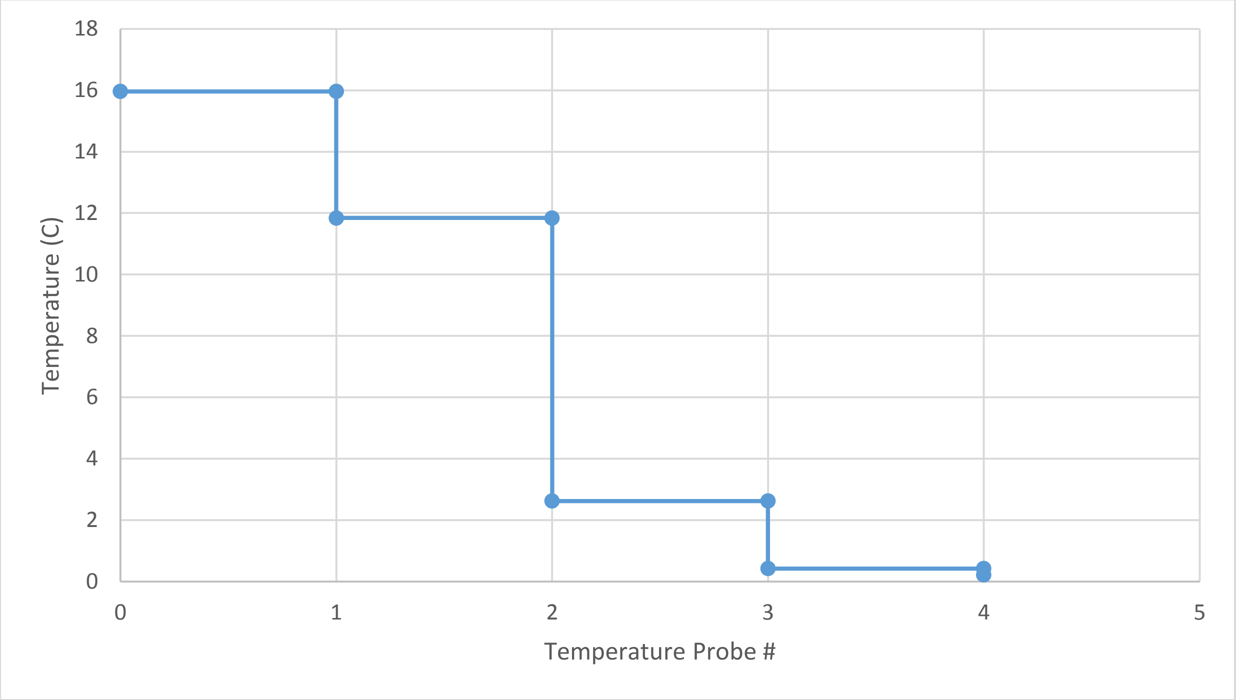


Figure 20: Differences in temperature at 50 seconds in a 250mL flask among the five temperature probes

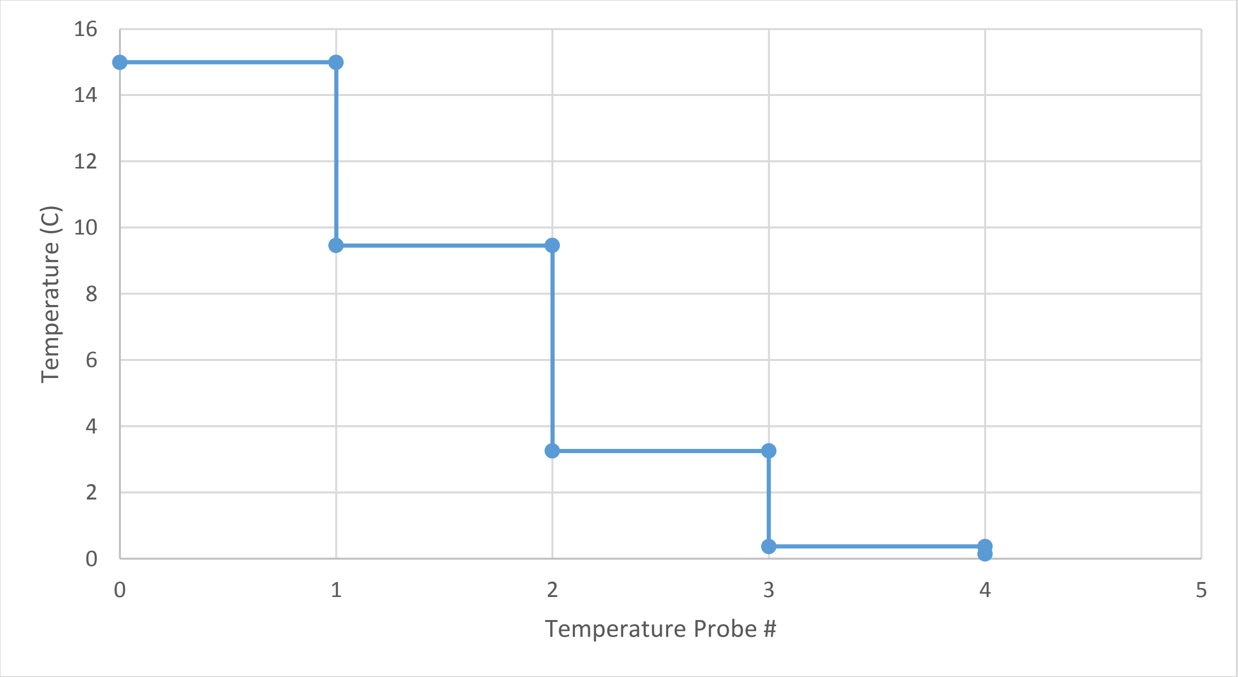


Figure 21: Differences in temperature at 50 seconds in a 500mL flask among the five temperature probes

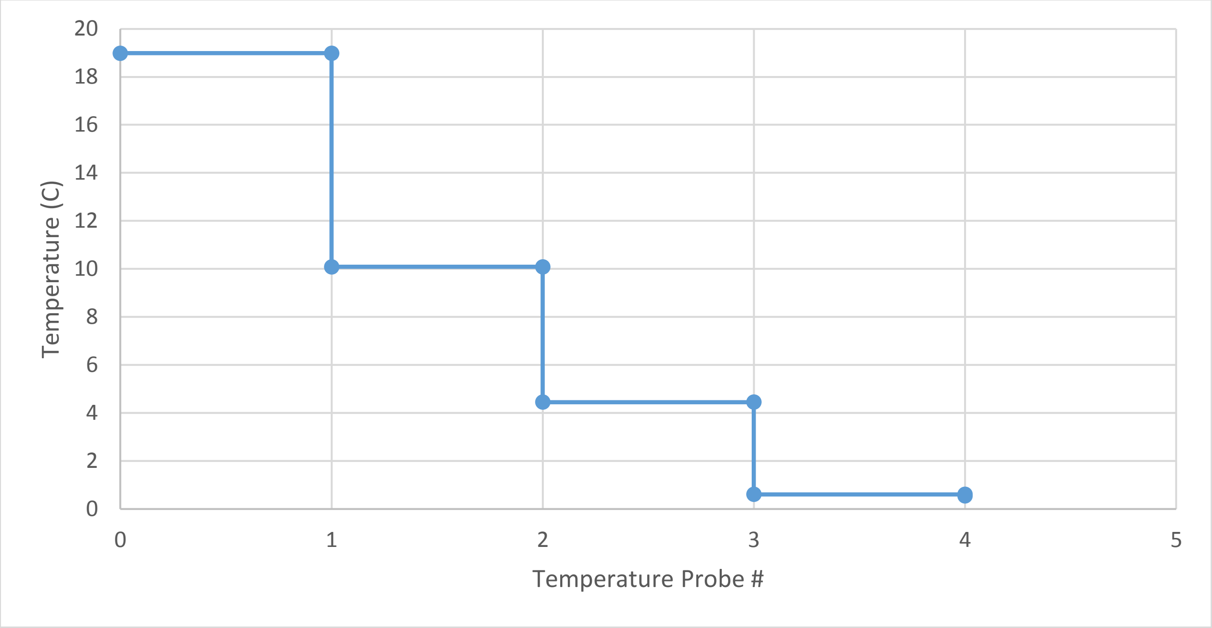


Figure 22: Differences in temperature at 50 seconds in a 1000mL flask among the five temperature probes

Hydrogen Peroxide Decomposition Reaction

The calorimeter experiment consisted of several types of trials. First, the reaction was run under near adiabatic conditions, to demonstrate how much heat it releases under non-cooling conditions. Next, the same reaction was scaled-up to appropriate proportions in 100 and 1,000 mL flasks to investigate the heat transfer differences in differently-sized vessels. The results of these studies carried out in an ice bath are summarized below.

Calculations of Calorimeter Heat Transfer Coefficient

The temperature profile of the mixture post hydrogen peroxide decomposition reaction is shown in Figure 23:

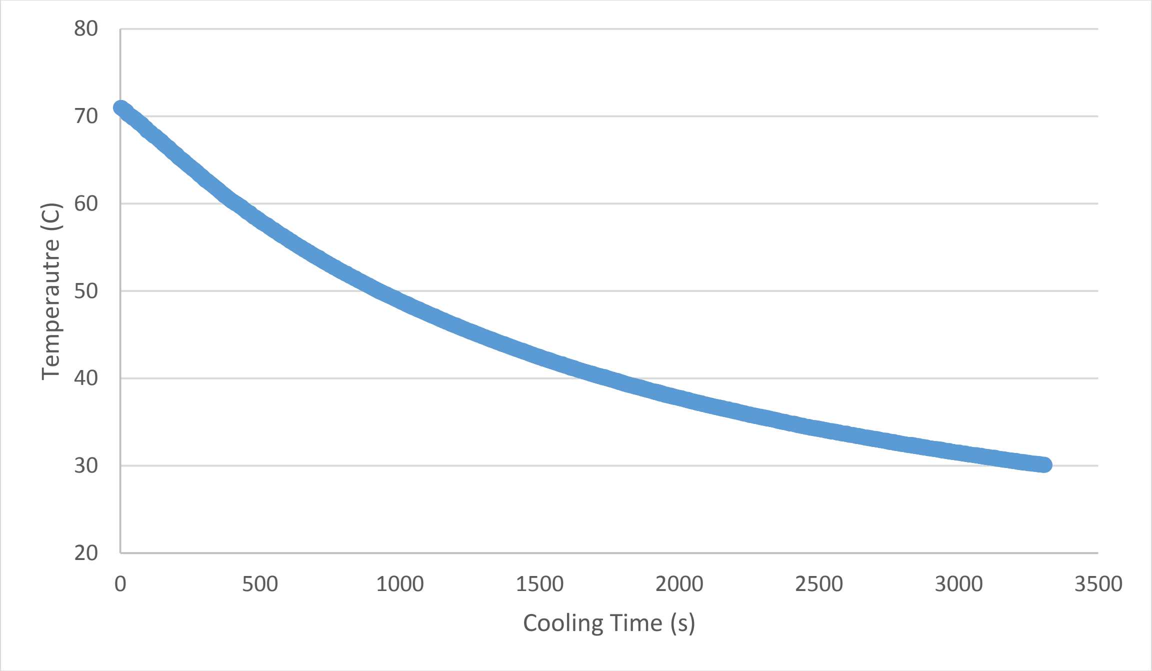


Figure 23: H_2O_2 Reaction Temperature vs. Time Cooling Profile

The data from the experiment was used to evaluate the heat transfer coefficient of the calorimeter made from two 8 ounce Styrofoam cups. The graph used for these calculations is presented below:

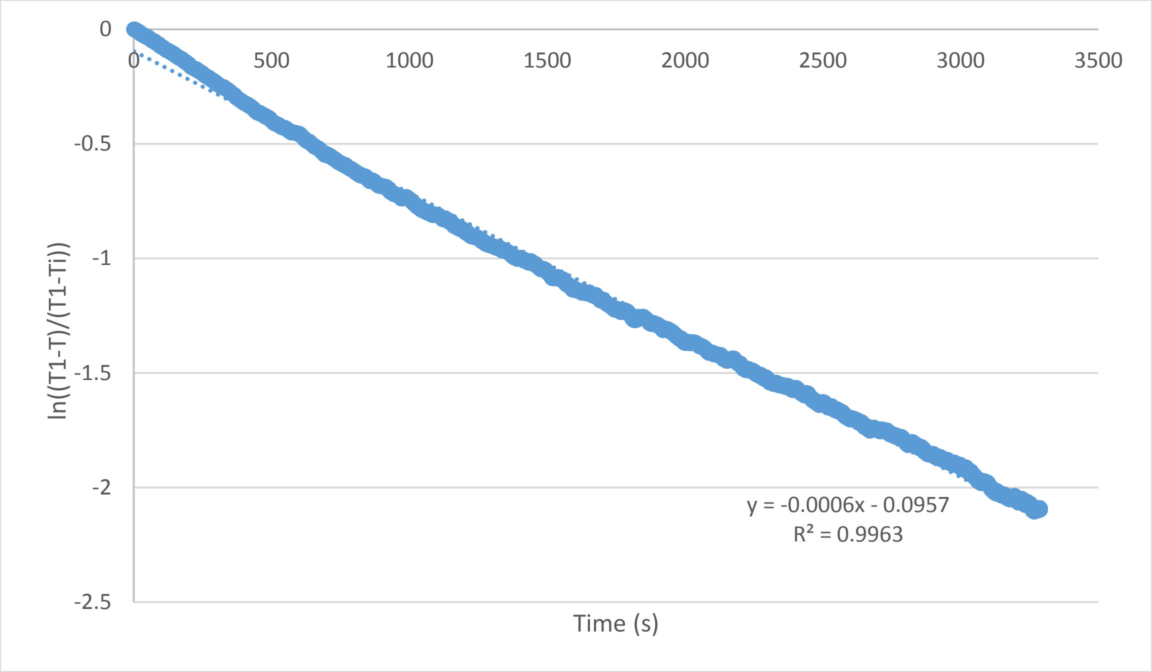


Figure 24: Calculation of Calorimeter Heat Transfer Coefficient

Based on the slope of the graph above, the overall heat transfer coefficient of the calorimeter was calculated to be 32 W/m^2*K. This value confirms the assumption that the Styrofoam cups used for the experiment are much poorer conductors of heat than the round bottom flasks used throughout the project. It was also suitable to imitate nearly adiabatic conditions for this experiment; however, it also demonstrates that the calorimeter allowed a notable amount of heat to escape during the experiment.

