Analysis of a Runaway Reaction

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Abstract

Safety is of utmost importance in the chemical industry. Inspired by an industrial accident that occurred in 2010, we explored the exothermic acid-catalyzed polymerization of furfuryl alcohol. In the accident, methanesulfonic acid entered a drum of furfuryl alcohol and caused an explosion due to a runaway reaction. In our investigation, we completed experiments to find the heat of reaction of furfuryl alcohol, heat capacity of polyfurfuryl alcohol, and overall heat transfer coefficient of furfuryl alcohol. We produced a model in Mathcad that can predict reaction temperature overtime and estimate the time for a runaway reaction to occur. We also investigated how mass and heat transfer can limit the reaction rate. Finally, we included the limitations of our experiments as well as safety recommendations for industry and future research.

Acknowledgements

We thank Professor Stephen Kmiotek of Worcester Polytechnic Institute (WPI) for the opportunity to work on this project. Professor Kmiotek provided constant feedback, support, and enthusiasm about our project over the course of the year.

We thank Professor James Dittami of WPI. Professor Dittami aided in our literature review early on in our project when we were looking for an approach to our complex problem. We also thank Professor Christopher Lambert of WPI. Professor Lambert gave us guidance on the techniques to gather data on our reaction, such as to inexpensively measure the heat of reaction by ice calorimetry.

Additionally, we thank Tom Partington and Doug White, Managers of WPI's Goddard Hall Unit Operations Lab. Both Tom and Doug helped us with creating our apparatuses for experimentation.

Finally, we thank Leslie Brodeur and Tiffany Royal of the WPI Chemical Engineering Department. Leslie and Tiffany helped us to gather the materials we needed to successfully experiment.

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1.0 Introduction

Safety is of utmost importance in the chemical industry. According to the AIChE code of ethics of a chemical engineer, a chemical engineer is to “hold paramount” the safety of both people and the environment (AIChE, 2015). When conditions are unsafe, a chemical engineer is required to take action.

We explored a chemical accident that resulted in an explosion in industry in 2010. Catalyzed furfuryl alcohol blew up a drum spraying an unknown black polymer. Luckily, no one was in the area of the explosion, but the environmental impact of this black polymer was unknown. An incident investigation team was formed to figure out the cause of the accident. Unknowingly, methanesulfonic acid entered a partly filled drum of furfuryl alcohol causing the exothermic reaction that resulted in the explosion. The incident investigation team was baffled at the lack of research on the polymerization of furfuryl alcohol. Our goal was to fill this gap by researching the acid catalyzed polymerization of furfuryl alcohol into polyfurfuryl alcohol.

To model the incident, we used the engineering software Mathcad. In our model, the parameters of vessel size, vessel material of construction, volume of furfuryl alcohol added, volume of acid added, and initial temperature of the reaction as the input variables. These independent variables can be manipulated to see if and when the polymerization of furfuryl alcohol will run away thus potentially causing unsafe conditions. The output of our model is a temperature versus time curve where an exotherm is noticeable if it occurs.

The goal of this research was to better understand the kinetics of the polymerization reaction which we did by creating a model to predict thermal runaway. With our model, in case there is contamination in the future, engineers can predict how long prior to the reaction and the severity of the reaction that is about to occur. We also developed safety recommendations that are applicable to prevent similar industrial situations from happening again in the future. Additionally, we have recommendations for how researchers can more safely handle our reactants to prevent any exposure throughout the course of further research.

All experimentation and data collection ceased on March 6, 2020 by WPI and governmental mandates due to the rapid spread of pandemic caused by the COVID-19 virus. This paper includes experimentation up to that date and a description of the activities that we had hoped to conduct after that date.

2.0 Background

2.1 Chemical Storage Practices and Hazards

2.1.1 Potential Safety Hazards

Handling chemicals in a safe manner is the responsibility of every employee in the chemical industry. Not only is it the job of the Safety Engineer to set and enforce policies, it is the responsibility of every operator, maintenance technician, and engineer to follow these policies and understand their importance. Even with complete cooperation, accidents have the potential of happening and this chance increases with a lack of cooperation. According to Dugas (2018), the four main causes of accidents in chemical plants are human error, improper training, manufacturing defects and improper maintenance. In 2017, 5,147 deaths in the United States occurred due to industrial accidents (US Bureau of Labor, 2018). This number correlates with a fatal injury rate of 3.5 per 100, 000 full-time workers (US Bureau of Labor, 2018). In order to reduce it to zero deaths in the chemical industry per year, it is critical to understand how accidents occur in order to prevent similar accidents from happening again in the future.

Human error causes the majority of industrial accidents (Dugas, 2018). Most human error accidents fault the worker who failed to follow the safety precautions of a procedure correctly. An example of a catastrophe resulting from human error is the explosion of the BP offshore drilling rig Deepwater Horizon. According to the Chemical Safety Board, if procedures were followed during the time of the upset, manual controls should have been reset which would have diverted fluids returning from the well instead of storing them onboard. This means the flammable gases would have never found an ignition source (McLeod, 2017). The Deepwater Horizon accident is evidence that emergency procedures are just as important as day-to-day procedures.

Without the proper training, there would be no purpose of having written procedures to promote safety. Employees, even those with ample experience, may not know how to respond to chemical spills. It is critical to assume this when training an employee of any skill level (Nichols, 2018). Training can include looking through standard operating procedures as well as hands-on training in the field. For example, in 2013 fires broke out on a barge in Mobile, Alabama due to workers not being trained on how to keep gas storing tanks clean. These tanks leaked and once an ignition source was present, a fire occurred. An intervention as simple as a presentation on the importance of clean storage tanks may have prevented this incident which left three people injured (Maritime Injury Center, n.d.).

Mechanical integrity of all pieces of equipment in a plant prevents any surprises from happening. It is best practice to follow the manufacturer’s recommendation for scheduled intervals of maintenance (Dugas, 2018). Without proper maintenance the operators that are closest to these pieces of equipment are at the highest risk of injury. Chevron fell victim to an incident due to inadequate mechanical integrity in an oil refinery in Richmond, California in 2012. Corrosion in a carbon steel pipe resulted in the vaporization of a highly flammable hydrocarbon process fluid (Chemical Safety and Hazard Investigation Board, n.d.). This accident could have been avoided if there was a preventative maintenance schedule that would have checked the pipes for levels of corrosion. Additionally, a pipe of a thicker or less corrosive material could have been used, but that pipe too would require maintenance just less frequent. Mechanical integrity is a balance between economic capital and the risk presented as proper maintenance per the manufacturer’s recommendation is not always feasible.

2.1.2 How to Handle Chemicals Safely

Handling chemicals is an important part of a chemical process as it is when an operator could come in direct contact with a chemical. For this reason, the safest approach to handling chemicals is documented on a Safety Data Sheet (SDS). According to the OSHA Hazard Communication Standard in 2012, it is required that every chemical manufacturer, distributor, or importer provide a SDS for each downstream user to have available (U.S. Department of Labor, n.d.). An SDS communicates the hazards of each chemical and the recommended safety measures needed to limit its hazard potential.

One major aspect of handling chemicals in Personal Protective Equipment (PPE). An SDS will recommend what amount of PPE is required per chemical in order to minimize exposure to any chemical. Just like wearing PPE, it is equally important that an employee knows how to properly wear any equipment. For example, if an operator is not trained on how to use an air-purifying respirator, it is possible that air-containing the toxic chemical will be inhaled. For this reason, OSHA recommends that each employee is required to know the following about any potential PPE that is to be worn.

I. When is it necessary?
II. What kind in particular is necessary?
III. How to properly wear, adjust, and take it off?
IV. What are the limitations of the equipment?
V. What is the proper care, maintenance required, life span, and intended disposal of the equipment (U.S. Department of Labor, n.d.)?

Information to answer these questions should be found in an SDS.

2.1.3 How to Store Chemicals

The storage of chemicals is a key component to safety in the chemical industry. Improperly storing chemicals can create hazardous conditions. For this reason, it is best practice to follow the rules of storage listed below.

I. Label all chemicals, in both primary and secondary containers.
II. Physically separate incompatible chemicals. Incompatible chemicals are ones that react or create dangerous conditions when mixed.
III. Separate chemicals by hazard class.
IV. Date all chemicals when received and opened. Have expiration date clearly labeled on container. Never ignore a chemicals expiration date.
V. Keep chemicals out of direct sunlight for a prolonged period of time.
VI. Keep emergency exits and walkways free from stored materials (Geary, n.d.).
VII. Keep up-to-date inventory of all chemicals on-site.
VIII. Store chemicals at or below eye level for easy access
IX. Ventilate any storage areas that require it (UCDavis Safety Service, 2018).

An SDS should provide details on how to properly store any chemical.

2.2 Incident Under Investigation

The reaction that this project is modeled after is an actual incident that happened at a local chemical company in Marlborough, MA on December 14th, 2010. On that day, a 55-gallon HDPE drum, partially filled with furfuryl alcohol, became over pressurized and exploded. Unknown to the engineers, some contaminant made its way into the drum which resulted in an exothermic reaction causing the drum to deform, shown in Figures 1 & 2. The heat produced by the reaction combined with the over pressurization caused the explosion. The drum was located in the "material preparation" or storage area of the plant, seen in Figure 3.

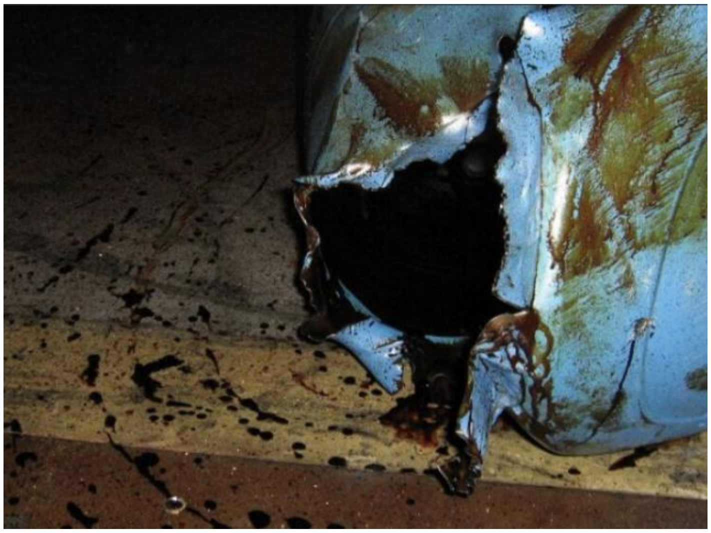


Figure 1. Hole caused from explosion of drum.

Figure 2. Over pressurized and overheated drum aftermath

Figure 3. The area of the plant where the accident occurred.

An incident of this magnitude resulted in a flurry of research and questions surrounding current operations and procedures for the plant. At the time of rupture, the drum was propelled 35 feet into the air where it hit the ceiling. A sticky black resin was sprayed in the immediate area of the accident. Thankfully, no people were hurt. Production in the plant was put on hold so a proper investigation could be conducted to find the root cause of the accident. The fire department was called to ensure the facility was safe.

The investigation revealed that a hand-pump was contaminated with trace amounts of methanesulfonic acid. This acid reacted with the furfuryl alcohol. A timeline of events was created by Prof. Stephen Kmiotek, who participated in the immediate accident investigation.

Table 1: Timeline of events the day of the accident (Kmiotek, n.d.).

Time	Event Description
12:00	Quantity of alcohol pumped into new, unused, clean drum for later use in a batch using previously used hand pump labeled “furfuryl alcohol.”
13:40	Drum ruptured; building evacuated. Fire Department arrives. At this time, the identity of the material is not known.
14:10	Entry teams (Level A) enter the area, collect air samples, take pictures. Identify the material. FD provides back-up. Team determines conditions are stable and the area is safe.
15:10	Building reopened and FD departed. Incident Commander established clean-up procedures. Teams re-enter, wash all affected areas with water. Ruptured drum isolated and bagged for future study. Contaminated disposable equipment discarded. Walls and major equipment brush-cleaned.
15:30	Operators in the general area interviewed.
19:00	All areas cleaned and the building turned back over to production.

2.3 Applicable Codes

Safety regulations were implemented into production and storage facilities to keep both citizens and employees safe. Safety codes and regulations all aim to minimize chances of hazardous situations. The main organizations that have implemented safety measures are the Environmental Protection Agency (EPA), National Fire Protection Association (NFPA), and the Occupational Safety and Health Administration (OSHA). Each of these institutions has released information with regards to storing and protecting hazardous or explosive materials. There are also specific regulations on furfuryl alcohol.

OSHA sets guidelines and regulations on chemical usage in industry. OSHA says that furfuryl alcohol is classified as a toxic chemical. Furfuryl alcohol can cause damage if inhaled or allowed to contact the skin. Repeated or prolonged contact can cause a skin rash, dryness and redness. Contact with the eyes can severely irritate and burn, leading to eye damage. Inhaling furfuryl alcohol can irritate the nose, throat and lungs causing coughing, wheezing and/or shortness of breath. Higher exposure may affect the nervous system causing headache, dizziness, nausea and even passing out.

OSHA also regulates exposure limits for employees in order to protect long term health. There are different levels of workspace exposure limits, depending on the amount of time around furfuryl alcohol. OSHA classifies the legal airborne permissible exposure limit (PEL) to be 50 ppm averaged over an 8-hour work shift. The National Institute for Occupational Safety and Health (NIOSH) recommends an airborne exposure limit of 10 ppm averaged over a 10-hour work shift and 15 ppm not to be exceeded during any 15-minute work period.

OSHA has also defined the necessary personal protective equipment (PPE) required when handling specific chemicals or materials. It is required by law that companies must follow OSHA guidelines in order to keep the public and their employees safe. 1910.132(a) states that

“Protective equipment, including personal protective equipment for eyes, face, head, and extremities, protective clothing, respiratory devices, and protective shields and barriers, shall be provided, used, and maintained in a sanitary and reliable condition wherever it is necessary by reason of hazards of processes or environment, chemical hazards, radiological hazards, or mechanical irritants encountered in a manner capable of causing injury or impairment in the function of any part of the body through absorption, inhalation or physical contact.”

The EPA was instituted by the US government with the simple goal of regulating policies to protect our environment. The EPA has instituted acts for the control and disposal of toxic substances like furfuryl alcohol. The Toxic Substances Control Act (TSCA) was created by the EPA in 1976 with the goal of regulating the introduction of new or already existing chemicals. When the TSCA was created, all existing chemicals were considered to be safe for use and subsequently grandfathered in. Before a “new chemical” can be utilized in industry, a pre-manufacturing form must be sent to the EPA for review before use.

The EPA also has a major focus on disposal efforts for hazardous materials, such as furfuryl alcohol. The EPA classifies a hazardous waste as “waste with properties that make it dangerous or capable of having a harmful effect on human health or the environment.” Hazardous wastes are created in various industries and must be properly controlled and disposed of in order to protect the public.

To protect the public and hold industries accountable, the Resource Conservation and Recovery Act (RCRA) was created. The RCRA gives EPA the authority to control hazardous waste from the "cradle-to-grave." This includes the generation, transportation, treatment, storage and disposal of hazardous waste. To achieve this, EPA develops regulations, guidance and policies that ensure the safe management and cleanup of solid and hazardous waste, as well as programs that encourage source reduction and beneficial reuse. Subsection C specifically deals with hazardous waste. To encourage safe disposal efforts, the EPA created an easy to follow flow diagram, as shown in Figure 4.