Next, the 100 mL flask experiment in an ice bath involved adding 6.6 mL of KI to 50 mL of 12% hydrogen peroxide solution. The temperature profile at a point inside the reactor as a function of time was as follows:

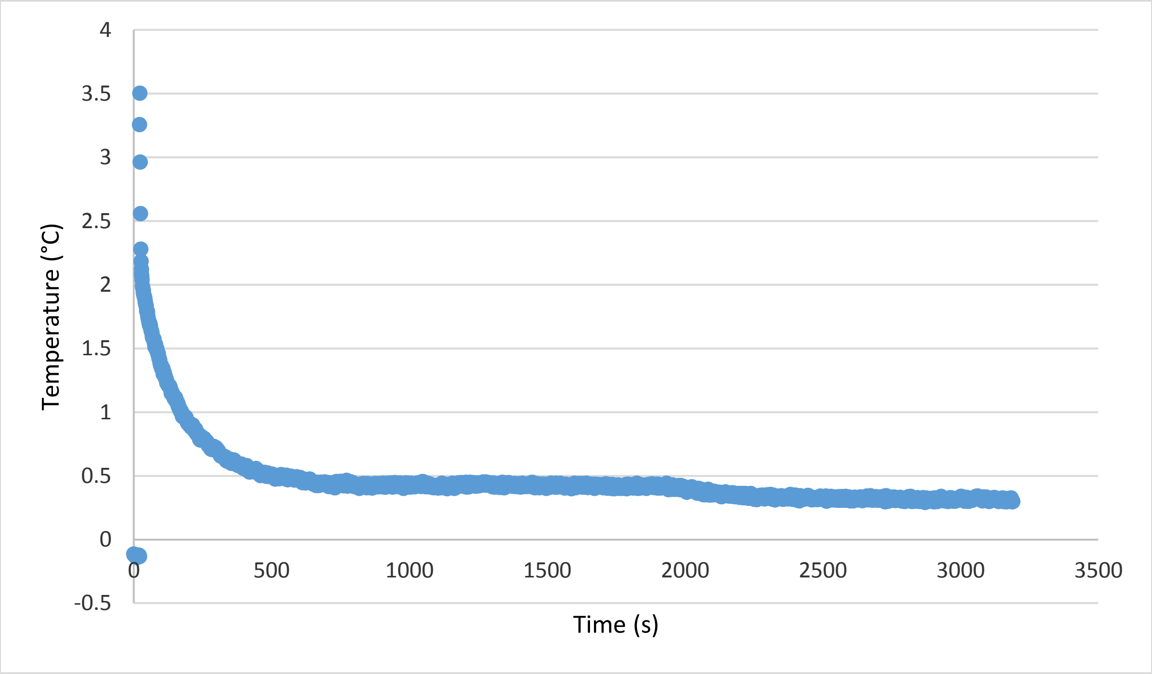


Figure 25: Temperature vs. Time Profile of H2O2 Reaction in 100 mL Round Bottom Flask

A similar trial was performed in a 1,000 mL flask as well. This time, the temperature profile had a different appearance, seen below:

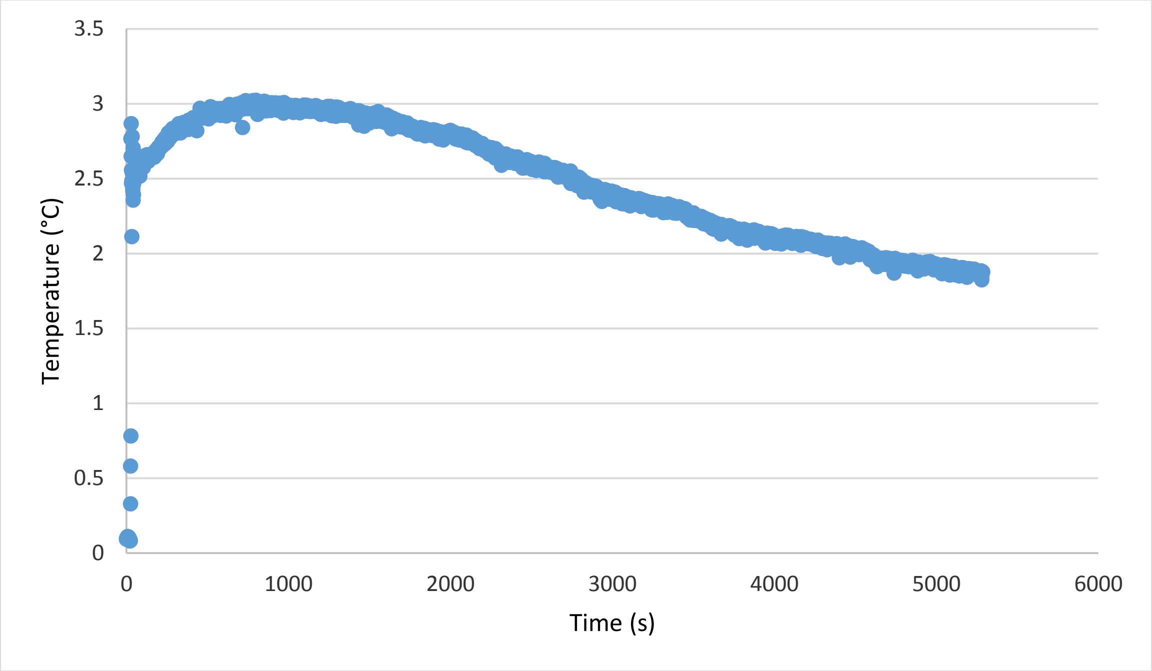


Figure 26: Temperature vs. Time Profile of H2O2 Reaction in 1000 mL Round Bottom Flask

As can be gathered from the trials shown above, the heat transfer effects between the two sized flasks differed to a small degree. In the initial 100 mL trial, the heat removal rate was rapid enough to remove all the heat generated by the reaction as it occurred over time. Therefore, after the initial spike in the profile when room-temperature KI was added to 0 °C hydrogen peroxide solution in the flask, the temperature steadily decreased for the remainder of the experiment. However, when the reaction was scaled-up to a 1,000 mL flask, the temperature profile had a visible increase in temperature post-mixing as well. This can be attributed to the rate of heat removal lagging behind the rate of heat production as the hydrogen peroxide decomposed under identical conditions as before, but with less surface area per unit volume available for heat transfer. It is expected that with increasing vessel size, such as the 2, 5, 12, and 22 L round bottom flasks whose overall heat transfer coefficients were extrapolated earlier, the heat transfer behavior observed in the 1 L flask would only be more pronounced.

Since pilot or industrial scale reactors cannot be directly compared to lab-size vessels due to various factors such as materials of construction and vessel geometry, the larger scale heat transfer was gauged using DynoChem.

Computer Modeling

COMSOL

Both the experimental and the COMSOL graphs for each size round bottom flask took the same amount of time to cool to 0 °C, because COMSOL was manipulated to do so. However, the temperature vs time curves of the COMSOL and the experimental graphs are noticeably different. In the COMSOL model, the water cooled very quickly at the beginning, then slowly cooled the rest of the way to 0 °C. In the lab experiment, the cooling was more linear. This variation could have been caused by several factors. It is important to remember that COMSOL is a model and that many assumptions were made while using this simulation. For example, many factors were assumed in making the model; the glass thickness was assumed to be uniform and the ice bath temperature was assumed to be constant and infinitely large. Also, glass properties were not only assumed, but the thermoconductivity was manipulated to aid in the cooling process, inducing a mixing effect. There was no mixing in the COMSOL model due to time restraints and no access to a COMSOL based model that has a stirring option. Therefore, to induce stirring, different variables were manipulated such as heat transfer coefficients, in order to mimic the heat transfer that was seen in the lab setting. All of these factors could have contributed to the differences seen between the curves of the temperature vs time plots for each size of round bottom flask.

Assumptions were also made on the neck of the flask. The round bottom flasks that were used in the lab either had two or three necks depending on the size. These types of flasks were used because it allowed hot water to be easily added into one neck, while a temperature probe was in the other. However, the COMSOL model used cannot model flasks with more than one neck because the model is built on an axis. Therefore, it was assumed that there was no difference in heat loss when comparing one, two, and three necks on a flask. This could have added to the error seen in COMSOL because it was assumed that heat transfer only occurred in 50% of the flask and that no heat was lost to the surrounding air, which is not true. These assumptions were made because this was a simplification of a model and assumptions were necessary to not over complicate it for the project's purposes. Also, the neck of the flasks were not considered an important feature to this project so time was not taken to perfect the dimensions, alignment, or scale-up of the neck on each flask in the COMSOL model. More attention was put into the rounded portion of the glass since there was technically no heat transfer outside of the rounded part of the flask in the model.

Another assumption that was made in the COMSOL modeling was the time it took for the laboratory experiment to cool to zero for each of the different flask sizes. The temperature sensors used in the lab were not accurate in that the temperature being read had an error of plus or minus a few tenths of a degree. Therefore, it was difficult to determine the exact time that the water reached a "true" 0 °C. For the sake of this project, it was assumed that the time it took for the water to cool to zero, was the time from the highest temperature read on the wall to the time where the inside wall first read a negative temperature reading. This time period was then used to model the different sized reactors in COMSOL.

A model of the 250, 500, and 1,000 mL flasks were also created in COMSOL in addition to the 100 mL flask. These models show that scale-up is not necessarily a linear process on all fronts. When the same heat flux inputs were made as the 100 mL flask, water in increasing flask sizes cooled faster. Therefore, adjustments were necessary to scale down the heat flux inputs so that the water would cool in the desired amount of time.

Therefore, the purpose of modeling in COMSOL was to show that an experiment in the lab can be modeled on the computer. However, COMSOL is not the best tool to make predictions during scale-up. Results for the 100, 250, 500, and 1,000 mL flasks can be viewed below.

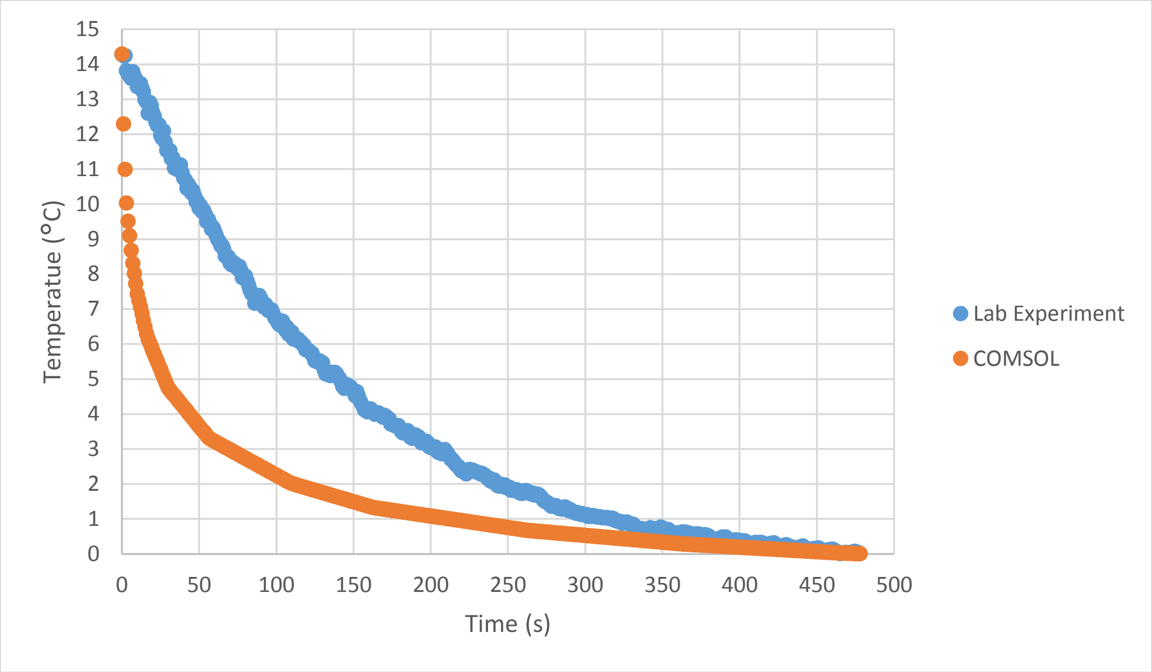


Figure 27: Comparison of Temperature vs. Time Profiles Between Experimental and COMSOL Model for 100 mL Round Bottom Flask

Table 8: Comparison of Initial Temperature and Time to Completion between Experiment and COMSOL for 100 mL RBF

	Lab Experiment	COMSOL
Initial Temperature (°C)	14.28	14.3
Time Until 0 °C (s)	479	479

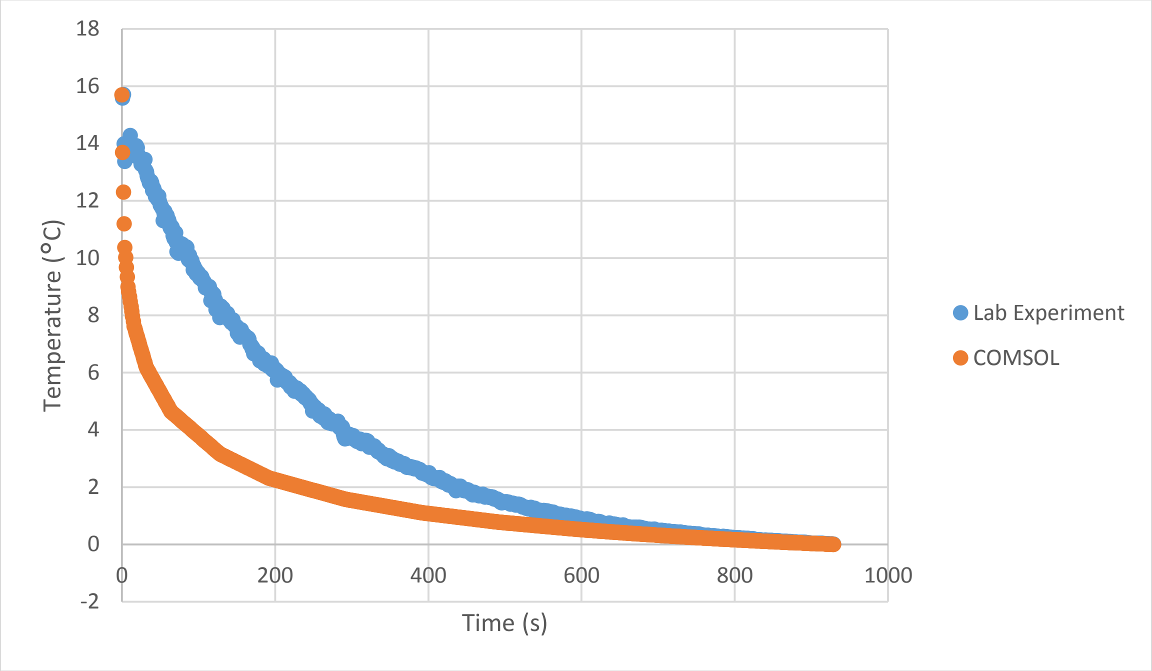


Figure 28: Comparison of Temperature vs. Time Profiles Between Experimental and COMSOL Model for 250 mL Round Bottom Flask

Table 9: Comparison of Initial Temperature and Time to Completion between Experiment and COMSOL for 250 mL RBF

	Lab Experiment	COMSOL
Initial Temperature (°C)	15.71	15.7
Time Until 0 °C (s)	929	929

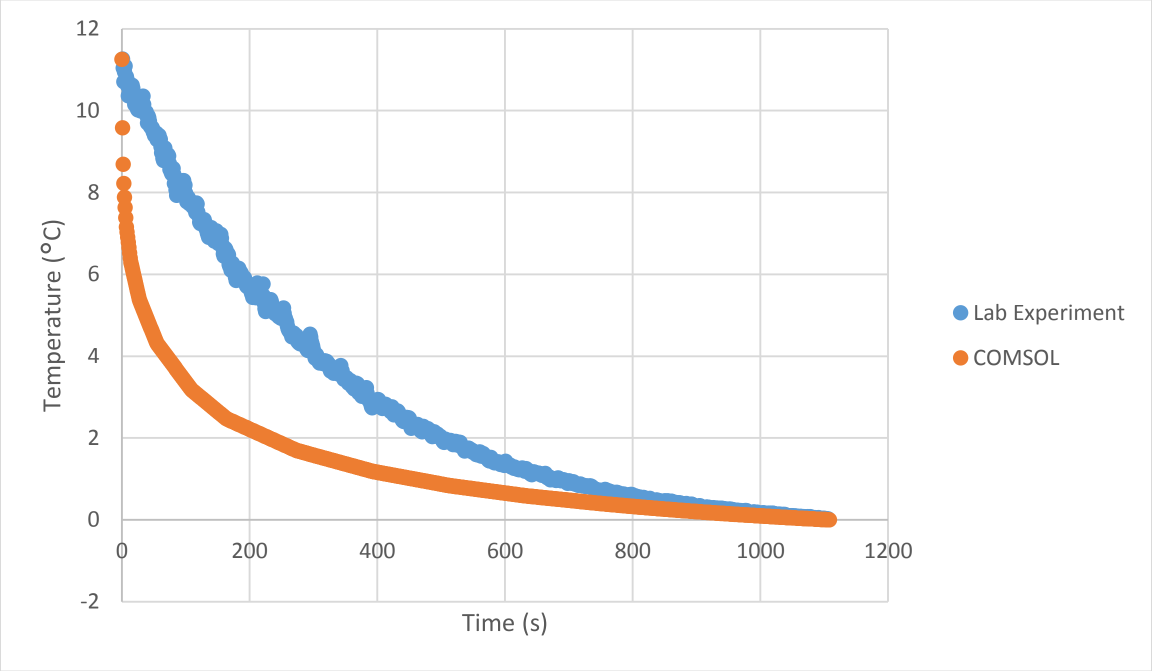


Figure 29: Comparison of Temperature vs. Time Profiles Between Experimental and COMSOL Model for 500 mL Round Bottom Flask

Table 10: Comparison of Initial Temperature and Time to Completion between Experiment and COMSOL for 500 mL RBF

	Lab Experiment	COMSOL
Initial Temperature (°C)	11.26	11.26
Time Until 0 °C (s)	1108	1108