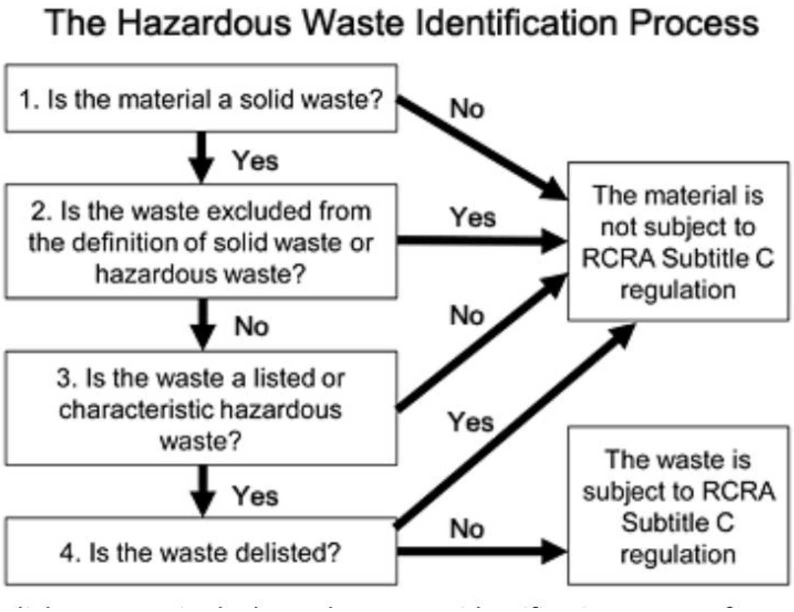


Figure 4. RCRA Subsection C flow diagram.

Another group called the National Fire Protection Agency (NFPA) has published a set of codes and standards to aid in fire suppression and fire safety. The NFPA has released more than 300 codes that are utilized in various industries. Some applicable codes are:

I. NFPA Code 1- Fire Code
II. NFPA Code 3 - Standard for Commissioning of Fire Protection and Life Safety Systems
III. NFPA Code 30 - Flammable and Combustible Liquids Code
IV. NFPA Code 33 - Standard for Spray Application Using Flammable or Combustible Materials
V. NFPA Code 45 - Standard on Fire Protection for Laboratories Using Chemicals
VI. NFPA Code 56 - Standard for Fire and Explosion Prevention During Cleaning and Purging of Flammable Gas Piping Systems
VII. NFPA Code 69 - Standard on Explosion Prevention Systems
VIII. NFPA 400 Code - Hazardous Materials Code
IX. NFPA 495 Code - Explosive Materials Code

A relevant code to this accident is the NFPA Code 69 - Standard on Explosion Prevention Systems. This code provides basic instructions to engineers, and other applicable personnel, on operating errors or flaws that could lead to an explosion or other accident. Codes are structured by chapters in order to make them more organized and easier to read, in turn making compliance more likely. Code 69 goes into different definitions and types of explosions in the initial chapters, and later addresses how each can be counteracted in later chapters. The term internal deflagration (explosion inside a vessel causing an explosion) is noted in Chapter 4, and then prevention measures are later addressed in Chapter 13.

2.4 Overview of Reactants

2.4.1 Furfuryl Alcohol

Furfuryl alcohol (FA) is a furan substituted with hydroxymethyl. Figure 5 shows the structure of FA.

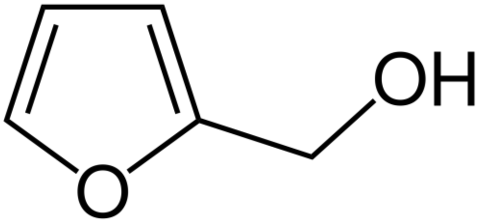


Figure 5. Furfuryl alcohol (Structural formula of furfuryl alcohol, n.d.).

At normal temperature and pressure, FA is a clear, colorless liquid. FA boils at 171°C and melts at -31°C (U.S. National Library of Medicine, n.d.). FA is miscible in water, ethanol, acetone, and most organic solvents (Kottke, 2005; McKillip & Sherman, 1978). FA is a possible carcinogen and is naturally present, in very small quantities, in several foods including wine, pineapple, and coffee (National Coffee Association, n.d.). The largest industrial use for furfuryl alcohol is as a monomer in the production of furan resins (see “Poly furfuryl alcohol”).

FA is typically synthesized by the hydrogenation of furfural. Furfural is typically produced by the dehydration of pentose sugars from lignocellulosic biomass (i.e., dry plant matter) (Adams & Voorhees, 1921). By these steps, FA and its polymers can be produced by "waste" biomass including corn cobs and oat hulls. In fact, Quaker Oats led the charge to industrially develop FA in the early twentieth century when they began to mass-produce the chemical from oat hulls (Brownlee & Miner, 1948).

FA is attractive as a monomer, in part, because it is non-petroleum based. FA, sourced from waste biomass, allows rich, renewable polymer chemistry. See 2.4.1 Poly Furfuryl Alcohol for uses for polymers of FA.

2.4.2 Poly Furfuryl Alcohol

Polymerized furfuryl alcohol is named, understandably, poly furfuryl alcohol (PFA). PFA, also called furan resin, is formed by the acid-catalyzed polycondensation of FA. Two reaction paths are possible, as shown in Figure 6, leading to two different repeating monomer units.

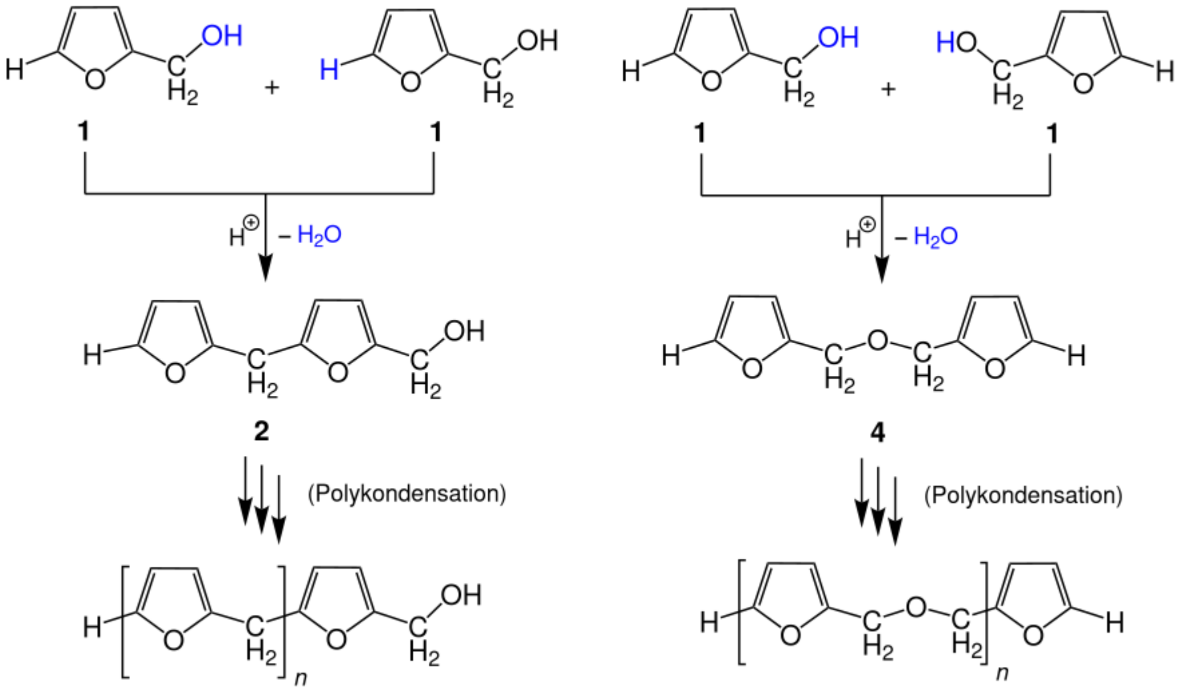


Figure 6. Reaction paths of polymerization of FA (Übersichtsreaktionen von Veretherung und Kernkondensation von Furfurylalkohol, n.d.).

Chains of furfuryl alcohol are expected to be colorless, but colorless polymers are not observed (Choura, Belgacerm, & Gandini 1996). The polymers are colored because they are not strictly linear but are also crosslinked (Choura, Belgacem, & Gandini, 1996). Crosslinking occurs when terminal hydroxyl groups react with double bonds outside of furan units. The polymerization of FA into PFA can be inhibited by the addition of sodium hydroxide; partially polymerized PFA is a viscous brown liquid. Fully cured PFA is a brittle black solid. PFA is highly resistant to acids and bases (Biron, 2014). Additionally, PFA has high thermal resistance and low flammability (Biron, 2014).

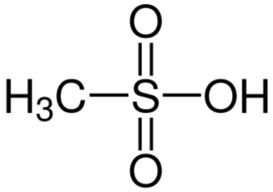
For its thermal and chemical resistance, PFA has namely two industrial applications. First, PFA is used as a binding agent for sand in foundry molds. By sand casting, molten metal is poured into a negative of the object in sand (Falco, Guigo, Vincent, & Sbirrazzuoli, 2018a). Second, PFA is used to reinforce wood. The low molecular weight of furfuryl alcohol allows it to penetrate the wood when it cures into PFA (Falco, Guigo, Vincent, & Sbirrazzuoli, 2018a).

Furan NO-BAKE, Furan HOT BOX, and Furan SO2 are brand names for furfuryl alcohol products to bind foundry sand (IFC, n.d.). Furan NO-BAKE is a furfuryl alcohol-based binder that uses sulfuric, sulfonic, or phosphoric acids as a catalyst (IFC, n.d.). Furan HOT BOX is like Furan NO-BAKE but is catalyzed by milder acids under higher temperatures (IFC, n.d.). Furan SO2 is catalyzed by SO_2 gas and is used for the fast production of small molds (IFC, n.d.). Furfuryl alcohol can be catalyzed by any acid, but few acids are used in practice (Zhang et al., 2014). P-xylenesulfonic acid is a typical acid catalyst used in Furan NO-BAKE, and Furan NO-BAKE binders release significant hazardous air pollutants (Zhang et al, 2014). Aromatic pollutants from Furan No-BAKE binders are thought to originate from the p-xylenesulfonic acid catalyst itself. For that reason, Zhang et al. explored the use of a nonaromatic sulfonic acid catalyst in the production of furan resins. The group found they could achieve a polymer of similar characteristics and fewer hazardous emissions by using methane sulfonic acid as the catalyst (Zhang et al., 2014).

FA also forms oligomers, chains of PFA only a few units in length. These oligomers form rather spontaneously (i.e., without the addition of an acid-catalyst). The year-old bottles of FA left by the previous MQP team were evidence of oligomer formation. While pure FA is clear, our year-old FA had an amber color, indicative of the presence of oligomer chromophores.

2.4.3 Methanesulfonic Acid

As stated before, PFA is produced by the acid-catalyzed condensation of FA. Methane sulfonic acid (MSA) does not necessarily have to be the acid-catalyst; any number of acids would suffice. We studied MSA because it was the acid that catalyzed the runaway reaction of interest. Figure 7 shows the structure of MSA.



$H_3C-S(=O)_2-OH$

Figure 7. Methane sulfonic acid (Structural formula of methanesulfonic acid, n.d.).

At normal temperature and pressure, MSA is a clear liquid (Lide, 2008). MSA melts at 20°C (Lide, 2008). MSA is nonvolatile; its boiling point under vacuum (10 mm Hg) is 167°C (Lide, 2008). MSA is soluble in water and ethanol (Lewis, 2007; Lide, 2008). MSA is favored as an acid-catalyst in organic chemistry due to its low volatility and solubility in organics. Also, MSA is an acid in which many salts are soluble, which makes its useful in the electroplating of tin-lead soldiers (Gernon, 1999).

2.4.4 Hydrochloric acid

Hydrochloric acid (HCl) is a strong acid. Anhydrous HCl is a colorless or slightly yellow gas at room temperature (U.S. National Library of Medicine, n.d.). HCl is completely soluble in water, and solutions of HCl are clear (U.S. National Library of Medicine, n.d.). HCl boils at -85°C and melts at -114°C (O'Neil, 2013).

HCl is a commodity chemical with many industrial uses. HCl is sold as “muriatic acid” in hardware stores for general cleaning, swimming pool treatment, and masonry. HCl is also used to remove rust and scale from steel and as a reagent in organic and inorganic chemical synthesis.

2.5 Reaction Kinetics

2.5.1 Rate Laws

Reaction kinetics concern the rates at which chemical reactions occur. By the law of mass action, the rate of a chemical reaction depends only on the concentrations of the substances involved when temperature is maintained constant (The Rate Law, 2019). Dependence may include the concentrations of reagents, products, and/or catalysts. A rate law expresses a reaction rate at a given temperature as the product of a constant and the exponentials of the concentrations on which the rate depends. In rate law expressions, rates are expressed in dimensions of amount per unit time per volume, typically: mol/L-s. Concentrations are expressed as mol/L. The dimensions of the constant, k, depend on the exponents of the concentrations. Equation 1 is a general rate law.

$$\text{rate} = k\,[A]^a[B]^b \qquad (1)$$

For the rate law expressed by Equation 1, the reaction it describes depends on the concentrations of components A and B; the bracket indicates that the quantity is a molar concentration. The reaction is said to be in the order of a + b. For instance, if a = 1 and b = 2; then the reaction is third order. The reaction is said to be in first order with respect to component A and is in second order with respect to component B.

The rate constant k has dependence on temperature, frequency and orientation of collisions, and the activation energy of the reaction. Equation 2 is the Arrhenius equation that defines the rate constant.

$$k = A \times e^{\frac{-Ea}{R\,T}} \qquad (2)$$

In Equation 2, A is the frequency factor, a pre-exponential factor that describes the frequency and orientation of collisions (Clark, 2013). Ea is the activation energy in J/mol. R is the ideal gas constant in J/(mol-K). T is temperature in K.

2.5.2 Kinetics of the Polymerization of Furfuryl Alcohol

While furfuryl alcohol is regularly polymerized for industrial applications, relatively little information is available on the kinetics of this reaction. It is possible that producers of furan resins understand the kinetics very well but protect this information. It is also possible that these producers have not described the reaction kinetics well but, instead, make resins by heuristics: they do what works experientially. We told engineer and researcher Abe Noe-Hays that it was odd that so little information is available on the reaction despite its industrial prevalence. Abe replied, “They probably just have a recipe.”

It is understood that the reaction kinetics vary considerably depending on the type and strength of acid, presence of water, and temperature (Choura, Belgacem, & Gandini, 1996). It is also known that those conditions control what reactions occur when FA polymerizes. Choura, Belgacem and Gandini found that mild conditions may limit cross linking. Falco, Guigo, Vincent, and Sbirrazzuoli (2018b) found that the presence of isopropyl alcohol or water solvents favors ring opening, which results in a polymer that is less rigid.

Sun et al. (2017) studied the kinetics of the polymerization of furfuryl alcohol in aqueous solution. The group isothermally reacted FA with a sulfuric acid catalyst at temperatures between 30°C and 70°C. The group determined that the polymerization in aqueous solution was first order with respect to hydrogen ions and first order with respect to furfuryl alcohol (Sun et al., 2017). The group determined an activation energy of 64.2±5.9 kJ/mol and a frequency factor of 4.89 x 10^9 L/mol-min (Sun et al., 2017). This information together forms a rate law for the polymerization of FA in aqueous solution with sulfuric acid catalyst, Equation 3.

$$rate = -(8.15 \times 10^7)\, e^{\frac{-7721}{T}}\, [H^+]\, [FA] \tag{3}$$

In Equation 3, r is the rate at which FA is consumed in mol/L-s. This rate law is a function of temperature. The reaction is exothermic. Some of the heat evolved by the reaction increases its temperature, and some heat leaves the system into the surroundings.

2.6 Reactor Scale Up

To predict the behavior of the reaction in different scales, it was necessary to understand the equations that describe reaction rate and heat transfer.

2.6.1 Energy Balance

A familiar form of the conservation equation is as follows for our reaction:

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Generation} \tag{4}$$

$$\text{Accumulation} = -\text{Out} + \text{Generation} \tag{5}$$

In the case of the acid-catalyzed polymerization of PFA, the heat of reaction accounts for heat generation. Normally, the system is at least the same temperature as its surroundings, so there is no heat transfer from the surroundings into the system. The accumulation term is approximated by the heat associated with the increase in temperature of the system. Heat moves out of the system because it is warmer than its surroundings. Heat flux from the system consists of conduction to the floor/benchtop, convection from the container's walls and free surface, and the evaporation of water and PFA from the system.

To describe heat transfer from the system, we used an experimentally determined overall heat transfer coefficient, U. Heat transfer from the system is as follows in Equation 6.

$$Q_{loss} = U\, A\, (T - T_\infty) \tag{6}$$

In Equation 6, Q_{loss} is the heat removed from the system in W; U is the overall heat transfer coefficient in W/m^2-K; A is the surface area available for heat transfer in m^2; T is the temperature of the system in K, and T_∞ is the temperature of the surroundings in K.

To describe heat generated by the reaction, the reaction rate, the reaction volume, and the heat of reaction are multiplied as illustrated in Equation 7.

$$Q_{gen} = r\,V\,\Delta H \tag{7}$$

In Equation 7, Q_{gen} is the heat released by the reaction in W; r is the reaction rate in mol/L-s (see 2.5.2); V is the volume of the reaction in L, and is the heat of reaction in J/mol.

The energy accumulated by the system is approximated by its heat capacity as illustrated in Equation 8.

$$Q_{accum} = m\,cp\,(T - T_i) \tag{8}$$

In Equation 8, Q_{accum} is the heat gained by the system in Joules, m is the mass of furfuryl alcohol in grams; cp is the heat capacity of the system's contents (a combination of FA and PFA) in J/g-K; T is temperature of the system in K, and T_i is the initial temperature of the system in K. Combining the expressions above, the overall energy balance can be written in the following differential form, Equation 9:

$$\frac{dT}{dt} = \frac{V\Delta\mathrm{H}\,r\; - UA\,(T - T_\infty)}{Cp\,m} \tag{9}$$

2.6.2 Mass Balance

A familiar form of the conservation equation is as follows for our reaction. Equation 10, shown below, simplifies to Equation 11 as there is no flow of mass into or out of the system for our batch reaction.

$$\text{Accumulation} = \text{In} - \text{Out} + \text{Generation} \tag{10}$$

$$\text{Accumulation} = \text{Generation} \tag{11}$$

In the case of the batch acid-catalyzed polymerization of PFA, there is no mass flow into the system. The mass flow out, due to some evaporation of water and FA, was assumed to be negligible. The generation term consists of the rate of consumption of FA by the reaction and is equal to the change in the amount of FA in the system.

To describe the rate of disappearance of FA, the reaction rate and the reaction volume are multiplied, resulting in Equation 12.

$$N_{FA} = -r\,V \tag{12}$$

Where N_{FA} is the rate of disappearance of FA in mol/s; r is the reaction rate in mol/L-s (see 2.5.2); and V is the volume of the reaction in L.

The mass balance on FA can be written in the following differential form, Equation 13.

$$\frac{dn_{FA}}{dt} = -Vr \tag{13}$$

2.7 Previous Experimentation

In 2019, the chemical incident described above was the subject of investigation by a team of WPI undergraduate students under the guidance of their advisor, Professor Kmiotek. Katherine Charla, Christopher Cyr, Sarah McKeage, and Kelly Vodola studied the behavior of the polymerization of furfuryl alcohol catalyzed by methanesulfonic acid and hydrochloric acid. The team measured the temperatures and pressures generated by the reaction for the different acid catalysts and different amounts of acid. Their goal was to better describe the acid catalyzed polymerization of furfuryl alcohol to improve process safety recommendations for the handling of furfuryl alcohol in the chemical processing industry.

The team modeled the reaction using the COMSOL modeling software. The simulation seemed to well-represent the expected mass transfer; high density acid remained sunken at the bottom of the furfuryl alcohol. The model, however, did not describe heat transfer as well. In the simulation, furfuryl alcohol far from the acid reached sub-zero Celsius temperatures over the course of the reaction. The team recognized that this temperature is likely a result of the temperature of the solution providing the activation energy for the reaction; but the team understood that these temperatures are unlikely to occur and are not experimentally observed.

In addition to modeling, the team conducted wet experiments. They catalyzed the reaction in 100mL and 1 L steel vessels capable of maintaining pressure up to 75 psig (before safely venting). The team observed an induction period, where the reaction very slowly progressed before thermal runaway occurred. Their experiments show that the reaction is highly variable. The team observed induction or “incubation periods” ranging from 500 seconds to 2000 seconds for the same amounts of FA and HCl in the same reactor vessel. The team observed a maximum temperature of 170.5°C and a maximum pressure of greater than 75 psig in these wet experiments. The 2019 team did a good job of describing the reaction behavior, and suggested, among other recommendations, that we study the reaction rate to more quantifiably describe kinetics.

3.0 Methodology

3.1 Initial Experimentation

Initial experimentation was conducted to become familiar with the reaction, to establish safety procedures, and to identify aspects of the reaction to explore in future experimentation. Our first experiments were modeled after some of the tests completed by the previous MQP group.

To begin, we slowly added MSA in 0.1mL increments to 22mL of FA in a 50mL beaker until the reaction ran away and FA was rapidly polymerized. We recorded temperature using a thermometer and took a video of the reaction. We conducted the same experiment with 12 M HCl in place of MSA. HCl is a more readily available acid than MSA; the previous MQP team frequently used HCl as a surrogate for MSA. We conducted these experiments to learn the approximate time before running away for different amounts of acid.

Next, we tested how mixing may affect the reaction. Mixing has the potential to eliminate inconsistencies within the reaction. We conducted a side-by-side test, comparing mixed and unmixed reactions of FA and HCl in open beakers. Two 50mL beakers were placed side by side, each with 22mL of FA. HCl, 12M, was added to each beaker simultaneously. Acid was added in 0.1mL increments.

Our experiments and the work of the previous MQP team show that HCl and MSA, strong acids, catalyze the reaction at room temperature. Literature reports that any acid can be used to catalyze the reaction (Zhang et al., 2014). In the interest of safety, we sought to use the least hazardous reagents in our experiments. We performed an experiment to determine whether the reaction could be catalyzed by vinegar (i.e., dilute acetic acid) at room temperature. Similar to the first tests with MSA and HCl, we added 0.1mL increments of PICS 5% acidity white vinegar to 22mL of FA in an unmixed 50mL beaker.

There is a possibility that a base could cleave hydrogen from the hydroxyl group on FA and catalyze polymerization (Interview with C. Lambert, 2020). To determine whether a strong base could catalyze polymerization, we added 12 M NaOH in 0.1mL increments to 22mL FA in an unmixed 50mL beaker.

3.2 Ice Calorimetry

3.2.1 Determining Heat of Reaction

Ice calorimetry (IC) is an inexpensive and reproducible experiment to determine the heat of reaction. In IC, the amount of ice melted by a reaction reflects the heat evolved by that reaction.

In IC, a test tube and graduated pipette are pushed into a rubber stopper, resting in a beaker filled with ice water. That beaker is then suspended in a larger ice bath. With such a setup, the internal bottle maintains a temperature of 0°C as the ice and water are in equilibrium. Heat evolved by an exothermic reaction in the test tube melts ice in the inner beaker. The melting of ice changes the volume of the ice-water mixture, which causes a change in volume measured by a graduated pipette pressed into the stopper. Figure 8 shows the general setup for IC.

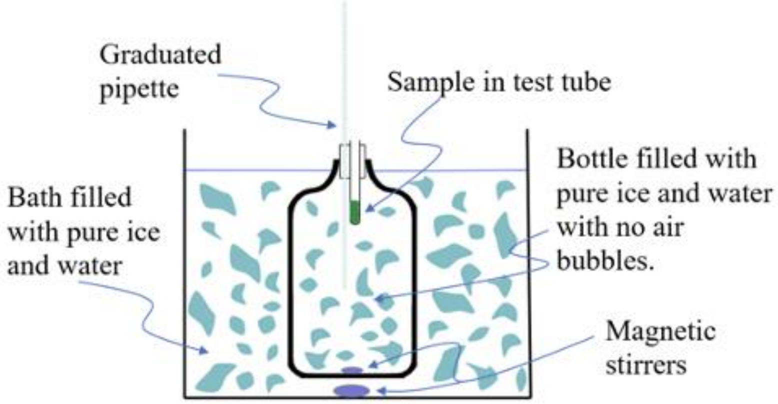


Figure 8. Basic IC Setup.

Total heat released (J) by the reaction can be solved for by using the following relationship, Equation 14:

$$Q = \Delta V * (\rho_{ice}/(1-\rho_{ice})) * (\Delta H_{fus}) \qquad (14)$$

In Equation 14, ΔV is the change in volume of the the pipette after ice melts (mL), ρ_{ice} is the density of ice (g/mL), and ΔH_{fus} is the heat of fusion of ice (J/g). Heat of reaction, expressed in either J/g or J/mol, can then be calculated by dividing the total heat released by either the mass or the total moles of reactants.

To conduct this experiment, we used a 1500mL beaker as the outermost container. We chose a glass beaker so we could see inside. Inside of this beaker was a large magnetic stir bar. This beaker sat on a stir plate and a ring stand. The ring stand was used to suspend the inner beaker, 100mL Berzelius style. The beaker was kept airtight by a size 11 rubber stopper. Inside of the beaker was a medium size stir bar. Holes were cut into the rubber beaker for the test tube (20mL) and the graduated pipette (2mL or 10mL). We initially used a 10mL graduated pipette but then switched to a 2mL once we realized the size of the volume change. To insert the glassware into the rubber stopper, we used glycerin as lubricant.

One key component of this experiment is to ensure that there were not air bubbles in the 100mL inner beaker. Air bubbles would affect the change in volume of water as when the escape it would seem as if more ice melted. To ensure this did not happen, the best way to seal the beaker was to submerge it completely in ice water. After first ensuring that the stir bar and sufficient ice was in the beaker, the beaker was inserted into a larger vessel of ice water so that the top of the beaker was below the water level. The rubber stopper, with the glassware already inserted in the top, was then pushed onto the beaker creating a seal. A visual inspection after this process was always completed to ensure that there were not air bubbles in the beaker. If there were bubbles, the rubber stopper was removed, and this process was completed until it was successful.

In the test tube, we first inserted 6mL of FA. Once the apparatus was set up, 0.1mL of HCl was added to catalyze the reaction. Acid addition was intended to be into the center of the test tube.

During experimentation, we used both larger ice cubes when we could not obtain crushed ice. We feel as though this variable affected the experimentation and would recommend that any future group use crushed ice for this experiment.

Additionally, to maximize heat transfer into the ice bath and not into the environment, we used a small stir bar in the 20mL beaker. Based on the distance between the test tube and the stir plate, we cannot say that the reaction was sufficiently mixed. Additionally, we would insert a small paper towel into the top of the beaker once the reactants were added. We hoped that the paper towel would keep heat in the beaker. A word of caution, as the experiment progresses, pressure builds up and will shoot the paper towel piece out of the beaker.

The starting temperature of the reactants was also taken into consideration. FA was inserted into the test tube and left in the apparatus until it reached 0^{o}C. HCl was kept on ice until it was inserted into the test tube. To be absolutely considerate of the starting temperature of the reactants, we put a micropipette tip in the freezer to ensure that it would not raise the temperature of the acid before it was inserted. If the starting temperature of the reactants is not 0^{o}C, ice will melt to bring the temperature to 0^{o}C thus adding error to the heat of reaction.

3.2.2 Determining Heat Capacity

In addition to the heat of reaction of the polymerization of FA, we used IC to determine the heat capacity of PFA. Except where specified otherwise, the setup and procedure of IC for heat capacity was the same as the setup for IC for heat of reaction.

The reaction is highly exothermic, so a relatively small volume of FA could cause a significant amount of ice to melt. Compared to the polymerization, relatively little heat is released from PFA as it cools. To accommodate this difference and determine the heat capacity of PFA, a few adjustments were made to the IC setup. These adjustments were made to maximize the amount of PFA in the inner test tube to release enough heat to measure a significant volume change of the melting ice.

In place of the 100mL inner beaker, we used a 1000mL Erlenmeyer flask and a large stir rod. This flask allowed us to press the test tube deeper into the stopper to fit more PFA in contact with the ice bath. We suspended the Erlenmeyer flask in a large stainless-steel pail.

We crushed samples of approximately five grams PFA using a stone mortar and pestle. Five grams was the maximum amount of PFA that could fit in the test tube while still sitting below the rubber stopper. We heated the samples to 100°C in a drying oven in ceramic crucibles.

Before adding the hot PFA to the test tube in the IC setup, we put approximately 7mL of chilled salt water in the test tube and allowed it to reach equilibrium (0°C) with the ice baths. The salt water served to conduct and convect the heat of the PFA to the walls of the test tube.

We added the 100°C PFA to the test tube and plugged the test tube with a piece of paper towel to limit heat loss through the top of the test tube. As with IC for the determination of the heat of reaction, the inner and outer ice baths were stirred by large magnetic stir rods. The test tube was not stirred as the pieces of PFA would prohibit stirring. We allowed the system to reach equilibrium.

In order to calculate the heat capacity, the specific heat formula shown in Equation 15 was used:

$$Q = m\, Cp\, \Delta T \tag{15}$$

In Equation 15, Q is heat (J), m is the mass of the substance (g), Cp is the specific heat capacity [J/(g^{o}*C)], and the ΔT is the change in temperature (^{o}C). Q was calculated using Equation 12 in Section 3.2.1.

3.3 Transfer Limiting Experimentation

Based on the inconsistencies observed in ice calorimetry, a series of different tests were conducted in order to better understand our curiosities of the mass and heat transfer within the reaction. Experiments were conducted that investigated mixing, acid addition technique, and the surface area to volume ratio of the vessel.

Our goal for conducting various mixing experiments was to see if we could manipulate mixing speed in order to more accurately predict the reaction time. When conducting experiments that investigated mixing, we used three different speeds of mixing that were controlled qualitatively between experiments. The three different speeds were a fast mixing, a slow mixing, and no mixing. Two separate mixing plates were used, one solely for fast mixing and one solely for slow mixing. These plates were set at the same rate of mixing every time so that the slow and fast rates are consistent across all tests.

In these mixing experiments, the amount of reactants added were controlled. Every experiment used 6mL of FA and 0.1mL of 12M HCl in a 20mL beaker. FA was added using a graduated pipette and HCl was added using a micropipette to ensure accuracy. Acid was dropped in the center of the beaker. All tests were conducted at room temperature at least three times. The no mix reaction was often quicker, so it was completed more. After the experiment, the beakers were cleaned out using acetone and then reused.

After the reaction, there were visible differences between the PFA that was produced in the slow mix and fast mix reaction. Because of this, a density test was conducted on both the slow and fast mix PFA. Density was determined by first taking its mass using a scale. Volume was found using water displacement since the volume of water is estimated to be 1g/mL. A 100mL beaker was filled to the rim when the PFA was inserted. A tray was around the beaker to collect the displaced water. The water was then weighed so that we could find the volume of PFA. Due to the surface tension of water and other areas of inaccuracies in this experiment, it was completed 10 times each. The same piece of PFA was used for each replicate of the test.

The method of acid addition was also investigated. Previously, acid was added into the center of the beaker. Still using a 20mL beaker with 6mL of FA and 0.1mL of 12M HCl, experiments were conducted by adding the acid down the side of the beaker. Acid was dropped from the micropipette onto the glass right above the FA liquid line. This test was completed for all three rates of mixing: fast, slow, and no mix.

All reactions were observed for a minimum 60 minutes unless they noticeably reacted quicker. A noticeable reaction would be due to thermal runaway. If thermal runaway did not occur, the viscosity of the PFA was measured using the level of mixing in the beaker. Once the acid was added, the liquid level was measured. As time progressed, the liquid level would continuously be measured until the 60-minute mark. This was conducted on most tests that did not react within the 60-minute time frame.

Lastly, tests were done in the 20mL, 50mL, 100mL, and 250mL beakers to investigate the volume to area ratio. Using the equations for area and volume of a cylinder, area directly relates to the radius of the beaker to the second power while volume directly relates to the radius to the third power. As beaker size increases, radius increases, thus the volume to surface area ratio increases. In each beaker, 6mL of FA and 0.1mL of 12M HCl was added. No mixing occurred and acid was added in the center of the beaker. Because of the explosiveness of these reactions, only one test in the 50mL, 100mL, and 250mL beaker were conducted. The 20mL tests were conducted earlier in duplicate when investigating mixing rates.