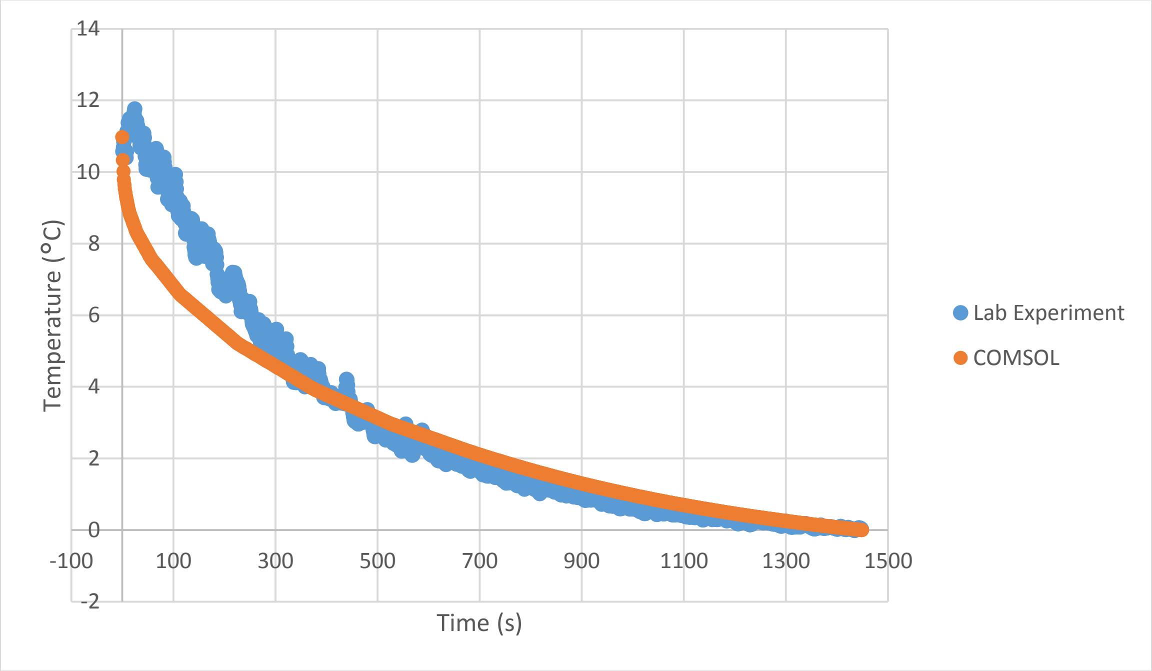


Figure 30: Comparison of Temperature vs. Time Profiles Between Experimental and COMSOL Model for 1000 mL Round Bottom Flask

Table 11: Comparison of Initial Temperature and Time to Completion between Experiment and COMSOL for 1000 mL RBF

	Lab Experiment	COMSOL
Initial Temperature (°C)	10.98	10.98
Time Until 0 °C (s)	1446	1449

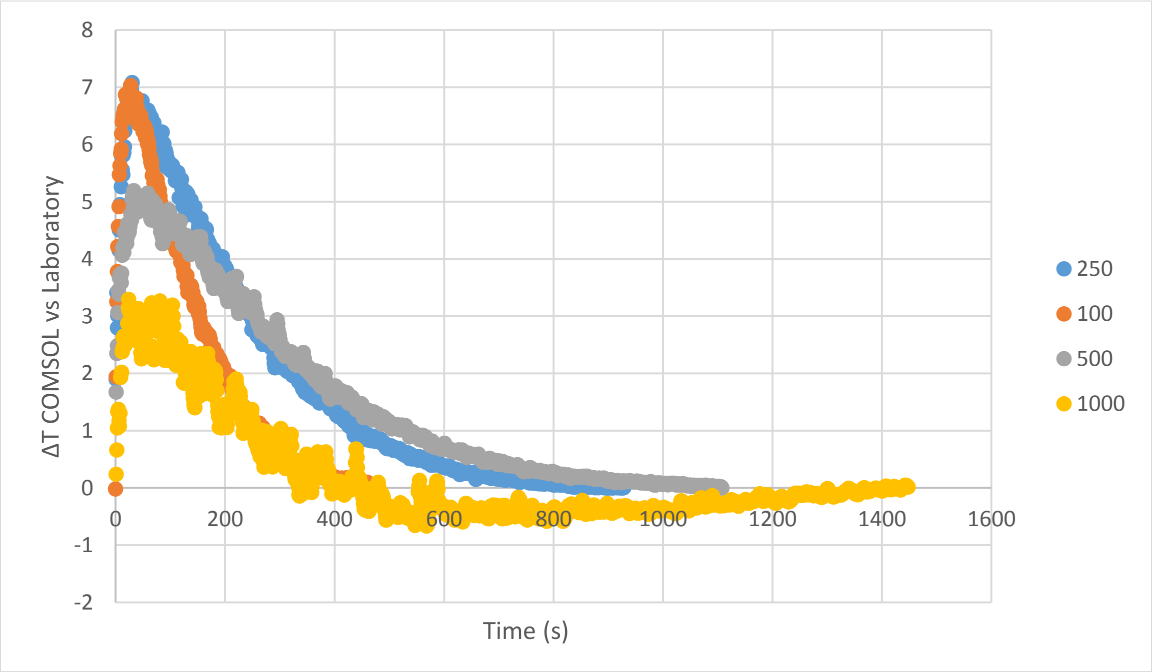


Figure 31: Difference in Temperature between COMSOL model and Experimental Data over time for all Flask Sizes

It is interesting to note, that with an increase in flask size, there was a noticeable drop in variation between the temperature vs. time curves when comparing the experimental curve to COMSOL. The graph above shows this drop, which is significant when comparing the 100 mL to the 1,000 mL plot. This suggests that with increasing flask size, the more accurate COMSOL was at mimicking the laboratory experiment. This trend may have been influenced by the fact that the stir bar size was not scaled up with increasing flask size during the laboratory experiments. This suggests that as the flask size increased, the stirring inside the flask was not as efficient. This caused the laboratory data to mimic COMSOL results closer, due to the insufficient stirring simulated in COMSOL. Therefore, this could explain why for the 1,000 mL flask, the COMSOL and laboratory plots of temperature vs time intersected, while the other flask sizes did not.

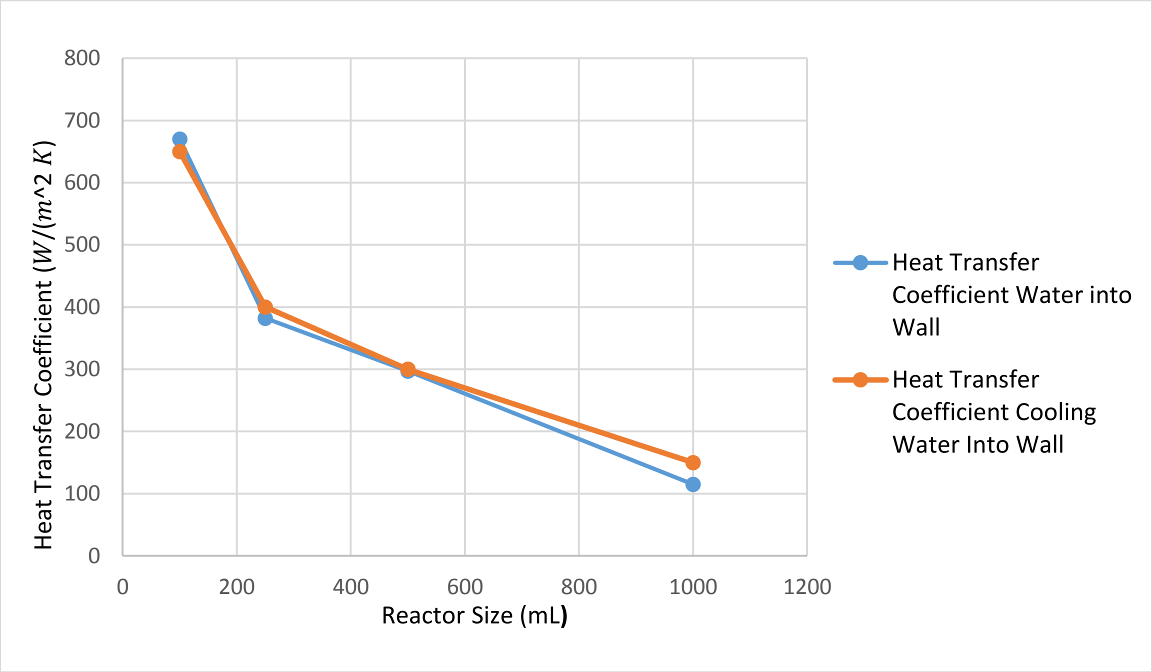


Figure 32: Heat Transfer Coefficient vs. Reactor Size Trend Based on COMSOL Model

The heat transfer coefficients used in COMSOL were graphed to compare how they changed with increasing flask size. The heat transfer coefficients of the water going into the wall and the cooling water going into the wall were examined. The heat transfer coefficient of the wall into the water was not examined because it was not changed with increasing flask size. As seen in the graph, there is a trend where both heat transfer coefficients decreased with increasing flask size. This graph could be used to extrapolate data for larger flask sizes.

DynoChem

To verify that DynoChem is a reliable computer modeling tool, hydrogen peroxide decomposition reactions identical to the experiments conducted in the lab were modeled using this software. Comparisons between experimental temperature vs time profiles and DynoChem results were completed. The following graphs show the experimental and DynoChem temperature vs time profiles for the calorimeter, the 100 mL, and the 1,000 mL round bottom flask experiments.

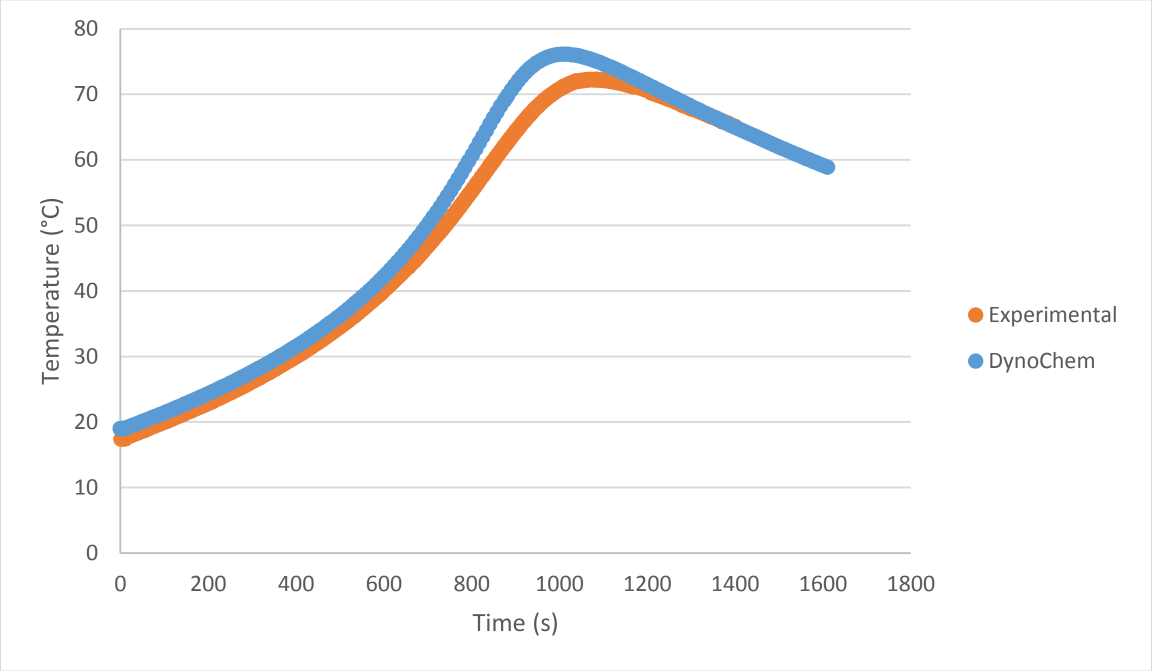


Figure 33: Temperature vs. Time Profiles for Styrofoam Cup Calorimeter

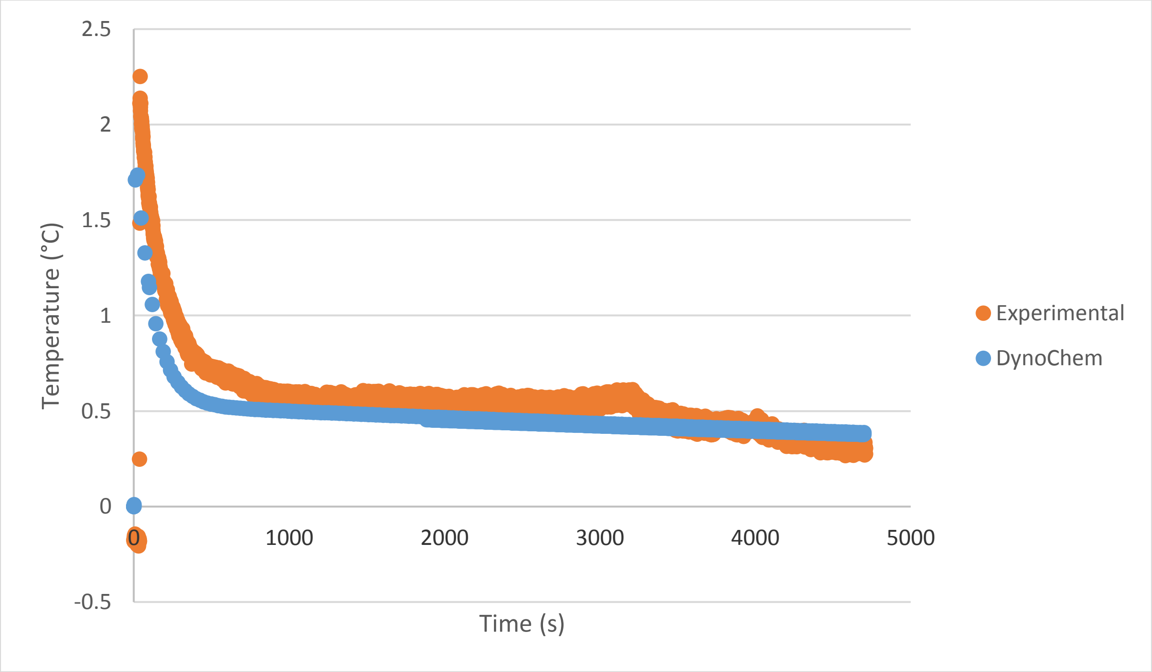


Figure 34: Temperature vs. Time Profiles for 100 mL Round Bottom Flask Trial 1

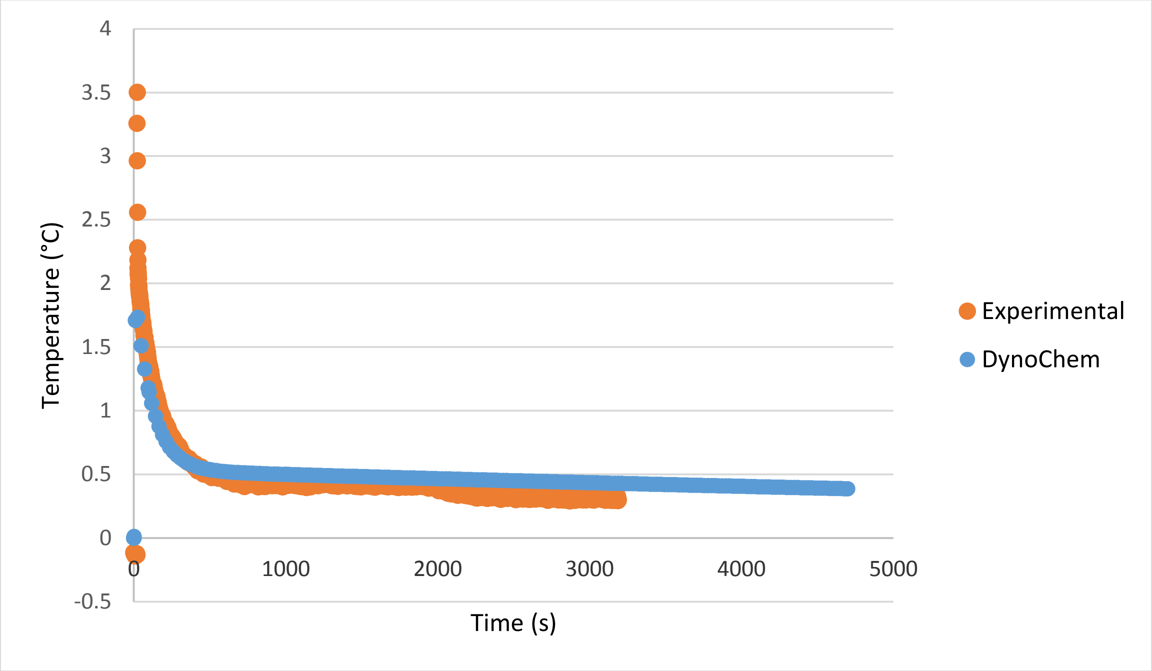


Figure 35: Temperature vs. Time Profiles for 100 mL Round Bottom Flask Trial 2

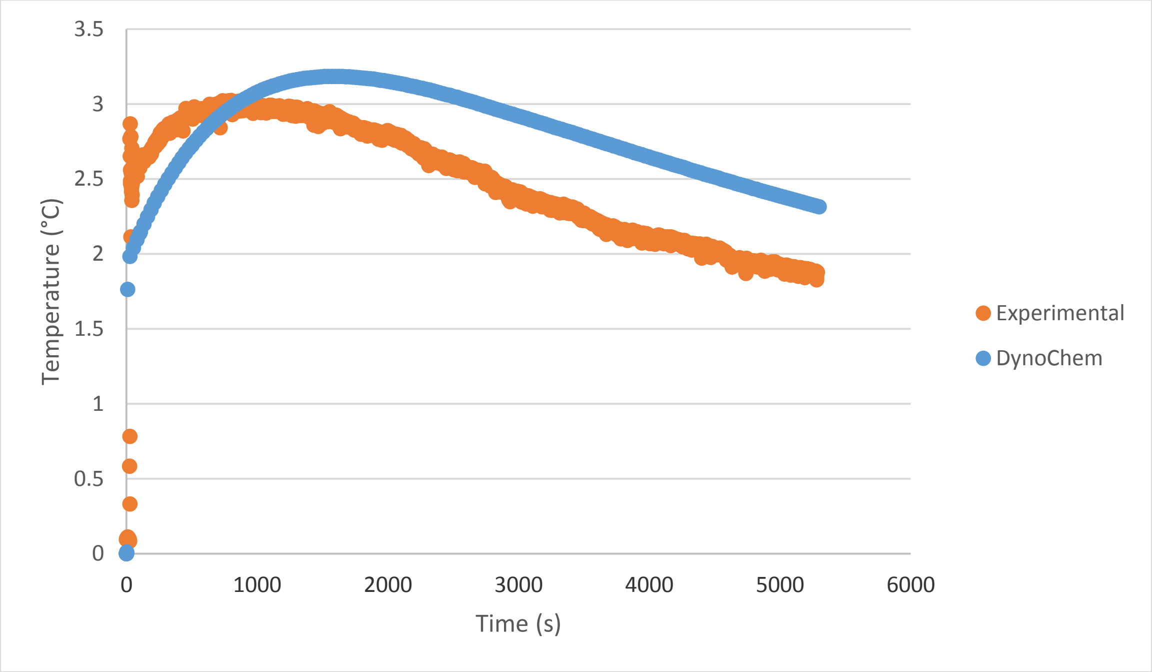


Figure 36: Temperature vs. Time Profiles for 1000 mL Round Bottom Flask

DynoChem predictions of reaction temperature over time was similar to experimental results. Deviations between experimental results and DynoChem predictions could be due to estimated rate constants. The rate constant of the first elementary reaction step was set to an arbitrarily chosen high number such that the reaction step would proceed quickly. Due to the rate constant, the rate of heat production predicted could be different from the experimental rate of heat production. Another difference between experiments and DynoChem simulations is the fact that DynoChem utilizes a cooling jacket while the round bottom flasks utilized an ice bath for cooling. Cooling jacket flowrates were estimated and iterated such that the max temperature of the reactor would match experimental results. DynoChem results for the calorimeter temperature profile yielded similar results to experimental data and can be expected as no cooling was used and hence there was no need to estimate a cooling jacket flowrate. Overall, DynoChem predictions were similar to data collected in the lab.

DynoChem predictions for the hydrogen peroxide decomposition in large scale reactors 100 L, 1000 L, and 10,000 L were also simulated since it was not feasible to conduct these experiments in the lab. A table of the max temperature of the decomposition reaction is shown below. Plots of the temperature vs. time profile for the 100 L, 1000 L, and 10,000 L reactors from DynoChem are provided in the Appendix.

Table 12: Max Temperature of Reaction Predicted by DynoChem

Reactor Size	Reactor Type	Max Temperature (°C)
adiabatic - 34 mL total	Styrofoam calorimeter	76.126
100 mL	RBF	1.735
1 L	RBF	3.183
100 L	AE100	7.961
1,000 L	AE1000	25.154
10,000 L	BE10000	55.739

As can be observed from the table above, the max temperature of the reactor increases with increasing reactor size. These results demonstrate the effect of decreasing surface area to volume ratio as reactor size increases. With a lower surface area to volume ratio, cooling becomes less efficient in removing the heat produced from the exothermic reaction. Heat that is not removed by cooling increases the reactor temperature and can increase the reaction rate leading to more heat production. In the 1 L round bottom flask, the ice bath was able to remove a sufficient amount of heat produced from the reaction so that the temperature increase was only 3 °C which turned out to be harmless. In the 10,000 L reactor, the cooling jacket was unable to maintain a heat removal rate equal to the rate of heat production resulting in the temperature increase to approximately 56 °C.

In addition to modeling the hydrogen peroxide decomposition reactions performed in the lab, additional studies of the reaction starting at 10 °C and controlling the jacket temperature to maintain the reactor at 10 °C were simulated. The maximum reactor temperature and lowest jacket temperature required to control the reactor temperature at 10 °C are shown below. Plots of the reactor temperature and jacket temperature over time for each of the reactors are provided in the Appendix.

Table 13: Max Reactor Temperature and Jacket Temperature to Control Reactor Temperature at 10 C

Reactor Size	Reactor Type	Max Reactor Temperature (°C)	Jacket Temperature (°C)
100 mL	RBF	10.295	4.101
1 L	RBF	11.82	-26.394
100 L	AE100	40.145	-40
1,000 L	AE1000	69.994	-40
10,000 L	BE10000	76.397	-40

Starting the decomposition reaction at 10 °C, it is relatively easy to maintain the reactor temperature at 10 °C for a 100 mL round bottom flask. A jacket temperature of 4 °C is also very achievable. DynoChem predicts that for a 1 L round bottom flask, a jacket temperature of -26 °C would be required to maintain the reactor temperature around 10 °C. This temperature is significantly colder and suggests that the starting temperature has a large effect on the rate of heat production. For the 100 L, 1000 L, and 10,000 L reactors, the jacket temperature reaches its set minimum temperature of -40 °C and the temperature increase in the reactors are significant. In the 10,000 L reactor, the temperature increases by 66 °C from its initial starting temperature of 10 °C. This further demonstrates that the rate of heat removal is not proportional in scale-ups and if not realized could lead to potentially harmful runaway reactions among other consequences.

Conclusions and Recommendations

After comprehensive research, testing, and computer modeling, it was confirmed that a direct scale-up from a round bottom flask to pilot plant equipment is not feasible, but involves multiple important scale-up steps and studies that can help make the process most efficient and safe. It was determined that in round bottom flasks of similar geometry, the overall heat transfer coefficient trend slowly declines with increasing size. This relationship was attributed to a similar trend in the heat transfer surface area to volume ratio of the same vessels. If the temperature of the cooling liquid is fixed, as it was in the experiments, this means that while the volume of hot water added is increased each time, the heat cannot escape the flask at a rate comparable to a smaller flask of similar geometry. In the case of a chemical reaction taking place in the same round bottom flasks, such as the hydrogen peroxide decomposition reactions tested following the water experiments, increased flask size implied larger amounts of reactants, with more heat released per every additional mole of substance added. The heat production became greater and faster in every round bottom flask of increasing size, while the rate of heat removal did not increase proportionally due to surface area depending on the radius squared while the volume depended on the radius cubed. In a 100 mL flask, the ice bath was able to remove the heat fast enough, as reflected by the temperature profile of the hydrogen peroxide as it reacted. However, the 1,000 mL flask temperature profile increased slightly for a short time period after the addition of the catalyst, when the heat production was at its peak, and the ice bath was unable to remove the heat fast enough. Apart from the obvious increase in heat production when the amounts of hot water or reactants were increased, factors such as the rate of reactant addition or stirring also affected the rate of reaction, which created more heat faster.

When it came down to computer modeling, COMSOL was a great tool for simulating a process, but it was not well suited for the purposes of this project. Making these models required a significant amount of time, since it is not possible to simply scale up a reactor in COMSOL; a completely new file and geometry had to be made to look into a new flask size. A person wanting to model a round bottom flask successfully needs extensive background training in COMSOL. For a more accurate result, a more updated version of COMSOL should be used, particularly a physics where stirring is an option. These COMSOL models are not suited for accurate scale up in a lab and can only prove that it is a useful simulation tool.

DynoChem results were comparable to experimental data for the Styrofoam cup calorimeter, 100 mL and 1,000 mL round bottom flasks helping to confirm the capabilities of DynoChem in modeling the hydrogen peroxide decomposition reaction. DynoChem scale-ups of the decomposition reaction further confirm conclusions made from experiments that the rate of heat removal does not increase proportionally in scale-up shown in the increasing reactor temperatures. Simulations attempting to control the reactor temperature at 10 °C proved to be difficult for industrial sized reactors. From the 100 mL round bottom flask to the 10,000 L reactor there was about a 56 °C increase in temperature with a cooling jacket temperature of -40 °C. This temperature increase supports the idea that proper scale-up procedures are necessary to ensure safety. The results of the hydrogen peroxide decomposition simulations also supported the proposed idea for the project that proper scale-up is crucial to process safety and usually has to be performed in systematic stages.

It can be concluded that DynoChem is a better scale-up software than COMSOL as it contains models of typical industrial reactors built into the program. Different modules of DynoChem can also be used to estimate the overall heat transfer coefficient UA and variables such as stirring rate, cooling jacket flowrate, fouling factors, and volume can be easily changed to study its effect on the overall heat transfer coefficient. Since DynoChem is Excel based, it is relatively easy to vary reactant or catalyst feed rate to model fed batch operations. Other DynoChem scale-up applications include fitting UA values to experimental data collected from the lab which yielded similar results to calculated UA values.

Future Recommendations

If the heat transfer reactor scale-up were to be continued, there are several recommendations on improving the process. First, running the experiments in flask sizes larger than 1 L would help confirm the extrapolations for 2, 5, 12 and 22 L vessels. These results would also aid in validating DynoChem's ability to accurately model heat transfer by incorporating lab data from the larger scale trials into the program and comparing the resulting data to experimental outcomes. Additionally, based on the temperature profiles produced from the round bottom flask trials, ensuring consistency across all trials would allow for the most accurate scale-up in terms of all variables affecting heat transfer. These profiles show the differences between inner and outer heat transfer coefficients, which allows one to adjust stirring inside the flask or in the ice bath to produce correct, scale-appropriate values.

To demonstrate the concept of how heat removal does not increase proportionally, it is recommended that students utilize experiments discussed in this report as a teaching tool. It is recommended that students perform these experiments themselves in 100 mL and 1,000 mL round bottom flasks with an ice bath for cooling. If a more dramatic temperature increase effect is desired than what was presented in this report, larger sized round bottom flasks up to 5,000 mL can be used. It is recommended that a teacher conduct the experiment as a demonstration while allowing students to perform the experiments on a smaller scale. Another option to create a more dramatic temperature increase effect is to repeat the experiments using 30% hydrogen peroxide rather than 12%. Caution should be exercised if using 30% hydrogen peroxide to ensure that the reactions can be conducted safely.

To make better use of COMSOL software, it is advised to use reaction engineering module to better model the heat transfer in round bottom flasks. Doing so would ensure that proper reaction rates are incorporated into the model, which in turn would produce realistic estimates of how big and how fast the heat production occurs in a studied vessel.

In future investigations of DynoChem modeling capabilities, fed batch operation can be utilized by varying the reactant or catalyst feed rate to better control exothermic reactions. Stirring speeds and coolant flow rates can also be changed to study its effect on heat transfer in the reactor. Varying stirring speed and coolant flow rates can also better demonstrate its effect on the inside and outside heat transfer coefficients. Various DynoChem modules for different applications can also be downloaded from DynoChem online resources.

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Appendix

Round Bottom Flask Experimental Data

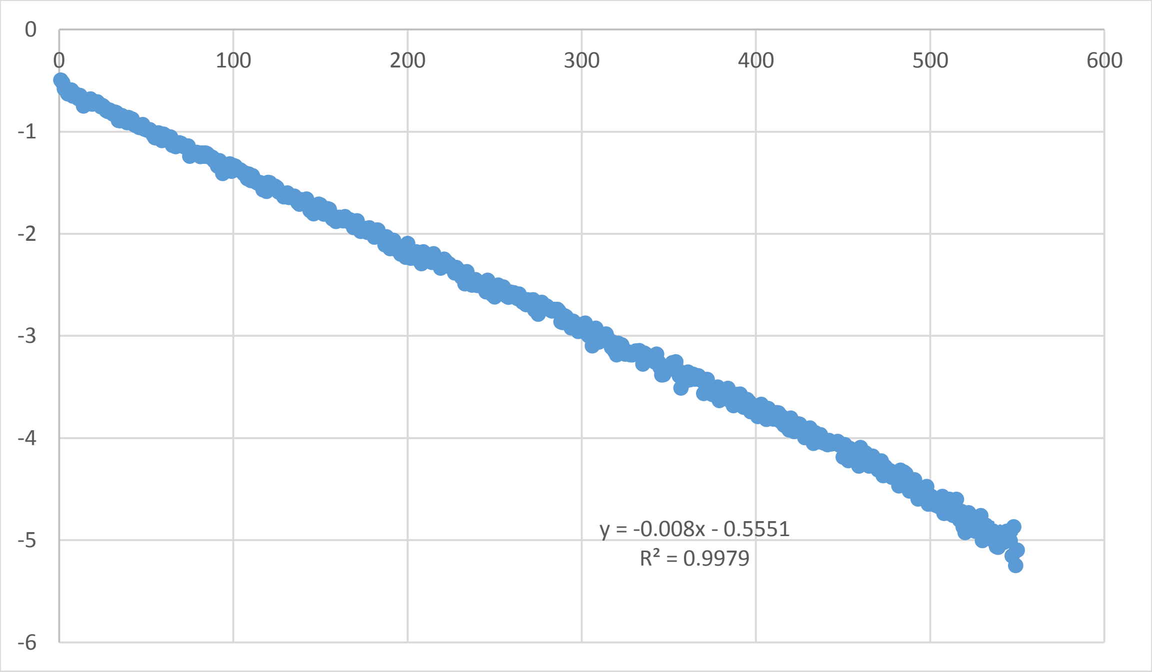


Figure 37: Calculation of Overall Heat Transfer Coefficient for 100 mL Round Bottom Flask Trial 1

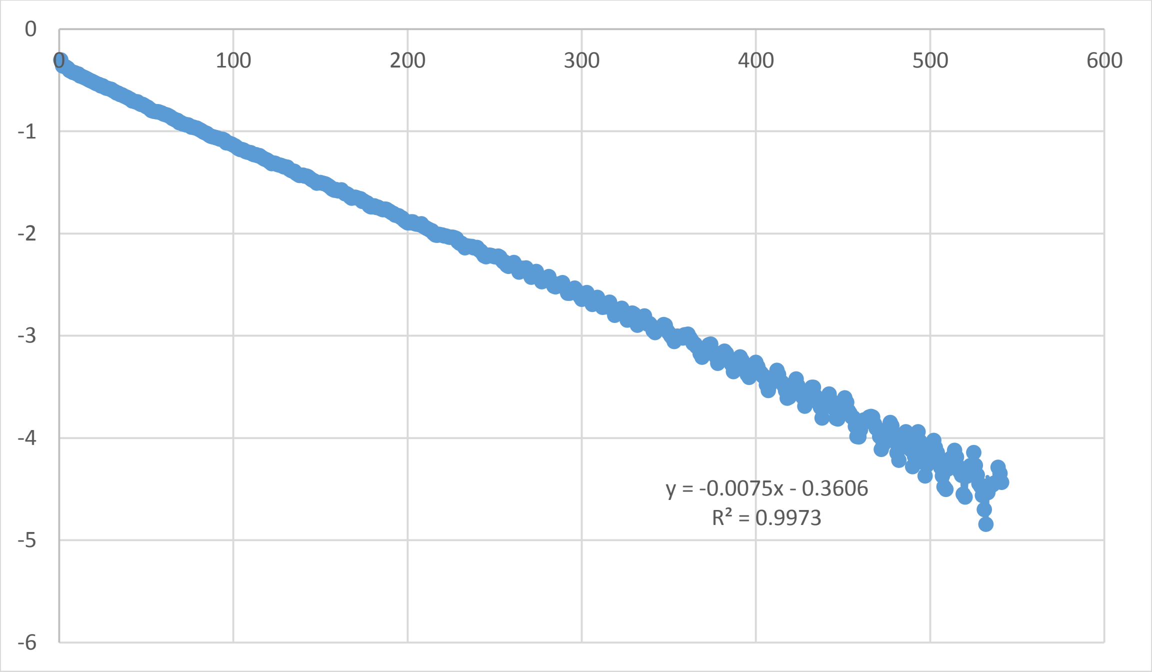


Figure 38: Calculation of Overall Heat Transfer Coefficient for 100 mL Round Bottom Flask Trial 2