3.4 Overall Heat Transfer Coefficient

For a cooling vessel with no reaction, the rate of heat removal to the surroundings is equal to the change in energy due to the material's temperature (i.e., thermal heat capacity). Equation 16, taken from a WPI Unit Operations Lab experiment, relates the change in temperature to the overall heat transfer coefficient (DiBiasio, Clark, n.d.):

$$\frac{(T_\infty - T_o)}{(T_\infty - T)} = \exp\left(\frac{UA(t - t_0)}{Cp\ m}\right) \tag{16}$$

In Equation 16, T_0 is the initial (high) temperature in K; T_∞ is the temperature of the surrounding air in K; and T is temperature in K. Cp is the heat capacity in J/(g-K); m is mass in g; A is area available for heat transfer in m^2; and t and t_0 are time and initial time, respectively, in seconds. Equation 16 can be rearranged, giving Equation 17 below:

$$\ln\left(\frac{(T_\infty - T_o)}{(T_\infty - T)}\right) = \left(\frac{UA}{Cp\ m}\right)(t - t_0) \tag{17}$$

$$y = (\text{slope})\ x$$

A plot of $\ln\left(\frac{T_\infty - T_0}{T_\infty - T}\right)$ versus t is linear when plotted against $(t - t_0)$ (DiBiasio, Clark, n.d.). The slope of that line is given by $\left(\frac{UA}{Cp\ m}\right)$; so to divide slope by $\left(\frac{A}{Cp\ m}\right)$ gives U, the overall heat transfer coefficient.

To complete the energy balance in our system, we determined the overall heat transfer coefficient of FA. The overall heat transfer coefficient is the ability of a substance to transfer heat. In our experiment, the reaction is nearly all FA, so we assume that any acid or water is negligible.

Experimentally, determining the overall heat transfer coefficient is fairly simplistic. The only data needed is the change in temperature versus time. We did not want to exceed the boiling point, or the freezing point but that is less feasible, of FA during our test. To record temperature data, we used a homemade thermocouple out of an Arduino board. If our thermocouple was not working that day, we used a thermometer and a stopwatch to record times at a regular interval.

We completed heat transfer coefficient testing for a 20mL, 50mL, 100mL and 250mL glass beaker to see how the coefficient changed with vessel size. We also tested a 250mL HDPE (high density polyethylene) bottle as HDPE is a common material used to make drums that are used in the chemical industry. Each test in the glass beakers were heated until the FA reached about 110°C on a hot plate. We then moved the beaker to a stir plate at room temperature. We measured the temperature of the FA for anywhere over 15 minutes so that the temperature would drop below 60°C, an arbitrary value that we picked. We heated and cooled the same FA each time and added more when we scaled up to a larger beaker. In the HDPE bottle, we did not want to melt the plastic, so we heated the FA to about 70°C and then let it cool to below 50°C. Each test included the same speed of mixing; the stir plate was set at one speed that remained consistent across all tests. Qualitatively, the speed was similar to the slow speed in the transfer limiting experiments (Section 3.3). Comparatively, the 20mL beaker had the fastest stir and the 250mL beaker/bottle had the slowest.

We completed each vessel's experiment in triplicate. In the 20mL beaker, we used 15mL of FA. In the 50mL beaker, we used 40mL of FA. In the 100mL beaker, we used 80mL of FA. In the 250mL beaker and HDPE bottle, we used 200mL of FA.

The same methodology can be used to determine the overall heat transfer coefficient of PFA. To conduct this, once the reaction ran away, we measured the rate of cooling of the PFA. At this point in the reaction, it is assumed that all the FA has converted to PFA. The rate of cooling is then just for PFA which can then be used to calculate the overall heat transfer coefficient of PFA.

3.5 Mathcad Model to Predict Thermal Runaway

3.5.1 Overview of the Model

We built a Mathcad document to predict the behavior of a furfuryl alcohol and strong acid mixture over time. Rather than attempting to arrive at a single equation to predict behavior, we used Mathcad to simultaneously solve the differential mass and energy balances of the system. The mass and energy balance equations have a reaction term. Little information is available on the kinetics of the acid-catalyzed polymerization of FA, so we used the rate law for FA's acid-catalyzed polymerization in aqueous solution as the starting point for our reaction term (Sun et al., 2017).

We wanted to make the model as versatile as possible, so that a user could input different volumes of FA, volumes and concentrations of strong acid, container dimensions, container material, and starting temperature. To accomplish this end, the main calculation (i.e., the solving of the differential equations over a time period) is preceded by some algebra that puts the variables in a form that can be input into the differential equation. Consider, for instance, the volume of FA and the dimensions of the container. Heat transfer to the environment occurs over the area that the FA is in contact with the vessel's walls, not over the entire area of the vessel. One equation uses the FA volume, container diameter, and container height to find this area. The Mathcad document with some sample inputs can be found in Appendix A.

3.5.2 Simplifying Assumptions

We made some simplifying assumptions in our model. We assumed that the reaction rate was zero-order with respect to FA. Sun et al. (2017) determined a rate law that was first-order in FA, but the reaction they studied involved low concentrations of FA in aqueous solution. We decided on a zero-order rate in FA because FA is the bulk of our system. Rate dependence on FA may be fairly described as pseudo-zero-order where FA concentration is very high so that only hydrogen ion concentration limits rate.

We also assumed that the system was well-mixed. As previously described, we carried out some unmixed reactions; but the behavior of these reactions was very inconsistent. A well-mixed system allowed us to consider average species concentration rather than local species concentration, eliminating any mass transfer limitations to the reaction. A well-mixed system also eliminated the need to consider internal heat transfer. The well-mixed system could be described as an average temperature.

We assumed that heat transfer occurred over the walls of the container and its top surface by conduction through the walls and convection from the walls. We did not consider evaporation in our model. Furfuryl alcohol and water (a product of the reaction) have the potential to evaporate. The evaporation of these species would, of course, reduce the mass of the system.

Their evaporation would also remove energy from the system (i.e., evaporative cooling). For temperatures less than the boiling point of water, very little material evaporates; so the model will hold up well. We were most interested in studying the reaction up to the point of thermal runaway (approximately 70°C), so it was reasonable to not consider evaporation.

Lastly, we considered an average heat capacity of furfuryl alcohol. In reality, heat capacity changes with temperature; and the specific heat capacity of PFA is about half that of FA. As described in the previous paragraph, however, we can study the reaction fairly accurately up until thermal runaway. Before thermal runaway, the mixture is mostly FA; and changes in temperature are not extreme.

3.5.3 Experiments to Inform the Model

We fit our Mathcad model to experimental data to better predict reaction behavior. We conducted 27 trials of FA and HCl reactions in different amounts of each and in different containers. We chose highly varied conditions in the hope of producing a robust and versatile model. We varied FA volume from 10mL to 50mL. For each volume of FA its container, we experimented with three different amounts of acid in an attempt to create three very different reactions: a reaction that ran away, a reaction that did not run away, and a third reaction between the two. We chose those amounts of acid based on some initial experiments and an early iteration of the model.

We also experimented with “recycled” and fresh FA. Recycled FA was the FA heated and cooled during heat transfer coefficient experiments. We were initially concerned that the recycled FA would contain a greater amount of oligomers and less furfuryl alcohol monomer due to auto polymerization that occurs at high temperatures. Ultimately, we determined that there was no difference between reactions of fresh and recycled FA, so the two were treated without distinction in the analysis of experimental results and the construction of the model.

Appendix B contains a table with all experiment conditions. In each trial, we allowed the reaction to progress until runaway or as long as feasible if runaway did not occur during the period of observation. We recorded temperature over the course of the reaction using a thermocouple and Arduino logger.

We fit the model to experimental data using a pre-exponential factor in the rate law. This preexponential “fudge” factor essentially adjusted the rate law frequency factor, A. To determine the pre-exponential factor for a set of conditions (e.g., FA volume, vessel size), we entered those conditions into the Mathcad document. Then we iterated the calculation with different values for the preexponential factor until the times to runaway (defined as the time to achieve 80°C) matched for the model and experimental data. We iterated to determine the pre-exponential factors (on the order of 10) to hundredths decimal point accuracy. If runaway did not occur, we iterated to match the last recorded temperature.

3.6 Final Experimentation to Validate Mathcad Model

As stated in the Introduction, all experimentation and data collection ceased on March 6, 2020 by WPI and governmental mandates due to the rapid spread of pandemic caused by the COVID-19 virus. Therefore, our team was unable to carry out all the experiments that we had planned on. We planned on conducting experiments to validate our Mathcad model. We would first generate a predicted temperature profile of a novel combination of (1) HCl amount and concentration, (2) FA amount, (3) container size and material, (4) initial temperature. Then we would react FA according to those four parameters and collect temperature data. Lastly, we would compare our prediction to experimental data to gauge the accuracy of our model.

3.7 Analysis of Industrial Accident

We explored conditions akin to those of the industrial accident using our Mathcad model to gauge the model's accuracy and to attempt to work out details about the accident. With Mathcad, we modeled the reaction of FA in a half-full 55-gallon HDPE drum over a 24-hour period. We input 1 to 10mL of strong acid, the average and the high pre-exponential factors, and initial temperatures between 20 and 25°C.

4.0 Results and Discussion

4.1 Initial Experimentation of Open Beaker Reactions

We reacted MSA and FA in an unmixed beaker, as shown in Figure 9.

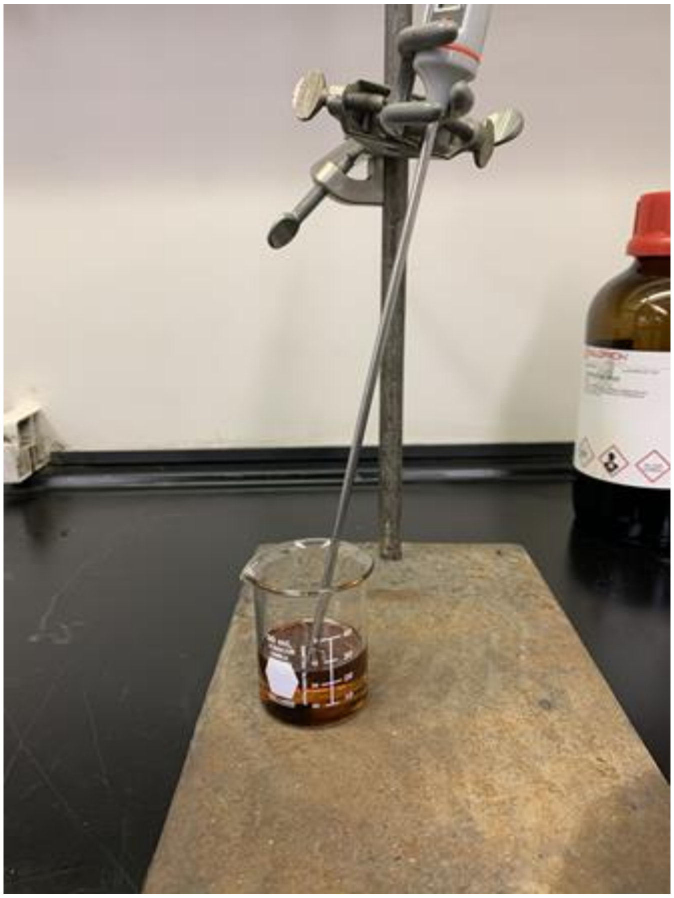


Figure 9. Initial open beaker experimental setup, 50mL beaker, 22mL of FA, 0.7mL of MSA.

The two goals of this experiment were to learn about the temperature profile of a runaway reaction, which contained 22mL of FA, and to approximate the amount of acid required to initiate the runaway reaction (by incrementally adding acid) for the given volume of FA. We plotted the temperature profile of the reaction, as shown in Figure 10. After the acid was added at the start of the reaction, the temperature climbed by 1℃ approximately every sixty seconds from 0 - 1000 seconds. The reaction did not show signs of runaway until 2,500 seconds and reached a maximum temperature of 120.5℃. The reaction tended to increase by 1℃ every ten seconds between 2500-3200 seconds. After the maximum temperature was reached, the reaction began to cool. The reaction tended to decrease by 1℃ every twenty seconds between 3200-3400 seconds.

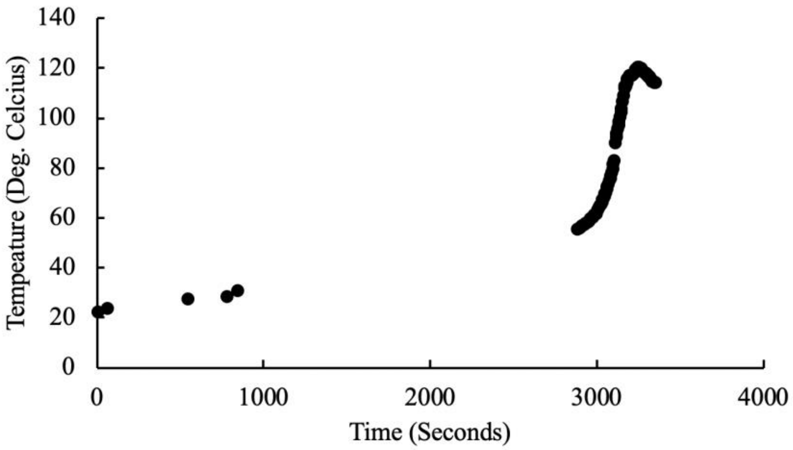


Figure 10. Temperature profile for the following conditions: 50mL beaker, 22mL of FA, 0.7mL of MSA.

Figure 11 is from the same FA and MSA reaction, but only shows the reaction runaway. Prior to reaction runaway, we observed that the reaction produces a vapor, some of which condenses on the walls of the beaker. The condensation (almost certainly water, a reaction product) became an indicator in future experimentation that the reaction was going to go to completion. For this individual experiment, 22mL of FA was catalyzed by 0.7mL of MSA and ran away in approximately 45 minutes. It is important to note that MSA was added in 0.1mL increments every five minutes. We added acid in 0.1mL increments in order to catalyze the reaction without overshooting the amount of acid necessary to cause thermal runaway.

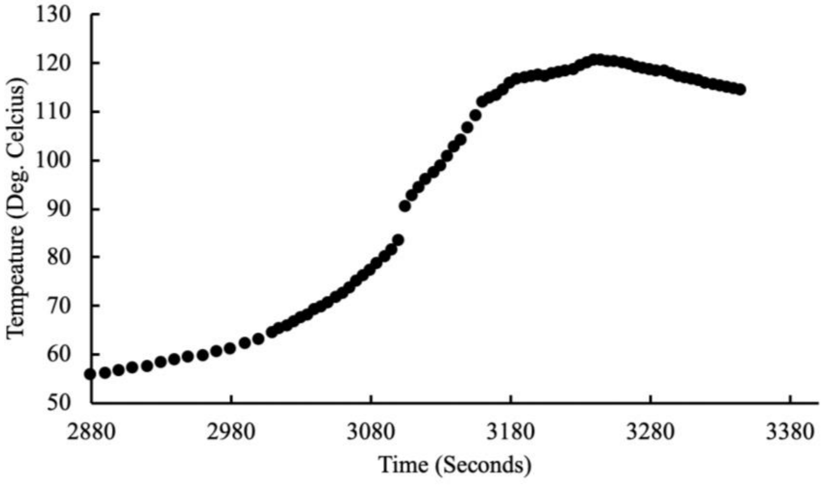


Figure 11. Profile of the exotherm for the following conditions: 50mL beaker, 22mL of FA, 0.7mL of MSA.

The second experiment used HCl as the catalyst. We set up the experiment in the same way for HCl as we did for MSA, as demonstrated in Figure 9. We observed similar characteristics in the two reactions. Both experiments had condensation on the side of the glassware prior to runaway. With both, the reaction increased in temperature over the course of several minutes, followed by an inflection and rapid increase in temperature to a maximum value of approximately 120°C. As the reactions cooled from their maximum temperatures, both polymers changed from a highly viscous resin to a brittle solid. One difference was the total volume of acid used. We used 0.5mL of HCl in experiment two, compared to 0.7mL of MSA in experiment one. It is important to note that acid was once again added in increments, but this experiment was not appropriately timed. Acid was added to the reaction at different intervals. Increasing or decreasing the rate at which these increments are added will impact the rate at which the reaction runs away. The HCl and FA reaction went to completion in 30 minutes, which was shorter than the MSA and FA reaction.

Based on inconsistencies in the time to runaway of previous reactions, we experimented with mixed and unmixed conditions side by side. Figure 12 shows the experimental setup and the unmixed beaker after it received its first 0.1mL increment of acid.

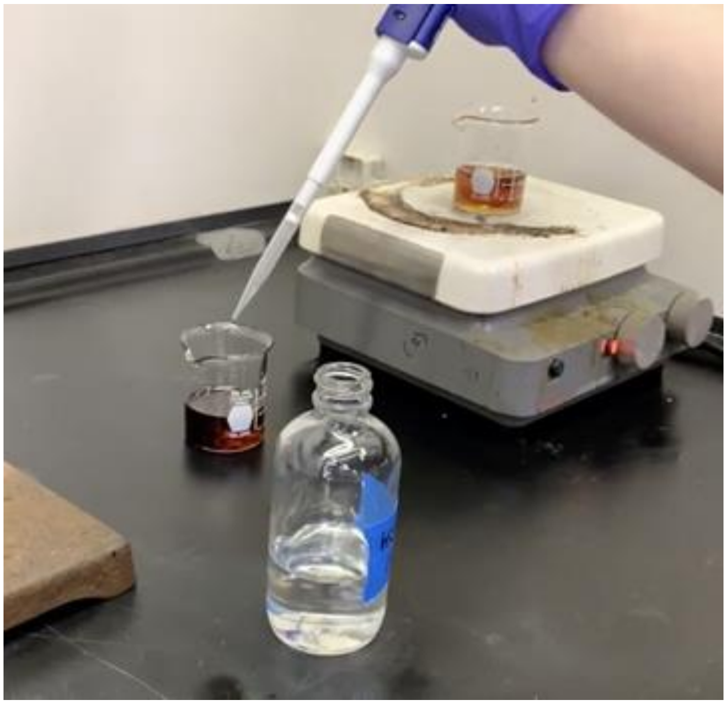


Figure 12. Mixed and unmixed reaction experimental setup.

We saw a noticeable color difference in the FA after the acid was added. The FA started as a light amber, and it became a dark amber as it began to polymerize. The unmixed beaker experienced a runaway at around four minutes, shown in Figure 13.

Figure 13. Mixed and unmixed runaway comparison, unmixed runaway (left).

This reaction was very similar to the previously described experiments. The reaction once again produced a vapor, which condensed on the walls of the beaker. The PFA was very porous after it solidified in the beaker. The mixed vessel experienced runaway at five minutes. When this sample erupted during runaway, the viscous PFA spilled over the walls of the beaker and onto the stir plate, shown in Figure 14. The sample hardened as it cooled.

Figure 14. Mixed and unmixed reaction comparison test, PFA spill-over in mixed beaker (right).

From this experiment, we learned that the reaction of MSA in FA can still be carried out under mixed conditions. Only one trial was conducted at this point in time. This experiment also demonstrated that the time to runaway was slower in the mixed beaker. From this single test, we speculated that the mixed reaction ran away slower because the act of stirring the solution had an effect on the mass or heat transfer of the reaction This test led to future experimentation on the rate of reaction for both mixed and unmixed solutions.

Any acid can carry out the polymerization of FA (Zhang et al., 2014). Our fourth experiment used a weak acid (acetic acid) in place of a strong acid (HCl or MSA). This experiment was conducted to avoid the use of more dangerous and corrosive reagents. We wanted to determine if a weaker and more dilute acid could still carry out the reaction. The HCl that we used in our other experiments was highly concentrated, 12 M. The concentration of our acetic acid was extremely low; we used a store-bought bottle of vinegar, which markets as 5% acetic acid per volume.

The acetic acid was added in 0.2mL increments to the FA. After several milliliters of acetic acid were added, we waited approximately 30 minutes and no noticeable reaction occurred. We concluded that the acetic acid we used was too dilute to carry out the reaction. If this test were to be replicated, it is recommended that a higher concentration of acetic acid should be utilized to carry out the reaction.

We attempted to initiate the runaway reaction with a strong base instead of an acid. We speculated that the base might be able to cleave a hydrogen from the hydroxyl group to promote polymerization. The addition of 0.1mL increments of 12 M NaOH into 22mL of FA did not result in runaway. The solution became slightly darker indicating that some polymerization did occur. Additionally, the beaker did not display any of the indicators of runaway, as demonstrated in reactions with acid catalysts.

4.2 Ice Calorimetry

4.2.1 Determining Heat of Reaction

Figure 15 shows the setup for the determination of heat of reaction.

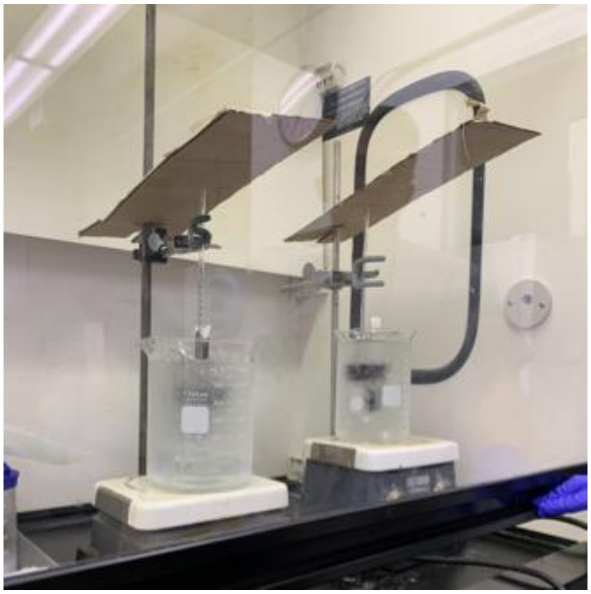


Figure 15. Heat of reaction setup.

We conducted several trials for the determination of heat of reaction. All experimental results are shown in Table 2. Example calculations to determine the experimental heat of reaction are found in Appendix C.

Table 2. Heat of reaction experimental results.

Trial	ΔV (change in pipette volume) [mL]	Heat of Reaction (unadjusted) [J/g]	Heat of Reaction (adjusted) [J/g]
1	0.83	-540	-772
2	0.56	-365	-521
3	0.292	-190	-272
4	0.84	-547	-781
5	0.57	-371	-530
6	1.45	-944	-1111
7	0.962	-626	-895
8	0.805	-524	-749
9	0.735	-479	-684

Trial 8 is an example of a successful experiment in which all of the FA is polymerized by a single charge of acid catalyst. Figure 16 gives the profile of the graduated pipette volume versus time for Trial 8.

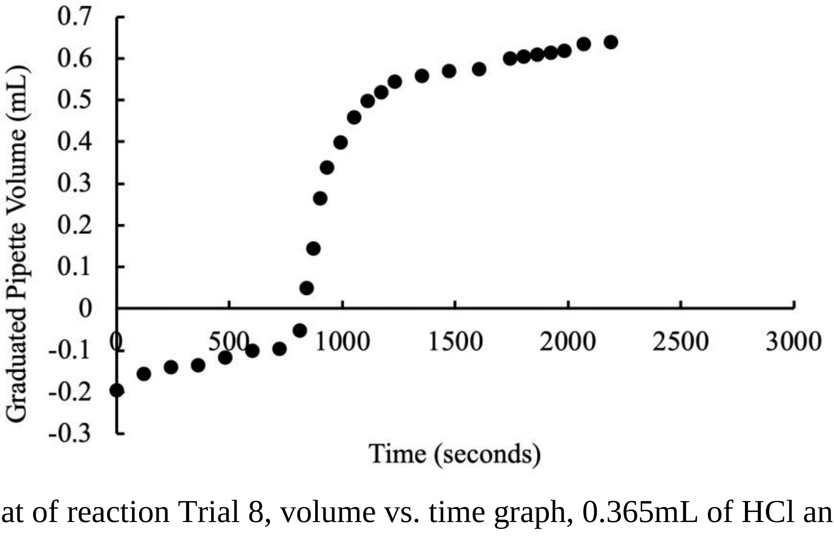


Figure 16. Heat of reaction Trial 8, volume vs. time graph, 0.365mL of HCl and 5mL of FA.

Three regions are shown on the graph above. Between 0 and 500 seconds, the volume slightly increased. It is important to note that as the actual volume in our apparatus decreases, the measured volume on our pipette increases due to inverted scale. This gradual and consistent volume change is because ice melted due to heat from the surroundings. This heat was conduction through the rubber stopper and through the test tube. These environmental effects were difficult to negate with our inexpensive setup.

After the pipette volume maintained a constant upward slope, we began the experiment. The addition of acid initiated the reaction and the temperature began to increase. Between approximately 700 and 1000 seconds, we observed the volume readings quickly increased. This is because the heat generated by the reaction melted more ice. We allowed the test tube contents to cool to 0℃ after the reaction took place. This reestablished the gradual increase in volume. The unadjusted heat of reaction values from Table 3 did not account for any heat loss to the surroundings.

We chose a value of 30% for our estimated heat loss factor. Heat loss is due to conduction through the stopper, conduction through walls of test tube upward, convection from uncovered surface of reaction, and evaporation. All trials and adjusted heats of reaction were assessed individually, to determine if the value was a good representation of the mean.

Trial 3 was an outlier because not all of the FA reacted. Its calculated heat of reaction was an underestimate. Trials 5 and 6 were also underestimates, but for a different reason from Trial 3. The capacity of our pipette limited the apparatus' volume in Trial 5 and 6. The water level in the pipette fell below the stopper. We recorded the lowest visible graduation, but it cannot be determined if this was the final volume because the reaction was still occurring. Trials 3, 5, and 6 were omitted from the average calculations.

The average heat of reaction (after corrected for heat loss) of FA was -734 ± 125 J/g. The limitations of the apparatus, as noted by the estimated heat loss factor, all contributed to heat loss that could not be accounted for in the heat of reaction equation. Post-accident, the incident investigation team estimated the heat of reaction for the polycondensation of furfuryl alcohol as -860 J/g (Kmiotek, personal communication on February 18, 2020). For comparison, the heat of polymerization of vinyl chloride is -964 J/g (D.E, Robert, Heats of Polymerization, n.d.). The similarity to FA's heat of polymerization to vinyl chloride leads us to believe that our experimental value is reasonable.

4.2.2 Determining Heat Capacity of Polyfurfuryl Alcohol

We also used IC to determine the heat capacity of PFA. Figure 17 shows the experimental setup.

Figure 17. IC apparatus setup for determining heat capacity.

Data from all trials are shown Table 3. A sample calculation to determine the experimental heat capacity of FA is found in Appendix D.

Table 3. Experimental Heat Capacities

Trial	ΔV [mL]	PFA Mass [g]	Q [J]	Heat Capacity, (Unadjusted) [J/(g-°C)]	Heat Capacity, (Adjusted) [J/(g-°C)]
1	0.0725	4.2173	267	0.632	0.703
2	0.0413	3.9538	152	0.384	0.427
3	0.1699	4.2075	625	1.486	1.651
4	0.1274	2.7896	469	1.680	1.867
5	0.7597	4.1053	624	1.521	1.690
6	0.0656	3.619	241	0.667	0.741

An example volume versus time graph is shown below as an example. Figure 18 shows the results of Trial 6.

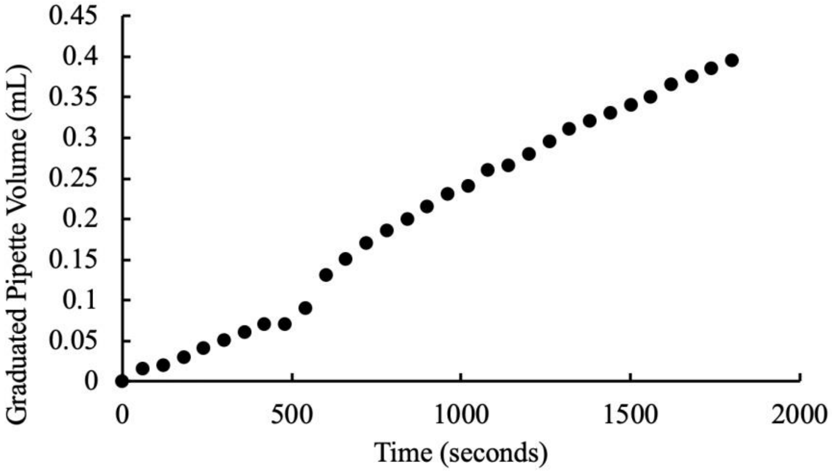


Figure 18. Heat capacity Trial 6, volume vs. time graph.

The volume was measured as the sample cooled down from 100°C to 0°C. Just like IC for heat of reaction, the heat from the PFA sample was transferred to the ice bath which melted ice. The heat exchanged is much less than the heat of reaction, so the slope is lesser. Between 0-500 seconds, the volume reading slightly increased as ice was melted from the heat of the surroundings.

The PFA sample was added when the volume interval read 0.075mL. After heated PFA was added and cooled, ice melted at a higher rate reflected in the greater slope between 500-600 seconds. Between 600-1800 seconds, the volume within the pipette began to return to the lesser slope similar to the start of the experiment. For Trial 6, the final pipette volume was 0.4mL.

The three regions are difficult to see, in comparison to heat of reaction, due to the low amount of heat exchanged in the experiment. We created Figure 19 to act as a model for the experiment, with exaggerated slopes to better explain the phenomenon seen during experimentation.

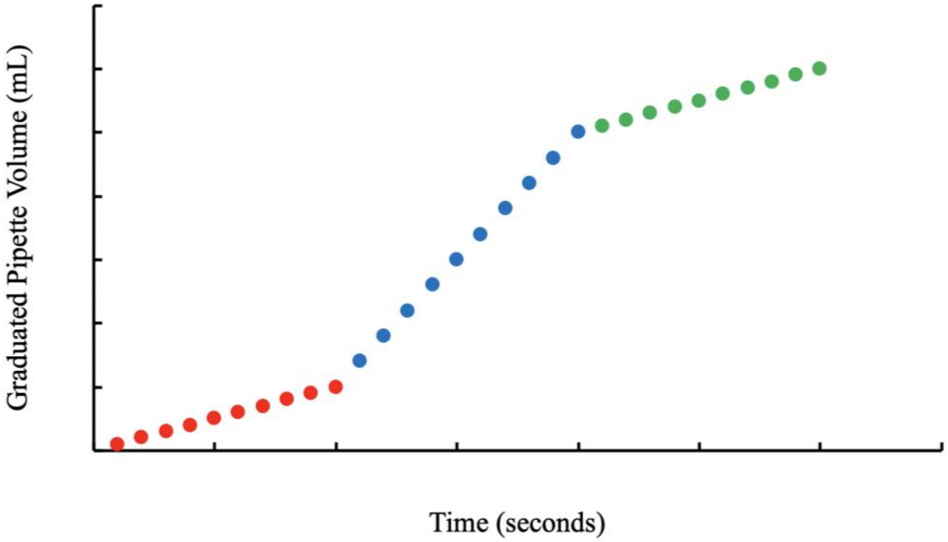


Figure 19. Theoretical heat capacity with exaggerated slopes.

Figure 19 is broken up into three sections, each with a corresponding color. The red section is the initial increase in volume found at the start of the experiment. This section has a very gentle slope because ideally, only a small quantity of ice has melted due to the heat from the surroundings. If the volume began to sharply decrease during this window of time, there was likely something wrong with the apparatus. Two common errors are a trapped air bubble within the inner vessel or that there was not enough ice in the outer vessel. If there is not a sharp increase in the volume, the experiment can be continued.

The blue section represents the addition of the heated PFA sample to the vessel. The addition of the sample caused ice to melt at a faster rate. This portion of the graph is exaggerated to better illustrate the change in slope. When conducted experimentally, this portion of the experiment lasted a few minutes because the sample was heated to 100°C. The green section is when the PFA has cooled to equilibrium with the ice (0°C), and the volume increase returns to its original rate.