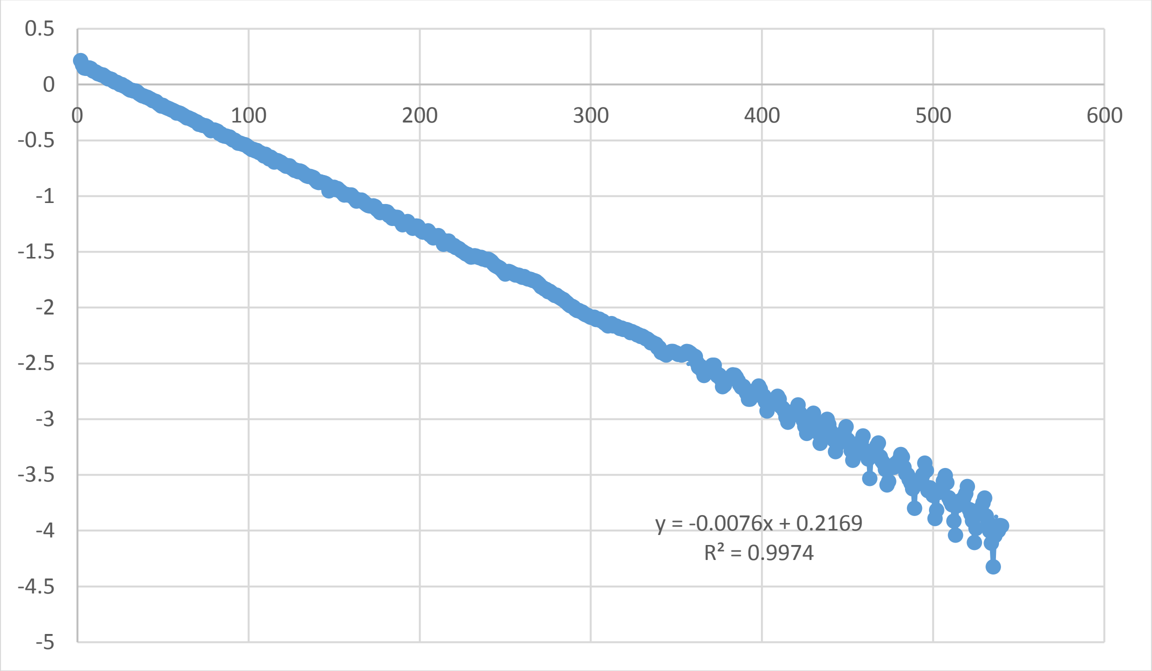


Figure 39: Calculation of Overall Heat Transfer Coefficient for 100 mL Round Bottom Flask Trial 3

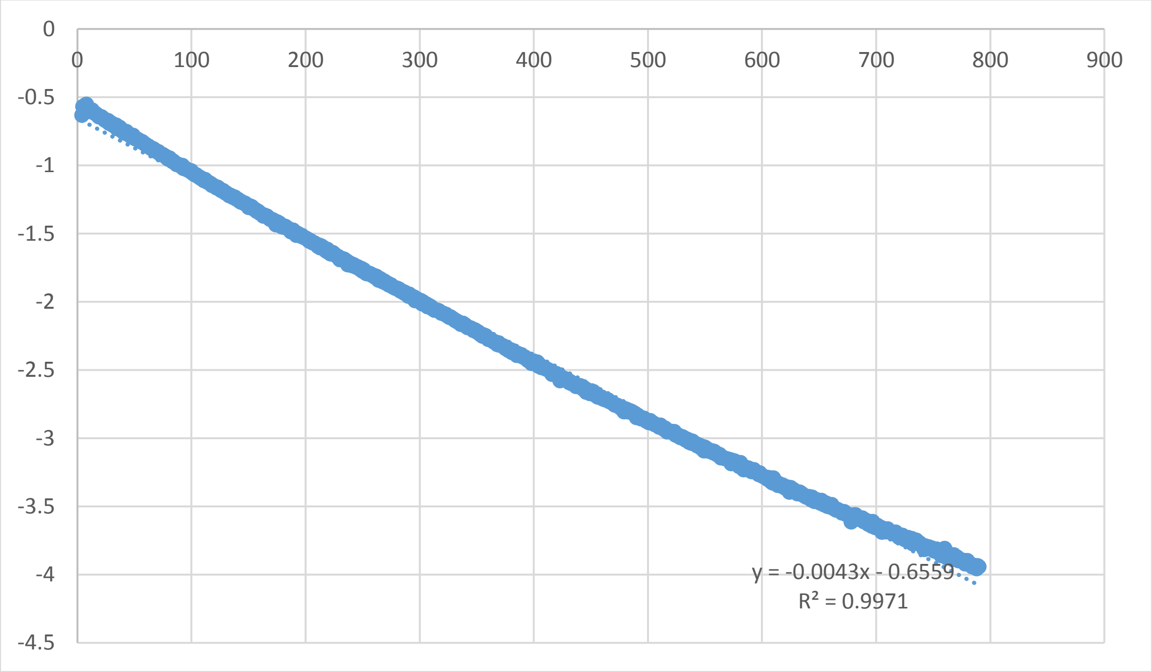


Figure 40: Calculation of Overall Heat Transfer Coefficient for 250 mL Round Bottom Flask Trial 1

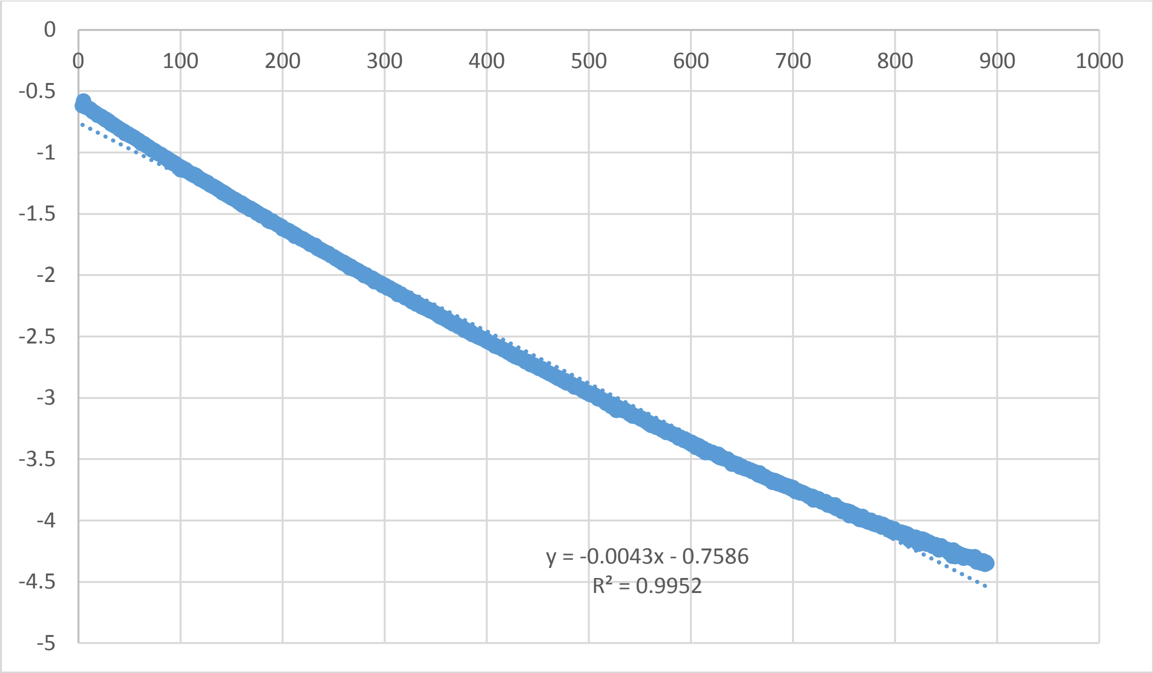


Figure 41: Calculation of Overall Heat Transfer Coefficient for 250 mL Round Bottom Flask Trial 2

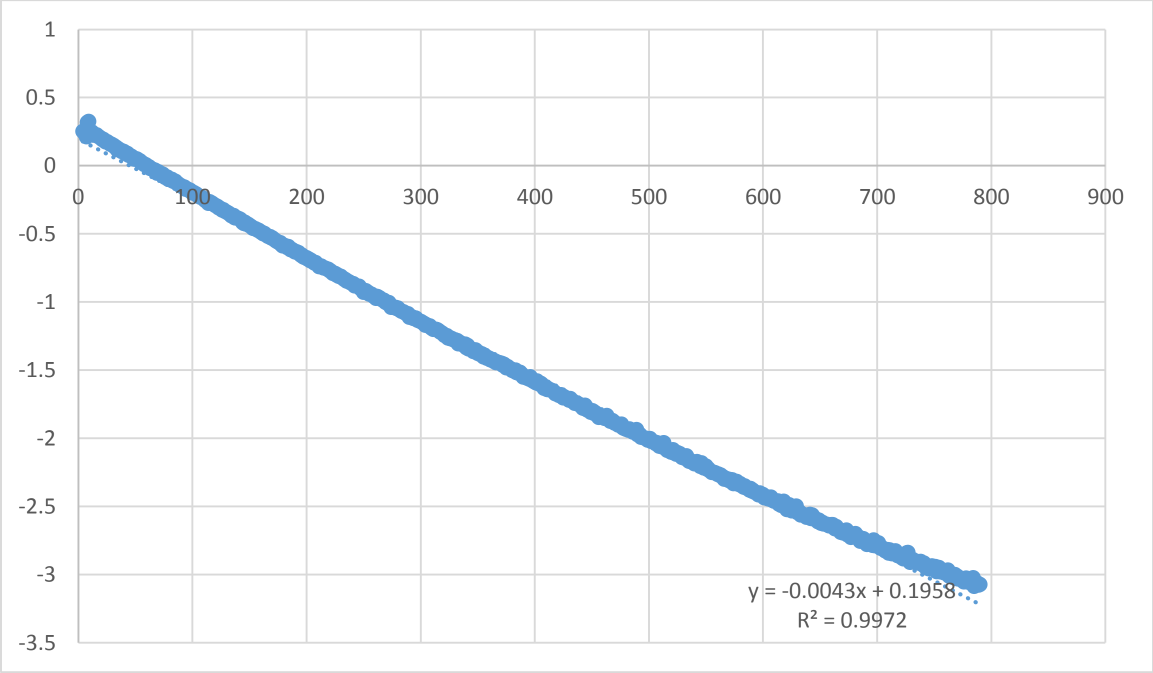


Figure 42: Calculation of Overall Heat Transfer Coefficient for 250 mL Round Bottom Flask Trial 3

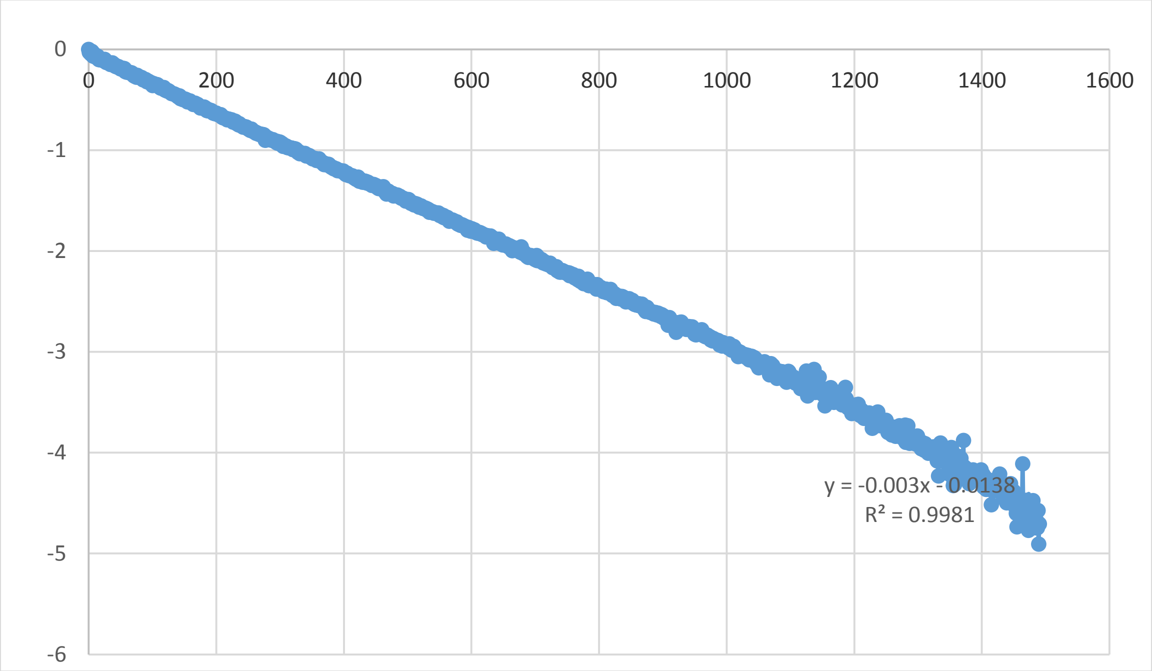


Figure 43: Calculation of Overall Heat Transfer Coefficient for 500 mL Round Bottom Flask Trial 1

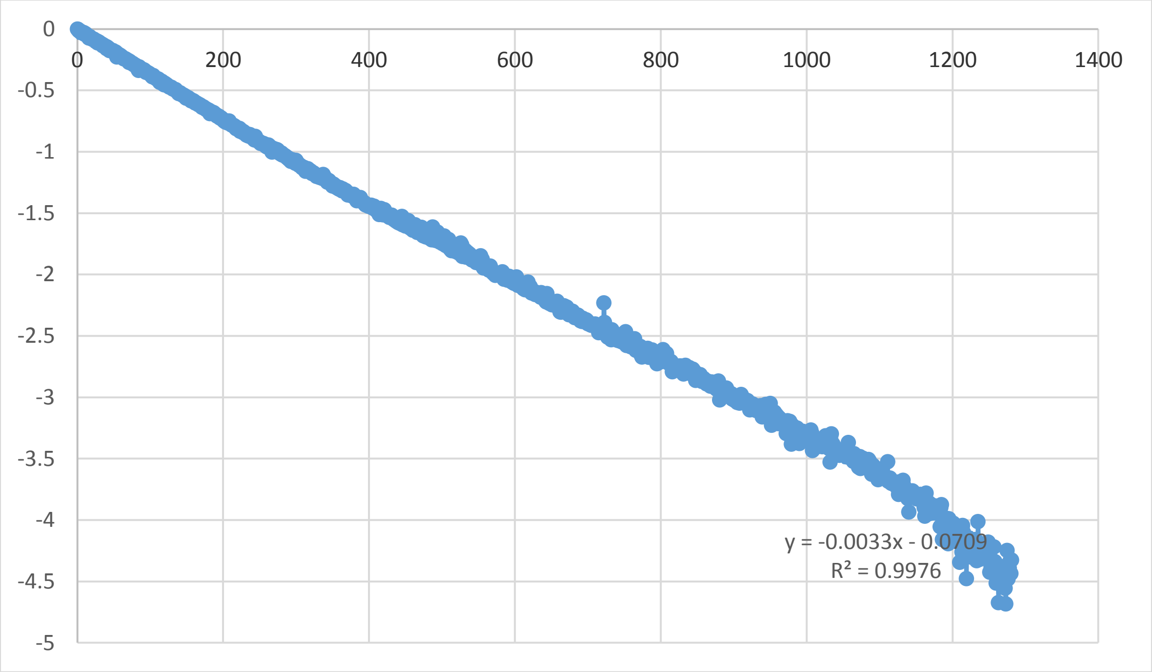


Figure 44: Calculation of Overall Heat Transfer Coefficient for 500 mL Round Bottom Flask Trial 2

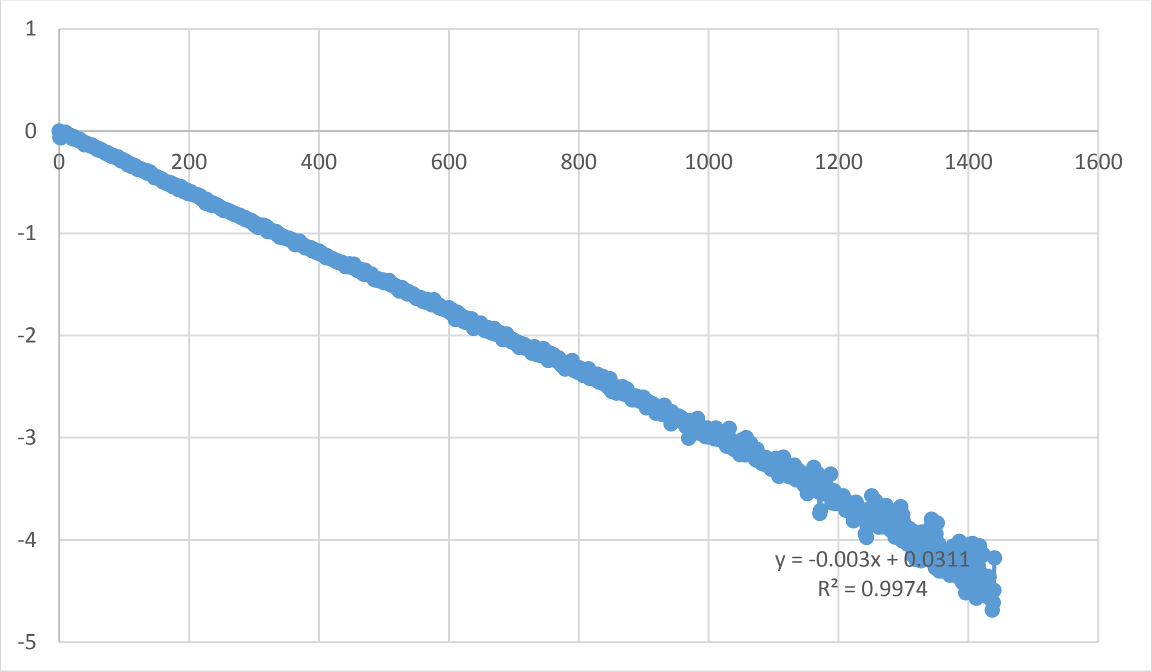


Figure 45: Calculation of Overall Heat Transfer Coefficient for 500 mL Round Bottom Flask Trial 3