We used the linear fits of the initial (red) and final (green) regions to determine the change in volume caused by the addition of the heated sample. Post experimentation, trend lines were fitted on to the graph to determine how much ice melted due to heat from the PFA. We plotted lines for the initial and final regions and subtracted their y-intercepts. This gives us the change in water volume (ΔV) in the pipette.

As for the heat of reaction experiments, we accounted for heat loss in our setup. We approximated 10% heat loss. Heat loss is due to conduction through the stopper, conduction through walls of test tube upward, convection from uncovered surface of the test tube, and any heat loss while the sample was transferred from the oven to the test tube.

Trial 2 was considered an outlier because of its low heat capacity. There was not enough salt water to cover the entirety of the PFA sample, which allowed for heat to escape out of the test tube and into the surroundings. Trial 2 was omitted from the average. It is important to note that heat capacity is typically a function of temperature, and our calculated value uses a known change in temperature of 100℃.

The average heat capacity (after adjusting for heat loss) was 1.33 ± 0.56J/(g-℃). We compared this value against other common plastics to see if our experimentally determined value was in the right order of magnitude. For comparison, PVC has a heat capacity of 0.88 J/(g-℃) at 0℃, and polyethylene has a heat capacity of 1.55 J/(g-℃) at 0℃ (Engineering ToolBox, 2013). The similarity of PFA's heat capacity to those of other polymers (approximately 1 J/(g-℃)) lead us to believe that our approximation is reasonable. The heat capacity of PFA is about half that of FA, a difference which informs an understanding about the rate of heat transfer in the reaction.

4.3 Mass and Heat Transfer Limiting Experimentation

In the first set of experiments, we varied the rate of stirring. We had three different speeds: fast, slow and no stir. Our setup is shown in Figure 20. The leftmost beaker was used for no stir and did not contain a stir bar. The middle beaker was the fast stir. The rightmost was the slow stir. Cardboard was used to contain any violent reaction and minimize the mess that was left in the lab hood.

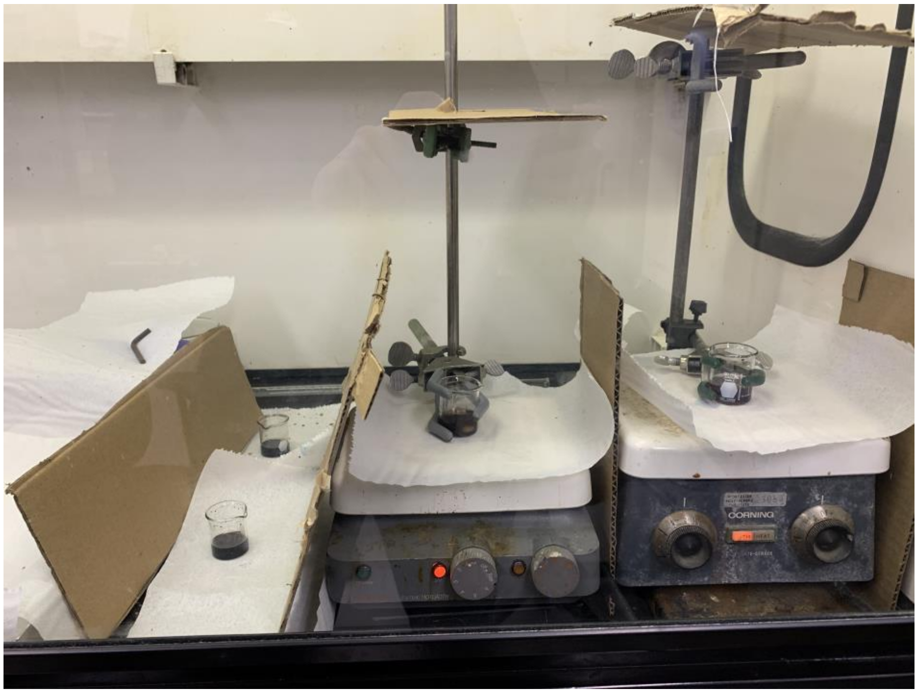


Figure 20. Experimental set up for changing the stir rate.

Reaction times from varying the stir rate are found in Table 4. The no stir reaction was unpredictable. In some cases, the reaction was instantaneous, in others the reaction did not run away for the hour that we conducted the experiment. The slow mix was the most predictable experiment. Every test that we conducted reacted to completion between 7 and 19 minutes. A 12-

minutes time prediction is far safer if we could estimate this in an industrial setting rather than having it be unpredictable. We speculate that when acid is added, it immediately catalyzes polymerization which is an exothermic reaction. When this occurs in the unmixed reaction, the heat can then speed up an adjacent reaction (increasing the temperature of a reaction will increase its reaction rate) or transfer into the environment. Heat transfers in the no mix reaction is unpredictable. In the slow mix, heat is transferred more consistently so the reaction is more consistent.

Table 4. Time elapsed before thermal runaway based on different stirring rates when acid is added in the center of the beaker

No Stir	Slow	Fast
No Runaway	18min, 30sec	12min, 30sec
8min, 15sec	12min, 36sec	13min, 31sec
Immediate Reaction	7min, 45sec	No Runaway
15min, 20sec	12min, 0 sec	No Runaway

Additionally, we must consider mass transfer in the reaction. Based on our results, we cannot hypothesize if the reaction is mass or heat transfer limited. Similarly to heat transfer, the way the acid transfers through the reaction will affect the temperature, based on the rate of reaction, which will affect the overall reaction rate. If the acid forms a pocket, it may not cause a reaction as shown in the first trial of the no stir. If the acid diffuses quickly based on the speed of it entering or the randomness of the reaction, it could react immediately as shown in the third trial of no mix. Mixing eliminates this randomness.

The fast stir reacted in a way that we did not know was possible. Prior to this experiment, we knew that some FA would polymerize when it came in contact with air. This is evident is the darker color of FA. But there was still enough FA present to react violently with acid thus causing thermal runaway. With a fast mix, the reaction often occurred at a controlled rate. The reaction did not run away, but after several hours, a hardened product is visible. To qualitatively measure this, we measured the height of the experiment in the beaker over time. As more reaction occurs, the mixture becomes more viscous because of the PFA, the height lowers. We found this result consistent in the two experiments where we measured height.

The method of acid addition may affect the reaction time if the reaction is not stirred. If the reaction is stirred, the mixing would prevent any inconsistencies with the mass or heat transfer. We conducted this test three times without mixing as shown in Table 5. In our limited sample size, none of the trials reacted immediately if acid was added down the side of the beaker. If it reacted, the time of the reaction is similar to when acid is added in the center of the beaker, about 12-15 minutes. Adding the acid down the side of the beaker limits how much acid and heat can transfer which can affect reaction rate. To make a more decisive claim, we could have conducted more tests adding the acid down the side of the beaker to see if it ever reacted immediately.

Table 5. Time elapsed before thermal runaway based on different stirring rates when acid is added down the side of the beaker.

No Stir	Slow	Fast
No Runaway	10min, 40sec	No Runaway*
15min, 30sec	N/A	13min, 0 sec
12min, 0sec	N/A	No Runaway*

*Represents that we kept track of height of reaction as time progressed

When the reaction took place in fast mixing and reacted without running away, the PFA was noticeably denser. There were no pockets for the vapor to escape during thermal runaway. The results of our quantitative density tests are shown in Table 6. Ten tests for each were completed because of the potential for error when filling the beakers prior to finding the water displacement of the PFA. Nevertheless, the experimental results matched what we predicted. The slow reaction created a PFA that was denser than the PFA that is created through the thermal runaway reaction. The slow reaction is closer to the density of industrial PFA that is estimated to have a density of 1.3-1.5 g/mL (Wang, Zheng, Zheng, 2011).

Table 6. Density testing of PFA where the slow reaction occurred in the fast mix and the fast reaction occurred during the slowly mixed sample.

Trial	Slow Reaction (solid piece) Density (g/mL)	Fast Reaction (vapor pockets) Density (g/mL)
1	1.26	1.065
2	0.903	1.313
3	1.35	0.7732
4	1.69	0.9562
5	0.910	0.78
6	1.15	0.81
7	1.23	0.74
8	1.48	1.041
9	1.38	0.978
10	1.13	0.852

During scale up on the industrial scale, it is dangerous because the rate of heat transferred into the environment is not linear with the amount of heat generated by the reaction. As vessel size increases, less heat is transferred into the environment thus cooling the product. This is why heat exchangers or other cooling options are necessary. This result was found when scaling up the reaction as shown in Table 7. While both the 50mL and 100mL beaker reactions had the same amount of reactants, they were qualitatively more violent than the 20mL size. Even though they reacted immediately, the amount of cracking and the intensity of the vapor bubbles increased as size increased. The 250mL did not run away because the volume of reaction was not enough. The 250mL beaker was too large in diameter for the FA to have a thin layer covering the bottom. Because of this, the acid formed a pocket in the beaker and was not able to mix with most of the FA in the beaker. We would expect that if it were not limited by this, the 250mL beaker reaction would have been the most violent.

Table 7. Time Elapsed before thermal runaway while varying glass beaker size. Stirring did not occur and acid was added in the center of the beaker.

50mL	100mL	250mL
Immediate Reaction	Immediate Reaction	No Runaway

Investigating heat and mass transfer confirmed the inconsistencies of the reaction that we found earlier. However, it told us that the mixing of the solution matters. If we mix rapidly, we can slow down the reaction to a rate that will not run away. This was completed in the 20mL beaker so there should be testing at larger sizes to see if this is feasible to do on the larger scale. Additionally, a slow mixed reaction would be the most predictable. When building a model to predict thermal runaway, it will be best to focus on a slowly mixed reaction as it will be the most accurate to predict.

4.4 Overall Heat Transfer Coefficient for Glassware and Plastic Containers

From our experiments conducted in triplicate, the overall heat transfer coefficient (U) of FA in varying vessel sizes and materials of construction can be found in Table 8. Data recorded utilized to calculate the overall heat transfer coefficient is found in Appendix E. A sample calculation is in Appendix F.

Table 8. Overall heat transfer coefficient of FA in glass beakers and a HDPE bottle.

	20mL beaker	50mL beaker	100mL beaker	250mL beaker	250mL HDPE bottle
Average U [W/(m^2*K)] of FA	17.3	14.9	14.6	14.7	15.5
Standard Deviation [W/(m^2*K)]	0.9	0.2	1.1	0.4	1.0

Our results were precise as they were all around 15 W/(m^2-K). This value is in the right order of magnitude as a liquid to gas overall heat transfer coefficient is estimated to be between 15-70 W/(m^2-K) (Engineers Edge, n.d.). Our system is liquid to gas because the heat is transferring from FA (the liquid) to the air (the gas). Being on the lower end of this range suggests that FA is not as good as transferring heat as other liquids.

A trend that is apparent in our results is that as the size of the glass beaker increases, the overall heat transfer coefficient decreases. In the beaker, heat is mostly lost through convective heat transfer through the glass or to the atmosphere. Additionally, since the mixing speed stayed the same, the internal velocity of the liquid will be less for the larger beakers. With a lower velocity, there will be less heat transfer which will result in a lower overall heat transfer coefficient.

The plastic bottle had a larger overall heat transfer coefficient than the glass beaker. This indicates that plastic is a better conductor than plastic. However, the plastic in our experiment was thinner than the glass, resulting in less resistance in plastic despite the higher per-meter conductivity of glass. In addition, the plastic bottle’s mouth was less than an inch while the glass beaker’s mouth was over two and one-half inches. Heat will more easily transfer to the air than through the sides of the vessel. With a bigger mouth we would expect more heat transfer, which is not what we found. Potentially, this difference could be due to the fact that we could not heat the FA up as hot in the plastic bottle so that we would not melt the container.

It is important to note that the thickness of our plastic bottle is not the same thickness of a drum used in industry. Our bottle is used in labs to hold water or acetone. Drums used in industry are thicker. If we wanted to be more accurate, we could complete more tests with different thickness HDPE plastic bottles and see how thickness correlates with the overall heat transfer coefficient. We predict that as thickness increases, the overall heat transfer coefficient will decrease.

4.5 Mathcad Model to Predict Thermal Runaway

4.5.1 Fit to Experimental Data

We determined pre-exponential coefficients between 8.8 and 20.1 when fitting our model to experimental data. We determined a coefficient for each unique set of HCl amount, FA amount, and container size. There was no clear relationship between the value of the coefficient and of HCl amount, FA amount, and container size. Because there was no clear relationship between the coefficient and these conditions, it was useful to also consider the average coefficient value in our simulations. The average coefficient was 13.9±3.5. Since this coefficient is greater than 1 indicates that the frequency factor for the rate law of the polymerization of FA in bulk is greater than the frequency factor for the rate law of the aqueous polymerization of FA. Therefore, there are more frequent reaction-favoring collisions of FA in bulk than when FA is dilute in water, as expected. Appendix G contains a table of experiments, their coefficients, and their approximated frequency factors.

The fit of our model was remarkably close to the experimental data for the experiments that informed the fit up until thermal runaway. Figure 21 shows the fit of a modeled reaction (20mL beaker, 10mL recycled FA, 0.2mL of HCl).

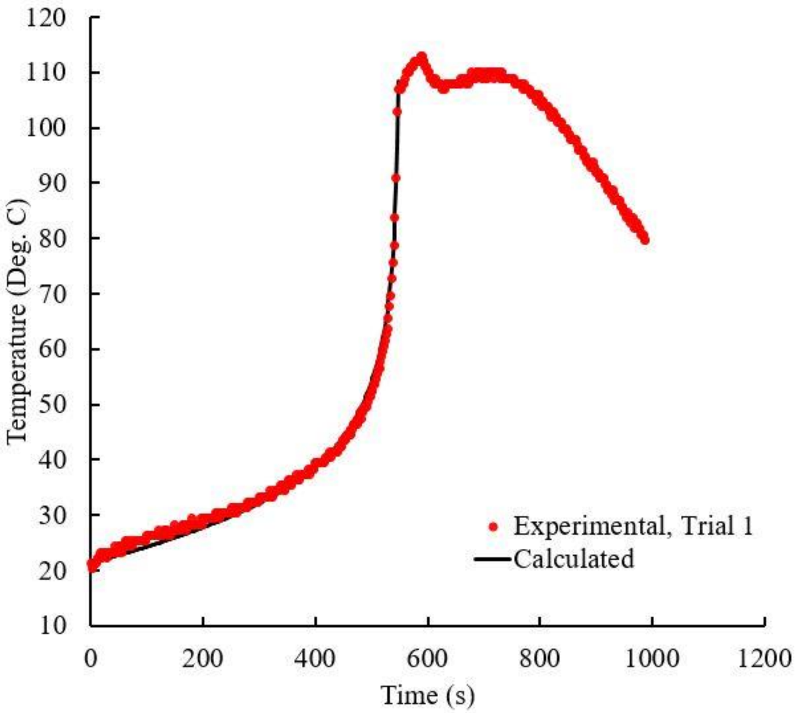


Figure 21. Experimental and calculated fit temperature profile for the following conditions: 20mL beaker, 10mL recycled FA, 0.2mL of HCl.

It should be noted that the graph above is a fit of our model to experimental data; it is not a prediction. The model's accuracy breaks down after the temperature reaches 100°C, as is expected given its assumptions (see section 3.5.2). After 100°C, the calculated temperature sharply increases to approximately 300°C. The model does not demonstrate the "double peak" observed in experimental temperature profiles. In experiments, temperature did not reach a single maximum before cooling but, instead, achieved a maximum; slightly decreased; and increased again to a local maximum temperature as shown above in Figure 21. The reason for this double peak is unclear.

In reality, evaporative cooling is significant at 100°C and above. The evaporation of water and FA from the beaker remove heat from the system that the model does not account for. Additionally, the model includes zero-order dependence on FA. At high FA conversion, dependence on FA is not zero-order. Nor is the system well-mixed at high FA conversion. At high conversion, the polymer is viscous; and there are almost certainly differences in temperature and concentration at different points in the system.

4.5.2 Capabilities

The model requires the following inputs from the user: initial temperature, FA volume, HCl volume, HCl concentration. The model also requires information on the container. The user inputs the diameter and height of a cylindrical container, and the user inputs the overall heat transfer coefficient on the container.

We measured the dimensions of and determined the overall heat transfer coefficients of a 20 L beaker, a 50mL beaker, a 100mL beaker, a 250mL beaker, and a 250mL HDPE bottle (see section 4.4). This data on the containers are built into the model. To type "U20" indicates to use the heat transfer coefficient of the 20mL beaker, for instance. The user could also enter the dimensions and/or heat transfer coefficient numerically to model a situation with a different container size or material.

Within the Mathcad document, variables are described, and instructions are included in plaintext (in blue). Arrows (in blue) indicated necessary inputs.

4.6 Final Experimentation to Validate Mathcad Model

As noted in 3.6 and the Introduction, all experimentation and data collection ceased on March 6, 2020 by WPI and governmental mandates due to the rapid spread of pandemic caused by the COVID-19 virus. We were unable to carry experiments to compare to our model. However, we conducted most experiments in triplicate and each individual trial tended to have a unique initial temperature due to day-to-day differences and because the stirring plate was warmed by preceding experiments. Although not ideal, we used duplicate and triplicate trials to compare to our prediction. For any set of conditions, the first trial informed the model fit that determined the pre-exponential coefficient. The second and/or third trial could be compared to a model determined by the first. Because there was no clear relationship between pre-exponential coefficient and reaction conditions, we also compared experiments to the model using the average coefficient.

The model seems to be a fair predictor of reaction behavior for the conditions that we experimented with on the benchtop-scale. Figure 22 shows the predicted temperature profile of a reaction (20mL beaker, 10mL recycled FA, 0.2mL of HCl). Figure 22 is our best prediction.

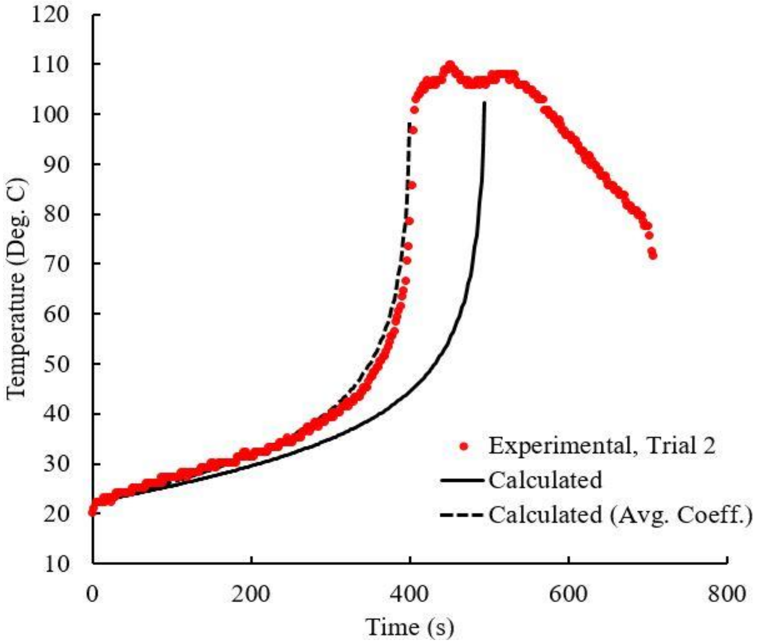


Figure 22. Experimental and predicted temperature profile for the following conditions: 20mL beaker, 10mL recycled FA, 0.2mL of HCl.

Figure 23 is a prediction and shows the predicted temperature profile of a reaction (50mL beaker, 30mL FA, 0.1mL HCl) that did not run away.

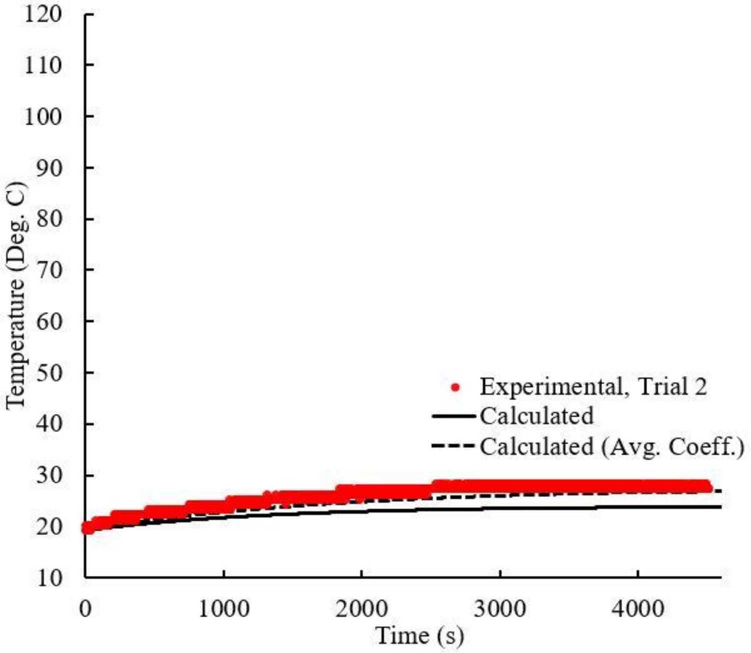


Figure 23. Experimental and predicted temperature profile for the following conditions: 50mL beaker, 30mL FA, 0.1mL HCl.

Figure 24 shows the predicted temperature profile of a reaction (100mL beaker, 50mL, 0.2mL HCl) and is our worst prediction.

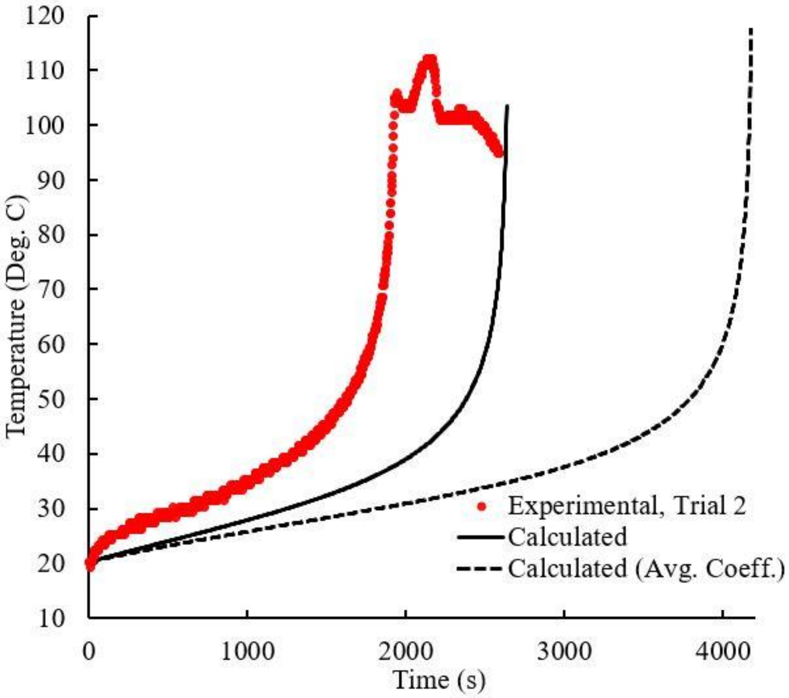


Figure 24. Experimental and predicted temperature profile for the following conditions: 100mL beaker, 50mL, 0.2mL HCl.

All models successfully predicted whether a reaction would or would not run away. For most models, the average pre-exponential coefficient created a more accurate prediction than the condition-determined coefficient. In addition to the best and worst predictions shown above, all comparisons of experimental data to predictions can be found in Appendix H. Please note, however, that the value of these predictions is limited. As noted in 4.5.1, the model is a good up to approximately 100°C and is not a good predictor of higher temperatures. Additionally, these models "predict" the behavior of reactions with sets of conditions nearly identical to those that generated the model. To carry out reactions with much different conditions (e.g., in a HDPE bottle rather than a beaker) would be a better measure of the accuracy of our predictions; but the COVID-19 pandemic resulted in the cessation of all experiments.

4.7 Analysis of Industrial Accident

With Mathcad, we modeled the reaction of FA in a half-full 55-gallon HDPE drum over a 24-hour period. We imputed 1 to 10mL of strong acid, the average and the high pre-exponential factors, and initial temperatures between 20 and 25°C. None of these models indicated thermal runaway. At most, the modeled temperature increased to approximately 30°C before leveling out then falling. Appendix I contains a Mathcad simulation for this study.

In reality, of course, the drum of FA reacted resulting in thermal runaway. It seems highly unlikely that the conditions of the incident were anywhere outside those that we tested (e.g., It is unlikely that more than 10mL strong acid entered the drum); so our model does not predict such a large scale up accurately. The simplification of our model likely limits its ability to accurately predict the behavior in the drum. The drum, for instance, was not well-mixed; it was not mixed at all. There were almost certainly areas of higher temperature where FA was reacting due to the small amount of acid contaminant. Areas of high temperature may have induced the auto polymerization of FA (a phenomenon that we observed in lab). Auto polymerization would generate more heat and propagate the reaction despite the low concentration and/or localization of acid. As previously noted, non-mixing, auto polymerization, and other effects are not present in the model. Changes in pressure are an example of one effect that is not present in the model because pressure has no place in non-gaseous rate expressions. Anecdotal evidence, however, suggests that the reaction may be sensitive to pressure (Cyr, Charla, Vodola, & McKeage, 2019). The absence of this effect and others and our simplifying assumptions limit the accuracy of the model's predictions for conditions that are very different from those directly studied by experimentation.

5.0 Conclusions and Recommendations

5.1 Mathcad Modeling

The Mathcad model is a good predictor for at least reactions with conditions like those we experimented with. With an average pre-exponential coefficient, we can predict whether a reaction of up to 50mL FA will run away. As previously mentioned, the model is a good prediction of reaction temperature up to approximately 100°C.

The model, however, has limitations due to its simplicity. For experiments with thermal runaway, predicted temperature increases higher than is experimentally observed largely because the model is of a closed system where no mass leaves. In the model, FA and water do not evaporate, a process that results in significant cooling in reality. Additionally, we assumed constant zero-order kinetics with respect to furfuryl alcohol but rate independence on FA is likely not the case for high conversion. At high conversion, PFA rather than FA dominates the reaction volume, and the concentration of FA likely limits the reaction rate.

We would be able to say with greater certainty how well our model predicts the behavior of benchtop reactions if we could conduct more experiments for comparison. These experiments would inform us on the robustness and versatility of our model. The COVID-19 pandemic, however, prevented us from conducting very different experiments to evaluate the model.

The Mathcad model also does not seem to be a good predictor of highly scaled up reactions without mixing. This shortcoming, we suspect, is because temperature and concentration are uniform throughout the reaction volume in both our model and in our mixed benchtop experiments. Such uniform concentration and temperature are unlikely to occur in a large unmixed container, such as a 55-gallon storage drum.

It may be possible to improve the Mathcad model, but changes would not be trivial. To add terms in the mass and energy balances that involve the vapor pressures of FA and water would allow for their evaporation to be considered. Vapor pressures are temperature dependent, of course, and to involve evaporation in the balances would introduce new variables (and possibly new differential equations) for the program to solve. The model may not survive the addition of evaporation terms; a few of our calculations could not converge to a solution, and our model as it seems to be near the upper limit of Mathcad's number-crunching ability. A wiser approach may be to use the program COMSOL, which is designed to efficiently perform calculations involving differential equations that model physical systems. Mass and heat transfer within the reaction volume may be modeled in COMSOL, eliminating the need to consider only mixed systems.

5.2 Process Safety Concerns

On an industrial scale, the best way to prevent an accident occurring from FA polymerizing is, of course, to keep it away from any acid or base. Our experiments show just how explosive and dangerous it can be on the small scale. On an industrial scale, it can only get worse. When both chemicals are onsite, it is best to inform all operators of the incompatibility of the reactants. Operators cannot prevent the combination if they do not know the dangers. Additionally, it is safer as well as more cost effective to use different pieces of equipment. The reaction occurred in industry previously because of contamination on a hand pump. It is best practice to use three separate pumps for acids, bases, and FA to avoid the reaction entirely. The effect of rinsing was not investigated, but it is evident that the consequence of not rinsing thoroughly is dangerous.

If both FA and MSA are used in a batch reactor, it will be necessary to charge them at separate times through separate piping units. One problem that occurs in batch reactors in reactant pooling which is when the reaction is not well mixed. If FA and MSA meet, they will form PFA which will be an unwanted side effect of the reaction. In addition to raising the temperature of the batch, the PFA will be sticky which could plug up or cause damage to equipment.

If PFA and a catalyst do end up mixing in a drum, the first step will be to clear the area around it. The reaction is unpredictable and if the drum is closed, the buildup of pressure is unknown. If it is safe to do so, for example the contamination of the FA drum just occurred, open the drum up in a vented area or in a place where respirators are required. FA is not to be breathed in directly. An open drum will prevent a buildup of pressure which will slow down the reaction. Next, add mixing to the drum, perhaps using an agitator. Pockets of polymerization form which spread throughout the drum. Mixing will prevent these pockets from forming. Then, add temperature tracking capabilities. From our experiments, the temperature rises slowly in the beginning but once it hits around 50^{o}C, it will be time to clear the area and prepare for an explosion. As long as the temperature remains below 50^{o}C, it should be safe to continue. Lastly, remove samples of the mixture to form lab-scale sizes and react them in a lab hood. Expect an explosive reaction in the hood so use proper PPE and blast shields. Since the drum is already contaminated, it is best to get rid of it safely by turning it into PFA. PFA can then be sent to a landfill as it is non-hazardous.

If contamination happens on a smaller scale in a lab, the same steps should be followed. Based on the size of the vessel, frequent checks with a temperature probe can be performed initially to make sure that thermal runaway is not occurring. Best practices are assuming the worst and being prepared for an explosion. If the vessel is glass, switching to a plastic bottle if the reaction is stable is recommended. To reiterate, the best way to avoid an explosive reaction is to keep the reactants separated in storage, usage, and disposal.

5.3 Future Experimentation

Overall, we explored many different aspects of this reaction, but there are still more areas that we could have pursued. We listed some key observations and recommendations that could be implemented into future projects.

Stopping the reaction: A safety instrument or chemical that could safely stop or detect an accident of this nature would be extremely beneficial to the chemical processing industry. From our experiments, we learned that volume and concentration of acid as well as reaction temperature play a key role in this reaction going to completion. If an HCl and FA reaction reached above 60°C, it began to rapidly heat up and run away Thus, further experimentation on the potential of stopping the reaction once it passes a certain temperature could be beneficial. If a device could detect this temperature and "pull an emergency switch", it would prevent an accident. We recommend first doing research on different chemicals that could prohibit further polymerization and then trying it in the small-scale in the lab.

Experimenting with weaker, or more dilute, acids: Although it was attempted in the beginning, we never fully explored the effects of weaker acids on FA. From our testing, only strong acids, like MSA and HCl, had the ability to make the reaction runaway. We tried a dilute acetic acid to initiate the reaction, but it did not work. One experiment could be using acetic acid at a similar molarity (12.5M) to what we used with HCl. Additionally, the concentration of HCl was not changed in any of our experiments. It would be safer to work with a less concentrated acid so that can be explored.

Go large scale (go big or go home): Our model has not been validated at larger volumes or vessels. In fact, due to COVID-19 we did not get to validate it at all. It would be exciting to do some larger scale tests to see if the model holds up. We made assumptions when building this model and are curious if they are accurate on a larger scale. Our largest volume ever tested against the model is a 100mL beaker. In this recommendation, the proper safety precautions are necessary. Since we have not conducted these larger scale tests, we do not know the volatility of the reaction. When we scaled up, the bursting vapor bubbles were powerful to make the beaker "jump" and have the potential to crack. A plastic bottle has the potential to melt similar to the drum in industry. Scale up should be down slowly and in a manner where a blast is a dangerous yet feasible option. In our testing, we used cardboard as a blast shield. Regardless of scale, we recommend using cardboard if not something sturdier in order to limit splatter after the reaction.