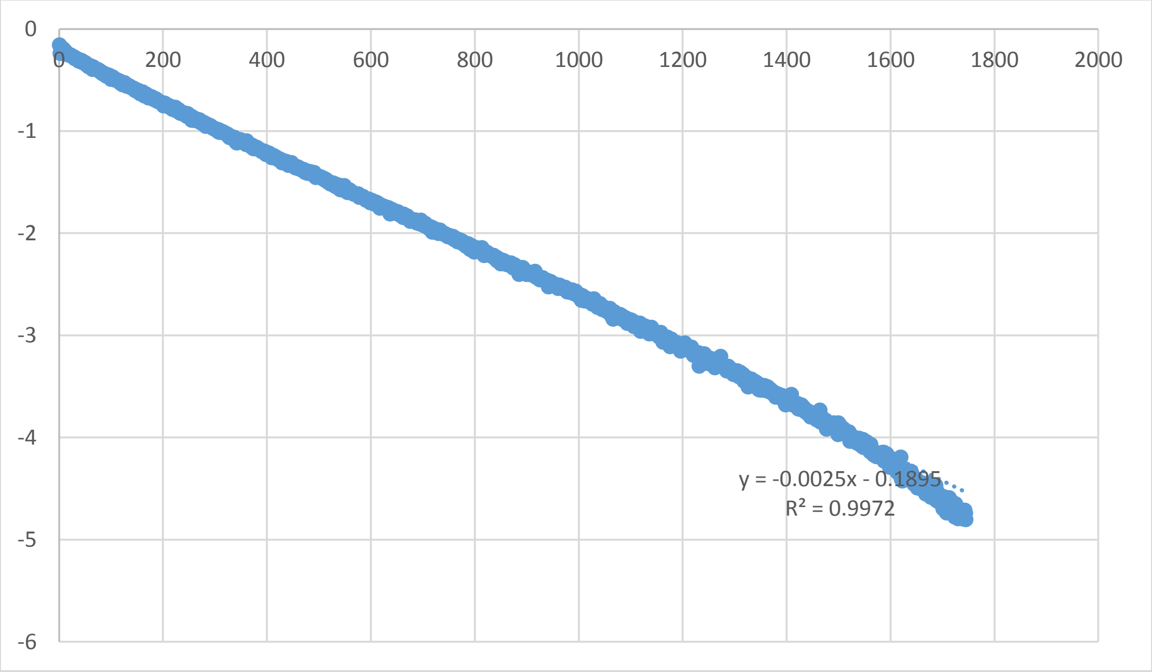


Figure 46: Calculation of Overall Heat Transfer Coefficient for 1000 mL Round Bottom Flask Trial 1

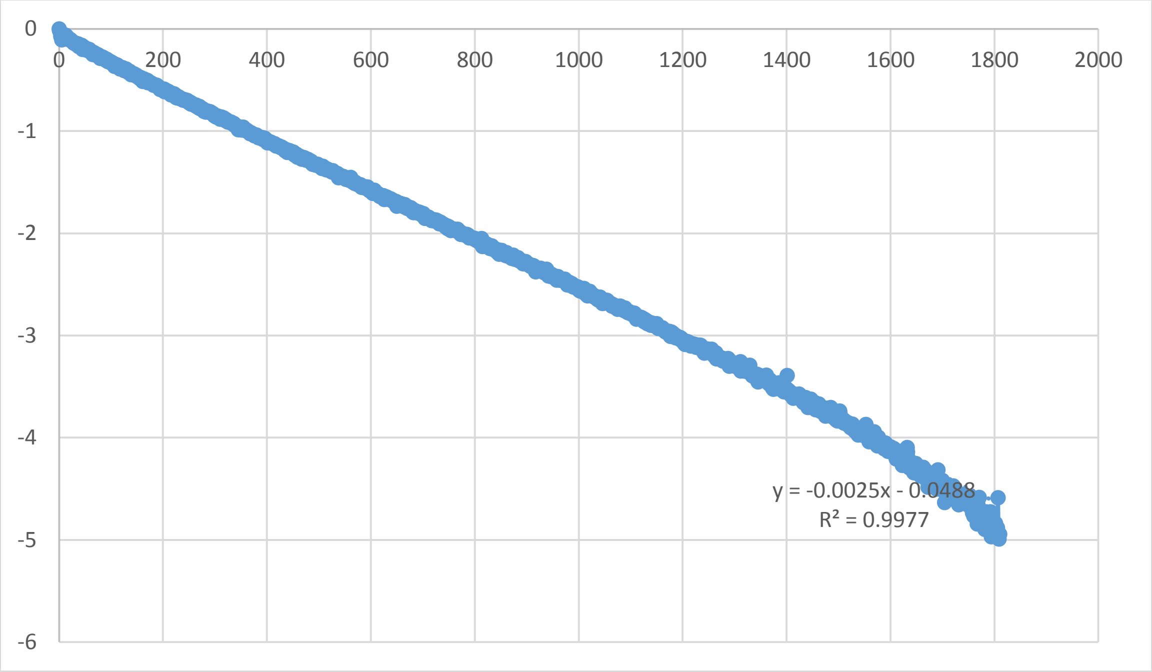


Figure 47: Calculation of Overall Heat Transfer Coefficient for 1000 mL Round Bottom Flask Trial 2

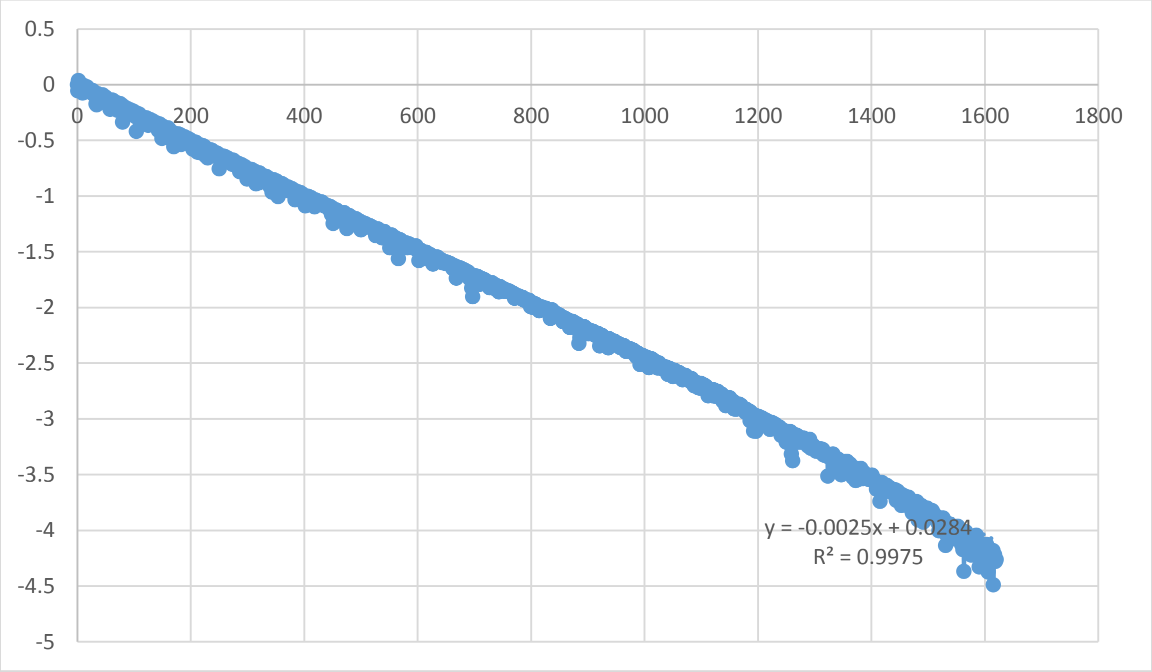


Figure 48: Calculation of Overall Heat Transfer Coefficient for 100 mL Round Bottom Flask Trial 7

Hydrogen Decomposition Reaction

For this experiment, 30% hydrogen peroxide solution was available. Since the experiment was designed for a 12% solution, the following calculations were performed to dilute the mixture:

For an 8 ounce calorimeter:

$Total\ reactant\ volume = 34\ mL, where\ 4\ mL = KI$

$34\ mL - 4\ mL = 30\ mL\ of\ H_2O_2\ solution;\ \ density\ of\ pure\ H_2O_2 = 1.45\ g/mL$

$1\ g\ 30\%\ solution:$

$$0.7\ g\frac{H_2O}{1\ \frac{g}{mL}} + 0.3\ g\frac{H_2O_2}{1.45\frac{g}{mL}} = 0.907\ mL\ 30\%\ solution;\ \frac{1\ g}{0.907\ mL} = 1.103\ g/mL$$

$1g\ 12\%\ solution:$

$$\frac{0.88\ g\ H_2O}{1\frac{g}{mL}} + \frac{0.12\ g\ H_2O_2}{1.45\frac{g}{mL}} = 0.963\ mL\ of\ 12\ \%\ solution;\ \frac{1\ g}{0.963\ mL} = 1.038\ g/mL$$

$Need\ 30\ mL\ of\ 12\ \%\ solution:$

$$30\ mL\frac{1.038\ g}{mL} = 31.14\ g\ solution$$

$31.14\ g\ (0.12) = 3.737\ g\ H_2O_2;\ \ 31.14\ g\ solution - 3.737\ g\ H_2O_2 = 27.403\ g\ H_2O$

$Need\ 3.737\ g\ H_2O_2\ from\ 30\%\ solution:$

$$\frac{3.737\ g}{0.3} = 12.457\ g\ 30\ \%\ solution;\quad 12.457\ g * 0.7 = 8.72\ gH_2O$$

$Total\ H_2O\ needed = 27.403\ g\ ;\ \ 27.403\ g - 8.72\ g = 18.663\ g\ H_2O\ to\ add\ to\ 30\%\ solution$

For a 100 mL flask, half volume was filled with the solution; therefore, similar calculations were done for 50 mL:

$$50\ mL * \left(1.038\frac{g}{mL}\right) = 51.9\ g\ solution$$

$0.12 * 51.9\ g = 6.228\ g\ H_2O_2;\ \ 51.9\ g - 6.228\ g = 45.672\ g\ H_2O$

$$\frac{6.228\ g\ H_2\ O_2}{0.3} = 20.76\ g\ of\ 30\%\ solution; 20.76\ g\ H_2O * 0.7 = 14.532\ g\ H_2O$$

$45.672\ g - 14.532g = 31.14\ g\ of\ additional\ H_2O$

For a 1000 mL flask,

$$500\ mL * \left(1.038\frac{g}{mL}\right) = 519\ g\ solution$$

$0.12 * 519\ g = 62.28\ g\ H_2O_2;\ \ 519\ g - 62.28\ g = 456.72\ g\ H_2O$

$$\frac{62.28\ g\ H_2\ O_2}{0.3} = 207.6\ g\ of\ 30\%\ solution; 207.6\ g\ H_2O * 0.7 = 145.32\ g\ H_2O$$

$$456.72\ g - 145.32g = 311.4\ g\ of\ additional\ H_2O$$

COMSOL Model Figures and Inputs

100 mL

Global Definitions

Parameters 1

Parameters

Name	**Expression**	**Description**

Model 1 (mod1)

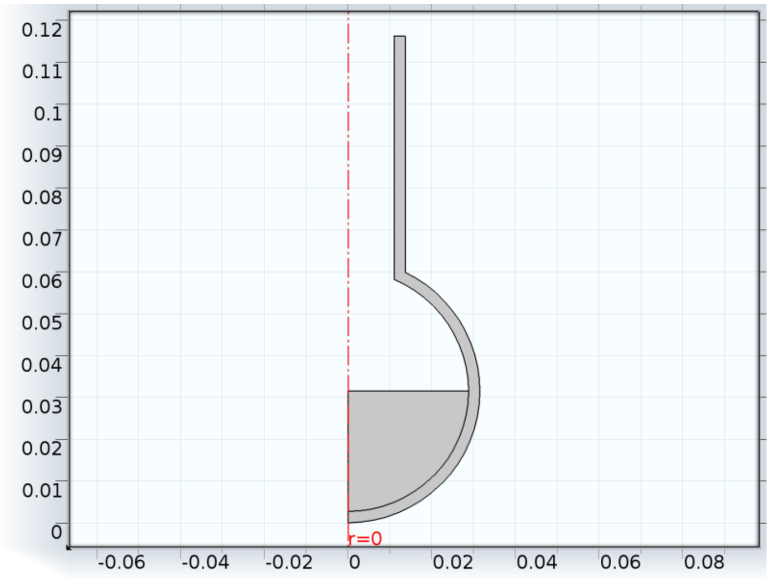
Definitions

Coordinate Systems

Boundary System 1

Coordinate system type	Boundary system
Identifier	sys1

Geometry 1



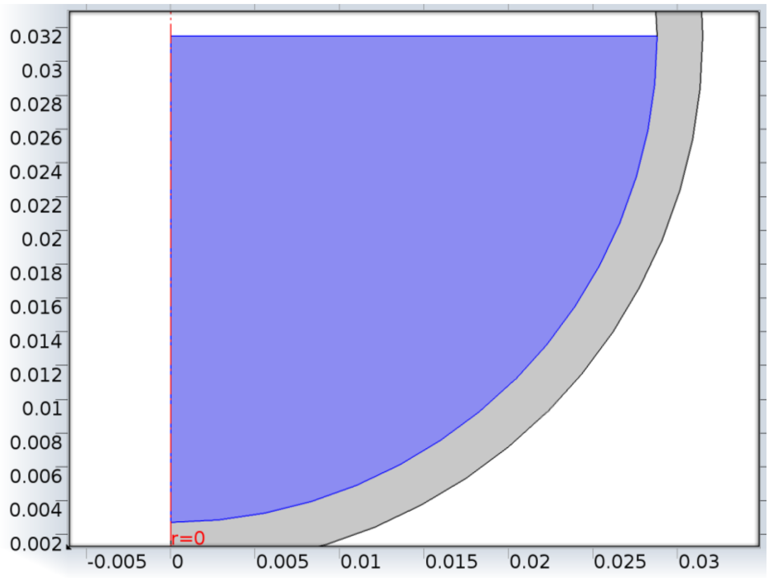
Geometry 1

Units

Length unit	m
Angular unit	deg

Materials

Water, liquid

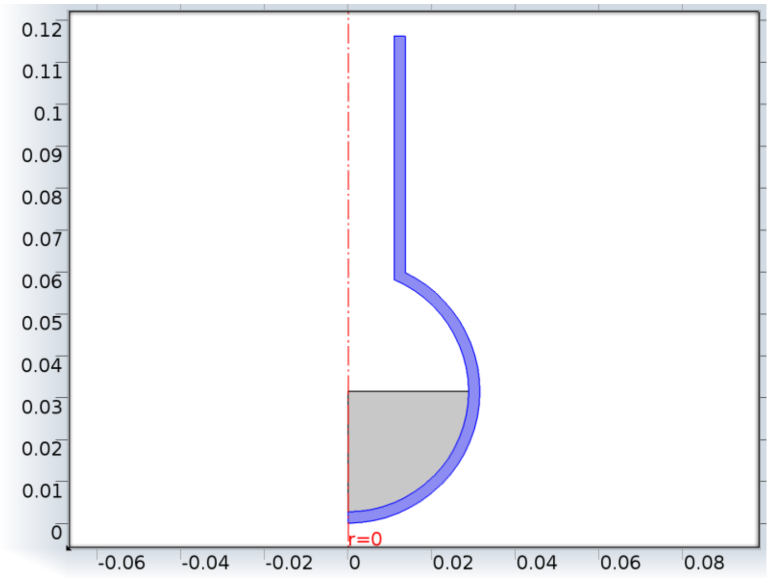


Water, liquid

Selection

Geometric entity level	Domain
Selection	Domain 2

Silica glass

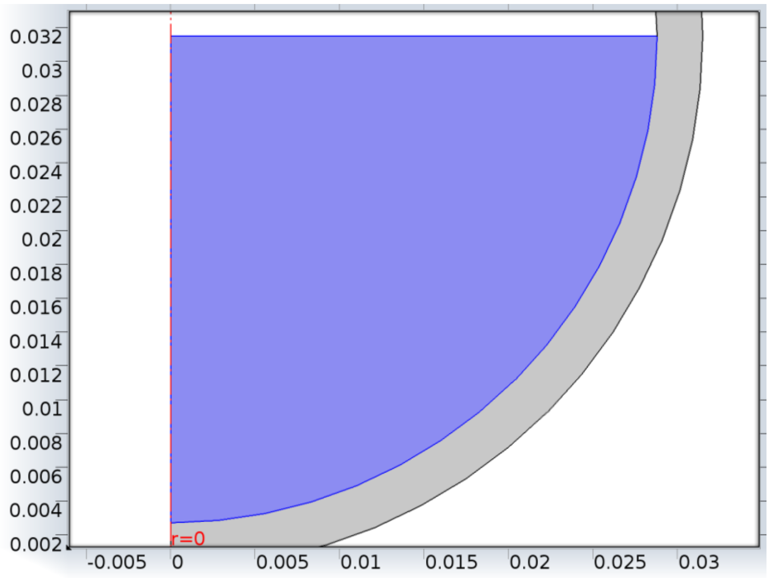


Silica glass

Selection

Geometric entity level	Domain
Selection	Domain 1

Heat Transfer in Solids (ht)

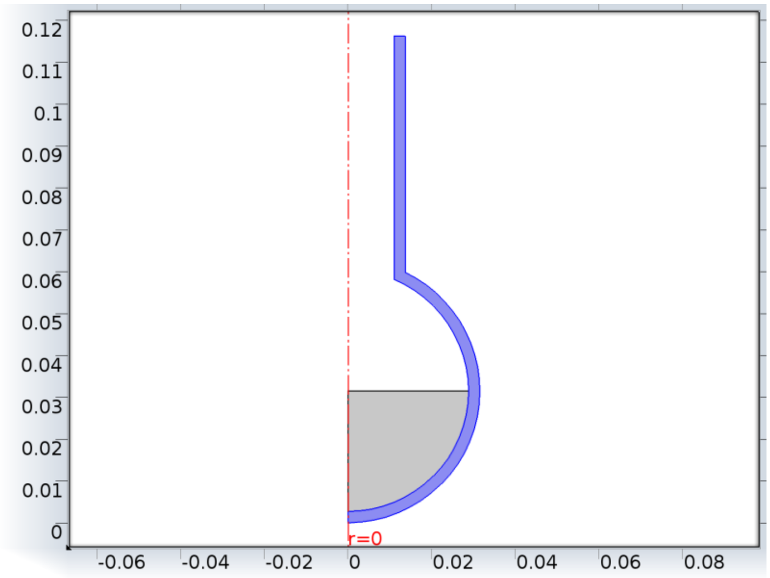


Heat Transfer in Solids

Features

Heat Transfer in Solids 1
Axial Symmetry 1
Thermal Insulation 1
Initial Values 1
Heat Flux 1

Heat Transfer in Solids 2 (ht2)

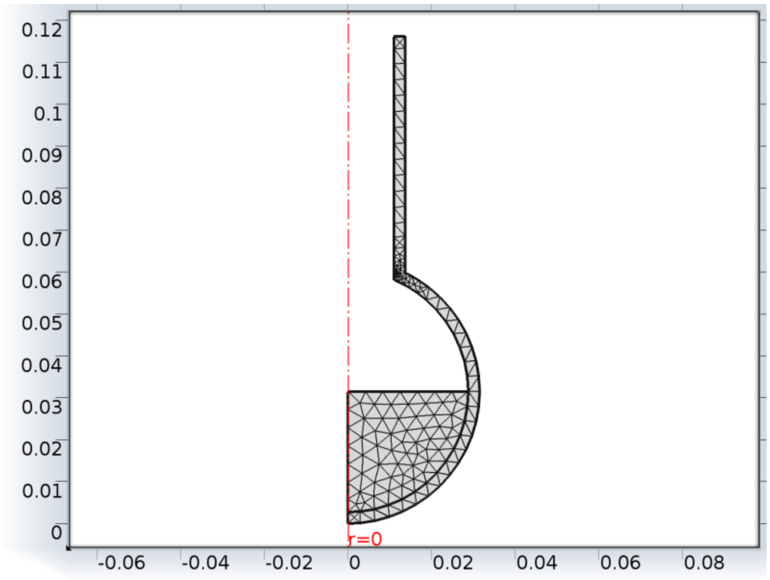


Heat Transfer in Solids 2

Features

Heat Transfer in Solids 1
Axial Symmetry 1
Thermal Insulation 1
Initial Values 1
Heat Flux 1
Heat Flux 2

Mesh 1



Mesh 1

Study 2

Time Dependent

Study settings

Property	Value
Include geometric nonlinearity	Off

Times: range(0,1,1000)

Mesh selection

Geometry	Mesh
Geometry 1 (geom1)	mesh1

Physics selection

Physics	Discretization
Heat Transfer in Solids (ht)	physics
Heat Transfer in Solids 2 (ht2)	physics

Results

Data Sets

Solution 2

Selection

Geometric entity level	Domain
Selection	Geometry geom1

Solution

Name	Value
Solution	Solver 2
Model	Save Point Geometry 1

Revolution 2D

Data

Name	Value
Data set	Solution 2

Revolution layers

Name	Value
Start angle	-90
Revolution angle	225

Revolution 2D 1

Data

Name	Value
Data set	Solution 2

Revolution layers

Name	Value
Start angle	-90
Revolution angle	225

Cut Point 2D 1

Data

Name	Value
Data set	Solution 2

Derived Values

Point Evaluation 1

Data

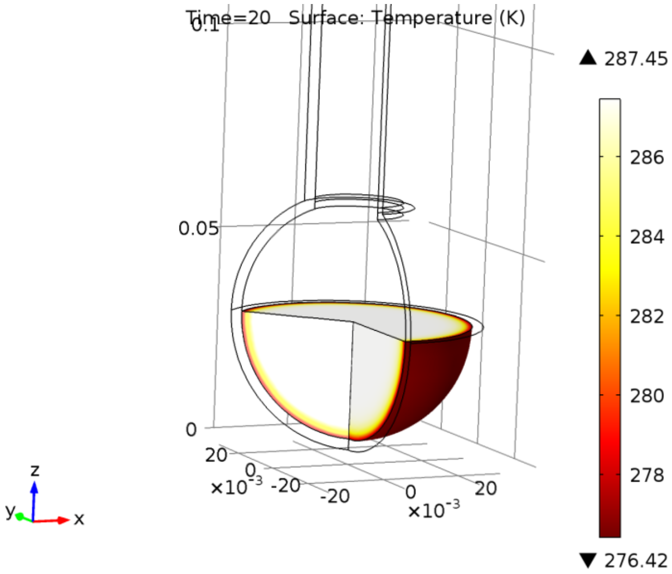
Name	Value
Data set	Cut Point 2D 1

Expression

Name	Value
Expression	T
Unit	K
Description	Temperature

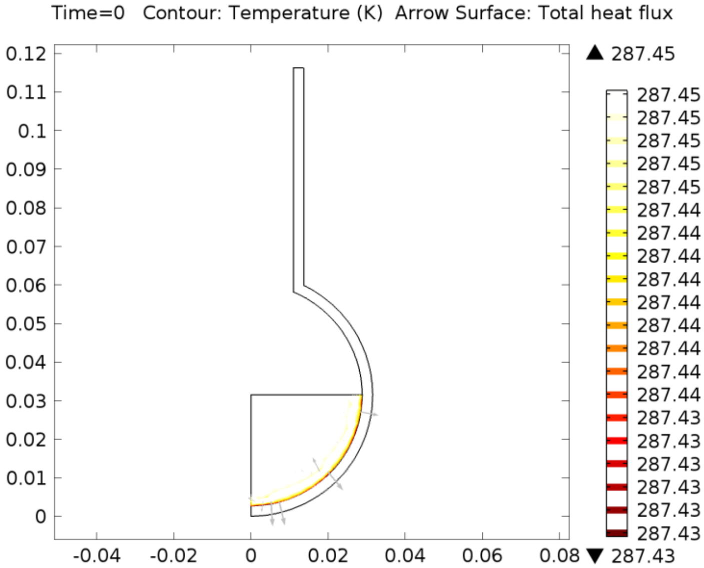
Plot Groups

Temperature, 3D (ht)



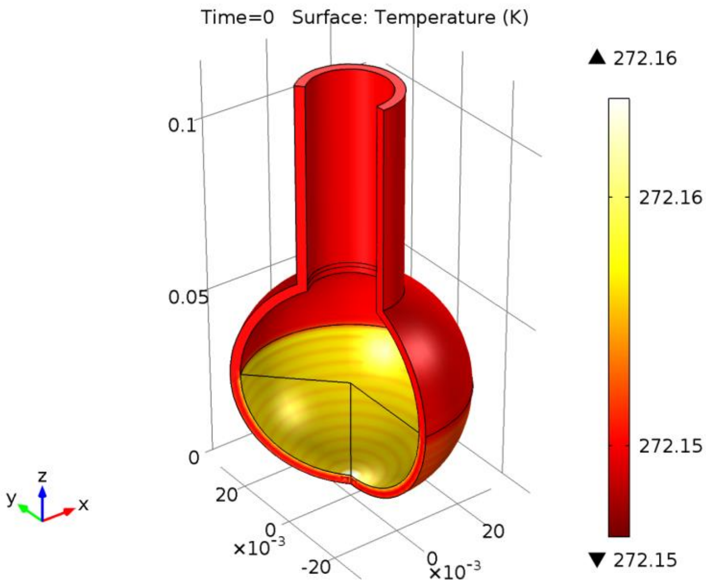
Time=20 Surface: Temperature (K)

Isothermal Contours (ht)



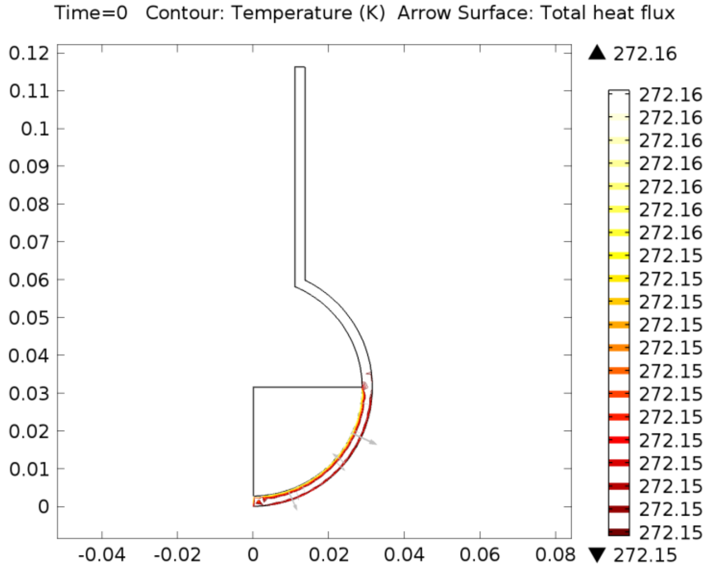
Time=0 Contour: Temperature (K) Arrow Surface: Total heat flux

Temperature, 3D (ht2)



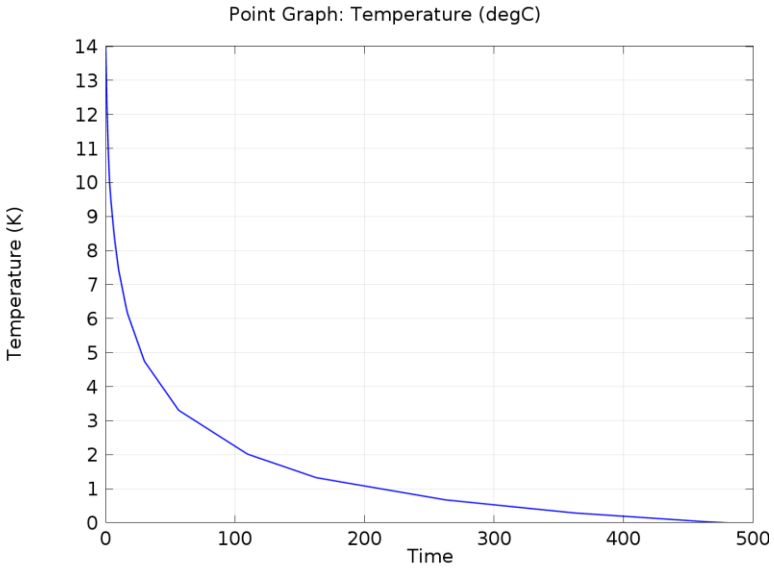
Time=0 Surface: Temperature (K)

Isothermal Contours (ht2)



Time=0 Contour: Temperature (K) Arrow Surface: Total heat flux

1D Plot Group 6



Point Graph: Temperature (degC)

DynoChem Model Figures and Inputs

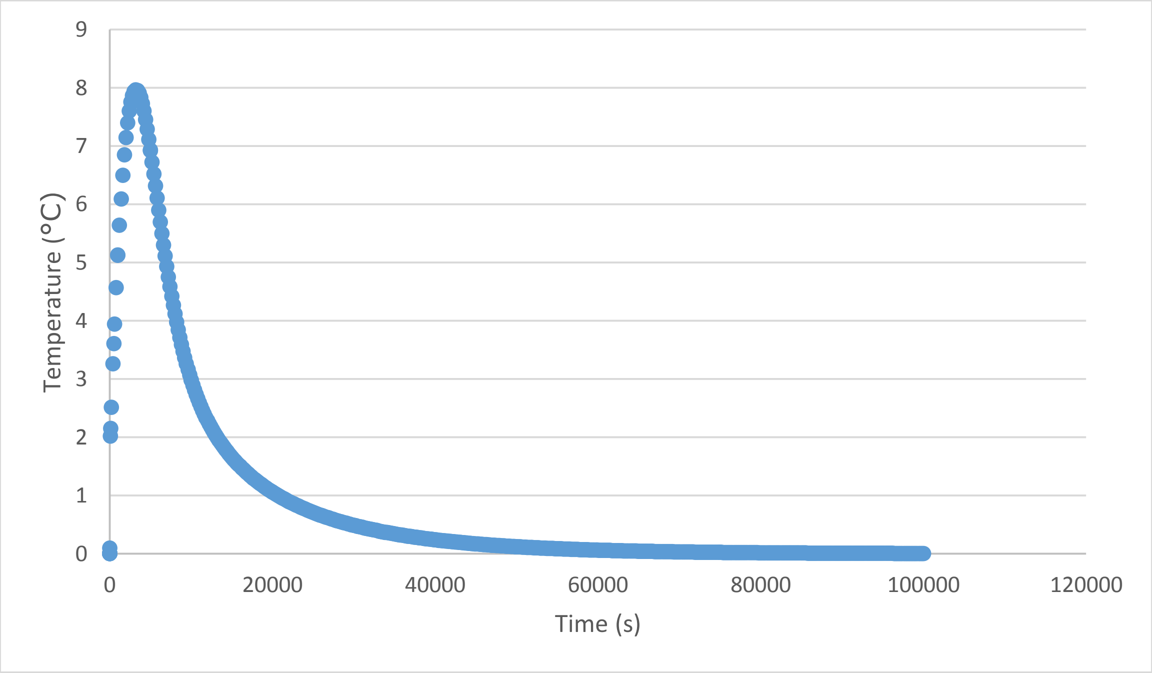


Figure 49: Temperature vs. Time Profile of Hydrogen Peroxide Decomposition Reaction in 100 L Reactor

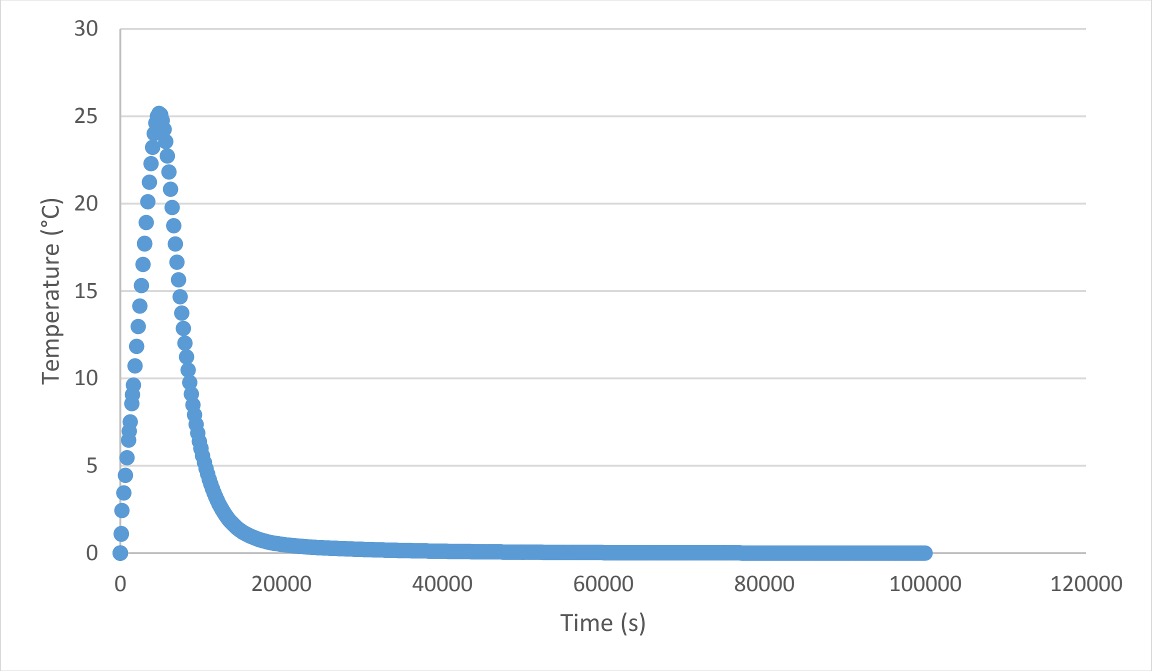


Figure 50: Temperature vs. Time Profile of Hydrogen Peroxide Decomposition Reaction in 1000 L Reactor

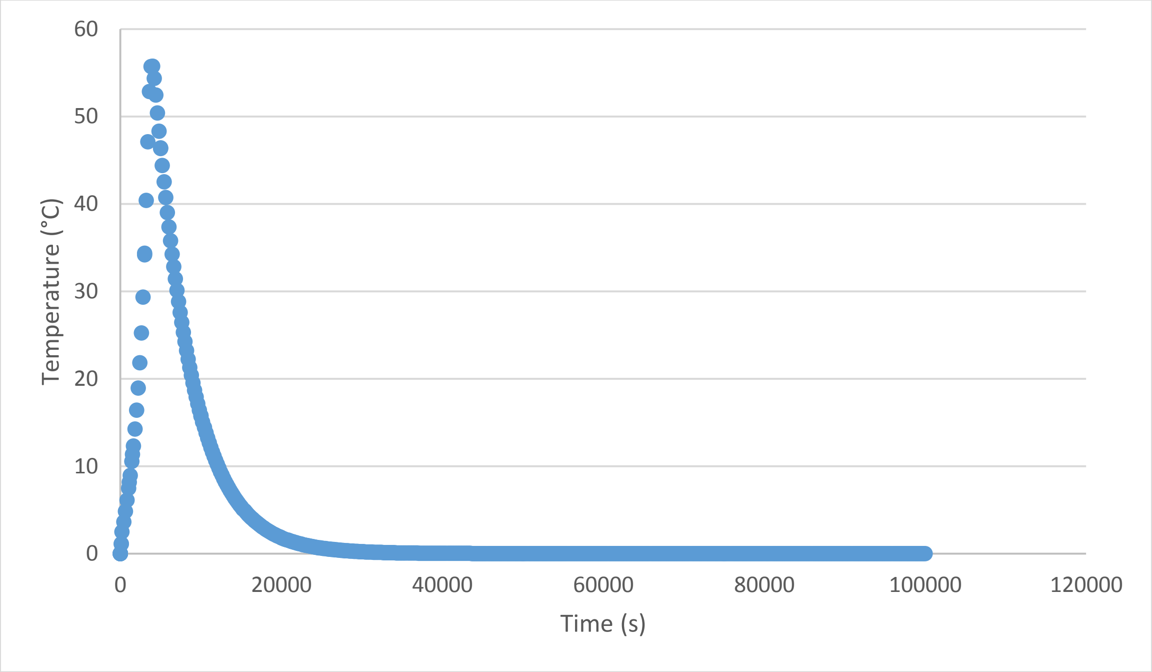


Figure 51: Temperature vs. Time Profile of Hydrogen Peroxide Decomposition Reaction in 10,000 L Reactor

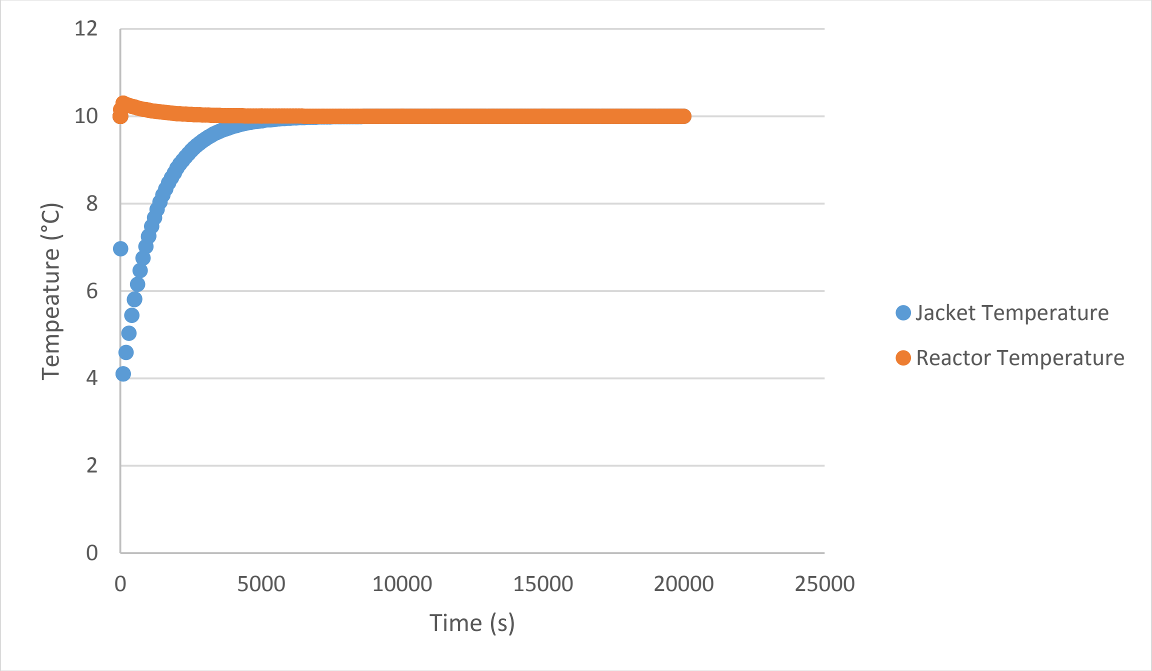


Figure 52: Temperature vs. Time Profile for Controlling Reactor Temperature at 10 °C in 100 mL Reactor

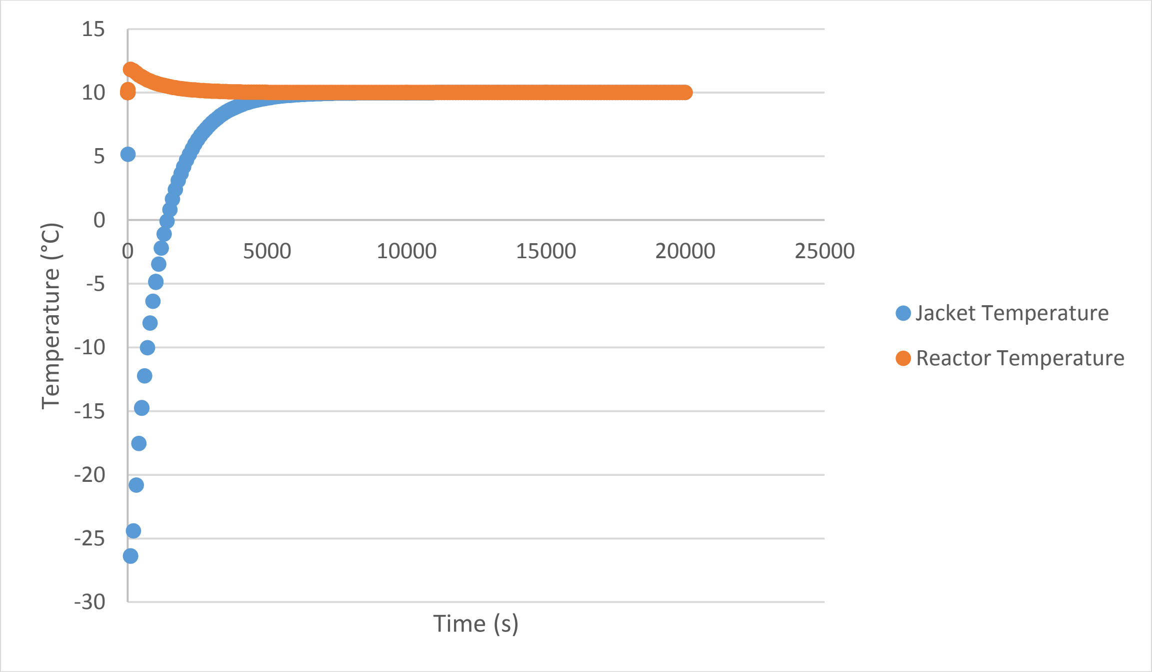


Figure 53: Temperature vs. Time Profile for Controlling Reactor Temperature at 10 °C in 1000 mL Round Bottom Flask

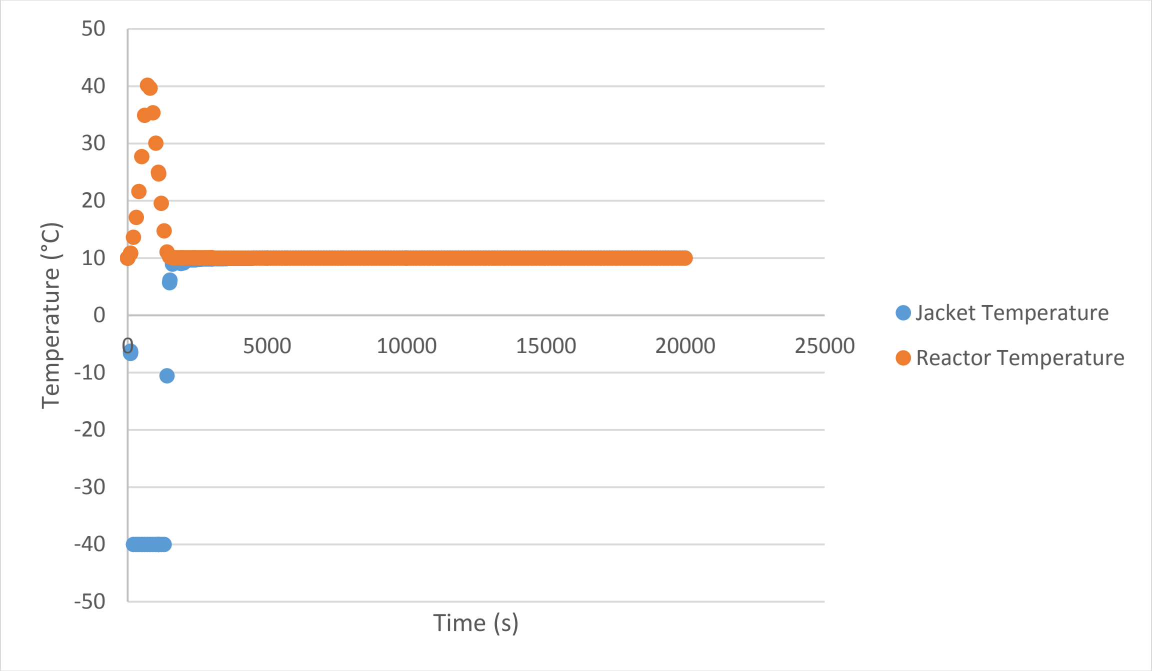


Figure 54: Temperature vs. Time Profile for Controlling Reactor Temperature at 10 °C in 100 L Reactor

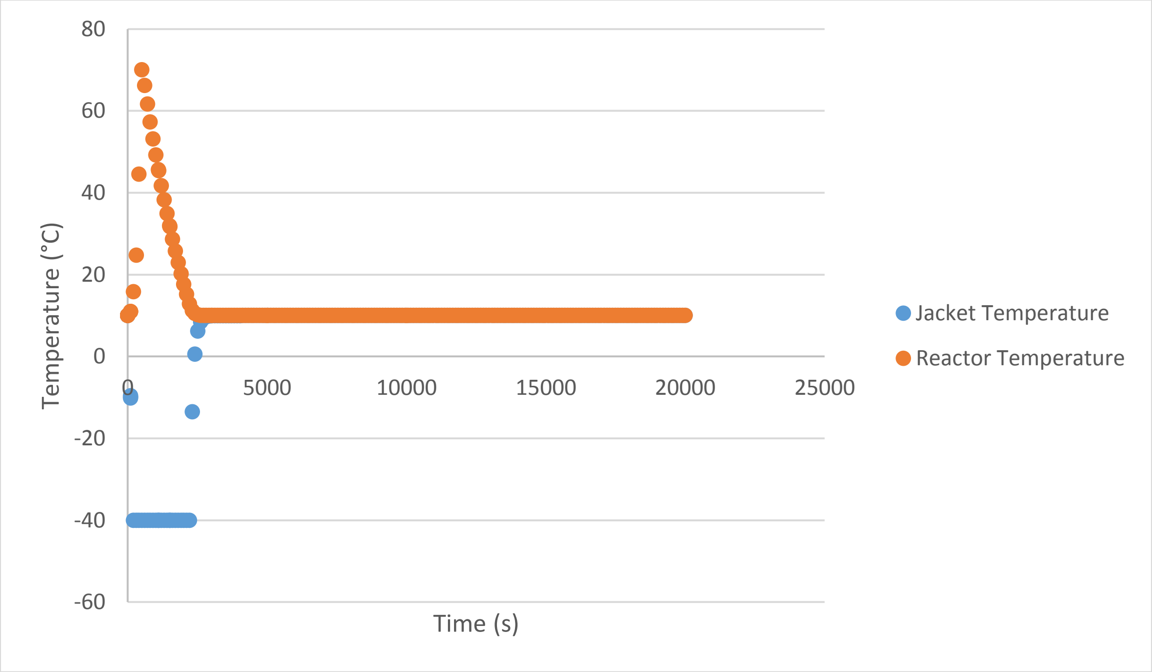


Figure 55: Temperature vs. Time Profile for Controlling Reactor Temperature at 10 °C in 1000 L Reactor

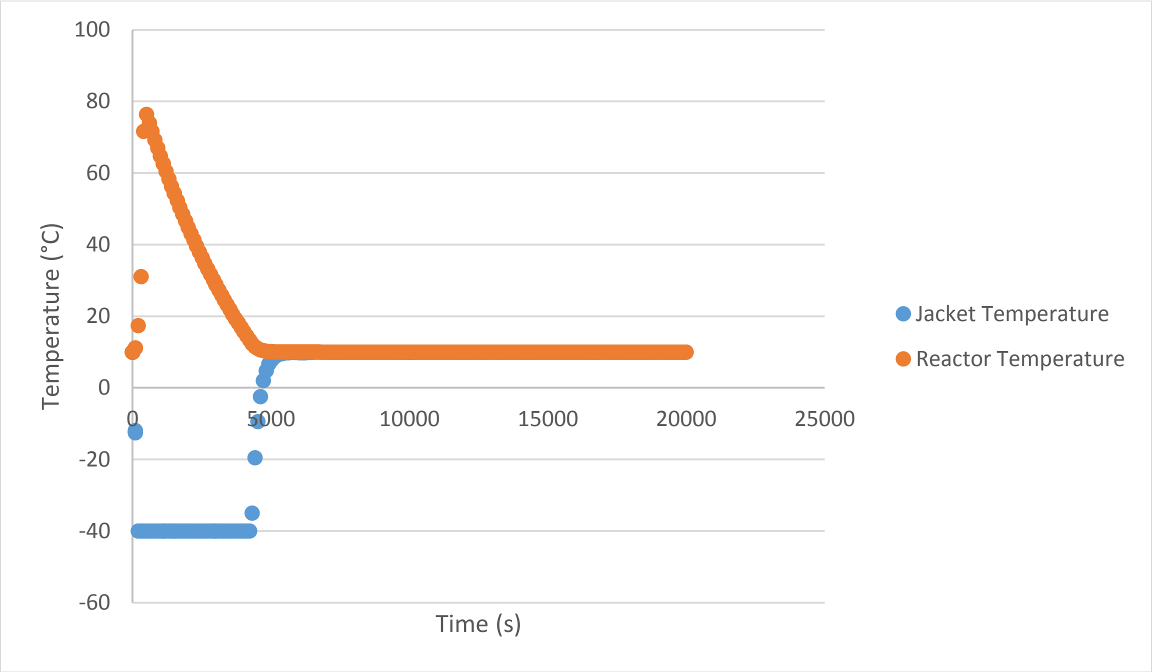


Figure 56: Temperature vs. Time Profile for Controlling Reactor Temperature at 10 °C in 10,000 L Reactor