Invest in a thermocouple: When validating the accuracy of our model, we constructed a thermocouple because we could not find one in the lab and they were too expensive to purchase. We recommend that future experimentation needing to log temperature vs. time data is done with a different thermocouple. Our homemade thermocouple was a great temporary tool, but it was not compatible for every laptop. Once calibrated, it did now stay calibrated based on which laptop it was plugged in to. Only the laptop that it was calibrated on showed the correct temperature. Other laptops were off by at least 7^{o}C or it was not compatible with Apple products.

Investigate the method of acid insertion: We experimented with inserting acid into the center and into the side of a beaker. We could not replicate the hand pump that contained the drum in industry. Potentially, future experimentation can investigate inserting acid into the middle of the beaker rather than the top. One method could be a pill capsule. Another method is to try and recreate the ineffective rinse of the hand pump that happened in industry.

Explore kinetics of reaction using GC or UV Spec: One potential path that we chose not to take is to use chromatography or spectroscopy to better understand kinetics. The basis of these experiments would be looking at the concentration of FA throughout the course of a runaway reaction. We modeled the reaction in terms of temperature, but it could also be modeled in terms of amount of reactant. One area of concern here is that PFA is a very sticky polymer and can cause problems in a machine such as GC. An aqueous reaction can be used to limit the stickiness. Still, it is best to consult a chemist with more experience before potentially causing damage to expensive equipment.

Catalyze monomers similar to FA: The actual chemistry behind the polymerization is not known. We predict the acid strips off the hydroxyl group (-OH) to create a polymer. We believe that the polymer chains are not long and are oligomers. Then, since there are bonding opportunities on the furan ring where there are double bonds, cross linking occurs between the oligomers. After polymerization, there are two available carbon atoms that can be used in cross-linking. We have not tested this hypothesis. To test it, additionally methyl (-CH_3) chains can be added on to the furan ring to the two available carbon atoms; this would no longer be FA. Chemical analysis on the product or a liquid product of a different color would prove that cross-linking is required to produce the solid PFA. Additionally, three methyl groups can be added to the FA to see if any reaction occurs. One limitation of this experiment is the chemical stability of these atoms. These chemicals are not common and may be expensive or not possible to purchase.

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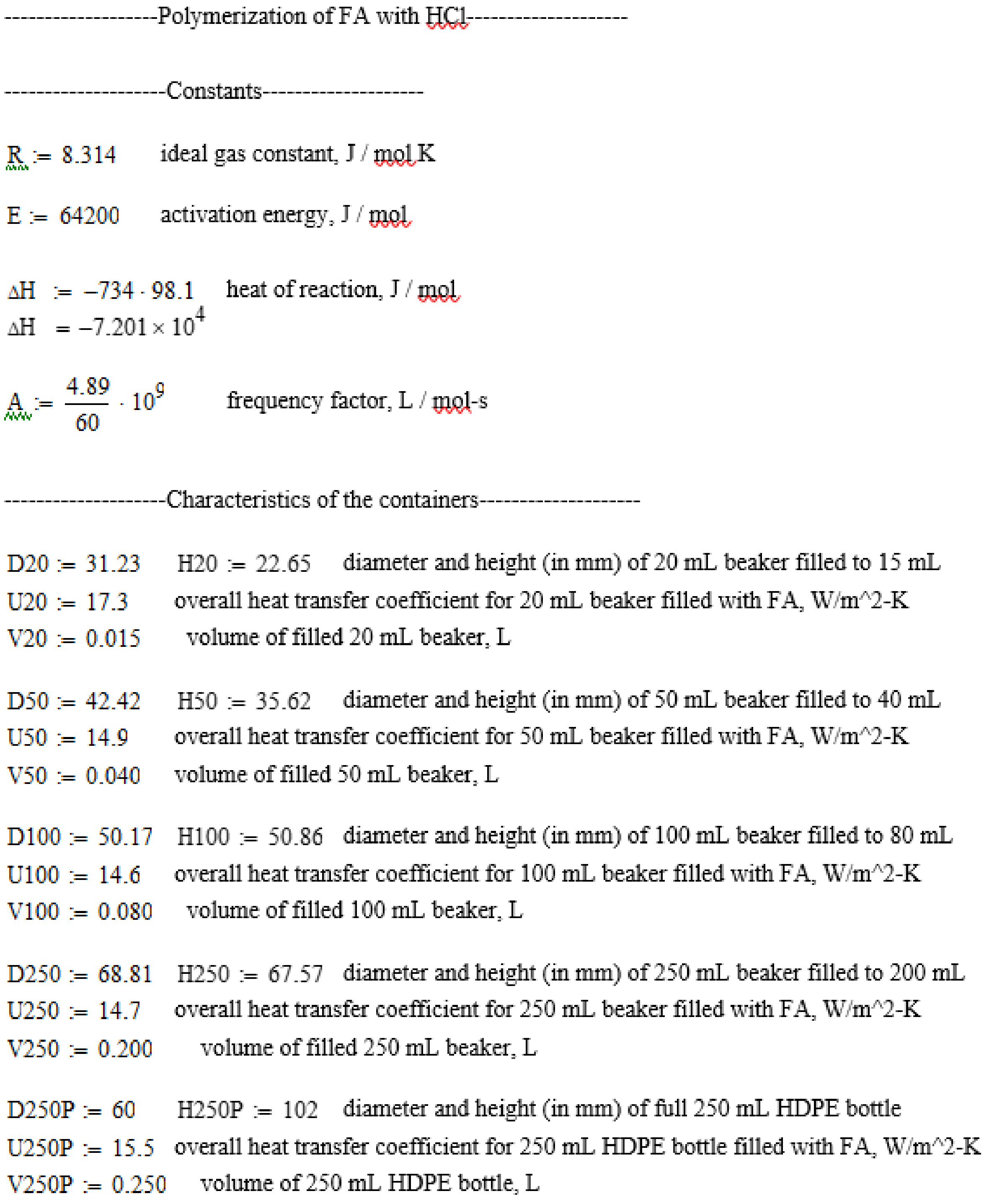
Appendices

Appendix A: Sample Mathcad Model



--------------------Polymerization of FA with HCl--------------------

--------------------Constants--------------------

$R := 8.314$ ideal gas constant, J / mol K

$E := 64200$ activation energy, J / mol

$\Delta H := -734 \cdot 98.1$ heat of reaction, J / mol
$\Delta H = -7.201 \times 10^{4}$

$A := \frac{4.89}{60} \cdot 10^{9}$ frequency factor, L / mol-s

--------------------Characteristics of the containers--------------------

$D20 := 31.23$ $H20 := 22.65$ diameter and height (in mm) of 20 mL beaker filled to 15 mL
$U20 := 17.3$ overall heat transfer coefficient for 20 mL beaker filled with FA, W/m^2-K
$V20 := 0.015$ volume of filled 20 mL beaker, L

$D50 := 42.42$ $H50 := 35.62$ diameter and height (in mm) of 50 mL beaker filled to 40 mL
$U50 := 14.9$ overall heat transfer coefficient for 50 mL beaker filled with FA, W/m^2-K
$V50 := 0.040$ volume of filled 50 mL beaker, L

$D100 := 50.17$ $H100 := 50.86$ diameter and height (in mm) of 100 mL beaker filled to 80 mL
$U100 := 14.6$ overall heat transfer coefficient for 100 mL beaker filled with FA, W/m^2-K
$V100 := 0.080$ volume of filled 100 mL beaker, L

$D250 := 68.81$ $H250 := 67.57$ diameter and height (in mm) of 250 mL beaker filled to 200 mL
$U250 := 14.7$ overall heat transfer coefficient for 250 mL beaker filled with FA, W/m^2-K
$V250 := 0.200$ volume of filled 250 mL beaker, L

$D250P := 60$ $H250P := 102$ diameter and height (in mm) of full 250 mL HDPE bottle
$U250P := 15.5$ overall heat transfer coefficient for 250 mL HDPE bottle filled with FA, W/m^2-K
$V250P := 0.250$ volume of 250 mL HDPE bottle, L

---------------------Variable inputs----------------------

Enter initial temperature in oC

Ti := 22.27 initial temperature, oC<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Ti := Ti + 273

Ti = 295.27 initial temperature, K

Enter the overall heat transfer coefficient for the container size and type. U20 for 20 mL beaker. U50 for 50 mL beaker. U100 for 100 mL beaker. U250 for 250 mL beaker. U250P for 250 mL HDPE bottle.

U := U20 <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

U = 17.3 overall heat transfer coefficient, W / m2 K

Enter the volume of furfuryl alcohol added, the volume of HCl added, and the concentration of HCl. Enter volumes in L and concentration in M.

VHo := $2 \cdot 10^{-4}$ volume of HCl added, L <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

CHo := 12 concentration of HCl added, M <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

VFAo := 0.01 volume of furfuryl alcohol, L<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Enter the diameter, height, and volume of the container. D20, H20, V20 for 20 mL beaker. D50, H50, V50 for 50 mL beaker. D100, H100, V100 for 100 mL beaker. D250, H250, V250 for 250 mL beaker. D250P, H250P, and V250P for 250 mL HDPE bottle.

Diameter := D20 <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Diameter = 31.23 Diameter of container, mm

Height := H20 <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Height = 22.65 Height of filled container, mm

Vfilled := V20 <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Vfilled = 0.015 Volume of filled container, L

Enter the "fudge factor" for the calculation.

Chocolate := 13.9 "fudge" factor <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Enter the endpoint of the solution interval for the calculation, in seconds.

te := 5500 endpoint of solution interval, s <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

--------------------Algebra and estimations--------------------

$CH := \frac{CHo \cdot VHo}{VHo + VFAo}$ concentraion of H+ in solution, M

$CH = 0.235$

$C := 2$ J / g K

$m := VFAo \cdot 1000 \cdot 1.13 = 11.3$ g

$Area := \left(Diameter \cdot Height \cdot \pi \cdot 10^{-6}\right) \cdot \frac{VFAo}{Vfilled} + Diameter^{2} \cdot \pi \cdot 0.25 \cdot 10^{-6}$

$Area = 2.247 \times 10^{-3}$ m2

--------------------Calculation--------------------

Giver

$$\frac{d}{dt}T(t) = \frac{VFA(t) \cdot -\Delta H \cdot \left(Chocolate \cdot A \cdot \exp\left(\frac{-E}{R \cdot T(t)}\right)\right) \cdot CH + U \cdot Area \cdot (Ti - T(t))}{C \cdot m}$$

$T(0) = Ti$

$$\frac{d}{dt}VFA(t) = VFA(t) \cdot \left(-A \cdot Chocolate \cdot \exp\left(\frac{-E}{R \cdot T(t)}\right)\right) \cdot CH \cdot \frac{98.10}{1.13 \cdot 1000}$$

$VFA(0) = VFAo$

$$\begin{pmatrix} T \\ VFA \end{pmatrix} := Odesolve\left[\begin{pmatrix} T \\ VFA \end{pmatrix}, t, te, 1 \times 10^{3}\right] \qquad t := 0, 2 .. te$$

$Tc(t) := T(t) - 273$

Appendix B: Experiments to Inform and Compare to the Mathcad Model

Table B-1. Experiments conducted to compare to the Mathcad model.

Conditions	Trial	Initial temperature (°C)	Pre-exponential Coefficient	Frequency Factor	Graph
20mL beaker, 10mL recycled FA, 0.2mL of HCl	1	21.27	11.69	$9.5\text{x}10^{8}$	Appendix G-1
20mL beaker, 10mL recycled FA, 0.2mL of HCl	2	22.27	-	-	Appendix H-1
20mL beaker, 10mL recycled FA, 0.2mL of HCl	3	23.28	-	-	-
20mL beaker, 10mL FA, 0.2mL of HCl	1	21.27	13.58	$1.1\text{x}10^{9}$	Appendix G-2
20mL beaker, 10mL FA, 0.2mL of HCl	2	22.27	-	-	Appendix H-2
20mL beaker, 10mL FA, 0.2mL of HCl	3	24.29	-	-	-
20mL beaker, 10mL FA, 0.2mL of HCl	4	24.29	-	-	-
20mL beaker, 10mL FA, 0.1mL of HCl	1	23.28	12.11	$9.9\text{x}10^{8}$	Appendix G-3
20mL beaker, 10mL FA, 0.1mL of HCl	2	24.29	-	-	Appendix H-3

20mL beaker, 10mL FA, 0.1mL of HCl	3	25.3	-	-	-
20mL beaker, 10mL FA, 0.05mL HCl	1	19.25	12.94	1.1x10^{9}	Appendix G-4
20mL beaker, 10mL FA, 0.05mL HCl	2	19.25	-	-	Appendix H-4
50mL beaker, 30mL FA, 0.1mL HCl	1	21.27	10.28	8.4x10^{8}	Appendix G-5
50mL beaker, 30mL FA, 0.1mL HCl	2	19.25	-	-	Appendix H-5
50mL beaker, 30mL FA, 0.1mL HCl	3	20.26	-	-	-
50mL beaker, 30mL FA, 0.2mL HCl	1	21.26	16.76	1.4x10^{9}	Appendix G-6
50mL beaker, 30mL FA, 0.2mL HCl	2	22.27	-	-	-
50mL beaker, 30mL FA, 0.2mL HCl	3	21.27	-	-	Appendix H-6
50mL beaker, 30mL FA, 0.3mL HCl	1	19.25	20.08	1.6x10^{9}	Appendix G-7
50mL beaker, 30mL FA, 0.3mL HCl	2	19.25	-	-	Appendix H-7
50mL beaker, 30mL FA, 0.3mL HCl	3	20.26	-	-	-
100mL beaker, 50mL, 0.2mL HCl	1	20.26	17.35	1.4x10^{9}	Appendix G-8

100mL beaker, 50mL, 0.2mL HCl	2	20.26	-	-	Appendix H-8
100mL beaker, 50mL, 0.2mL HCl	3	20.26	-	-	-
100mL beaker, 50mL, 0.15mL HCl	1	23.28	8.82	7.2x10^{8}	Appendix G-9
100mL beaker, 50mL, 0.3mL HCl	1	20.26	15.06	1.2x10^{9}	Appendix G-10
100mL beaker, 50mL, 0.3mL HCl	2	20.26	-	-	Appendix H-9

Appendix C. Sample Calculations to Determine Heat of Reaction

For Trial 8

Constants:
The Density of Water = 1.000g/cm^3 = δ_w
The Density of Ice = 0.917g/cm^3 = δ_i
The Density of FA = 1.130g/cm^3 = δ_{FA}
(Densities are at 0^{o}C)
The Heat of Fusion of Ice = 333.000J/g = L_F
Known Values:
Volume (V) of FA Added = 5.000mL = V_{FA}
Need to Know
The change in water level in the pipette = ΔV
Experimentally Determined Values
The initial water level in the pipette = -0.095mL
The final water level in the pipette = 0.640mL

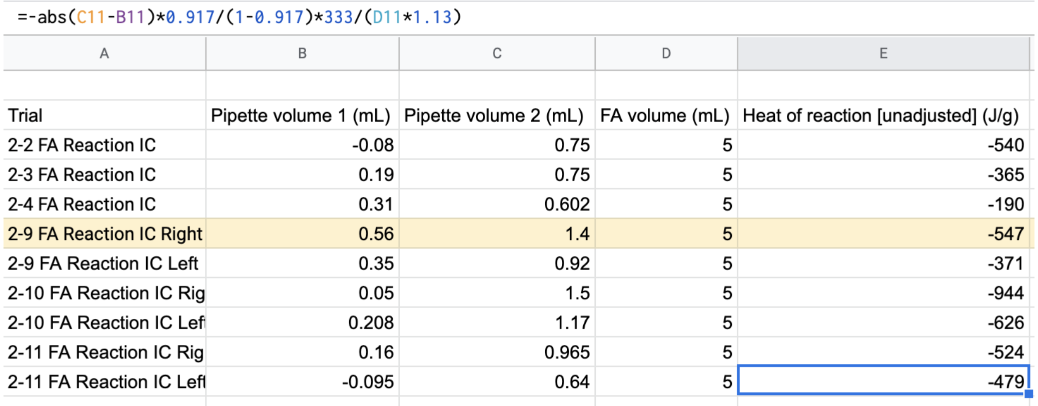
To start, we first needed to identify the change in the water level in the pipette. This is the final volume minus the initial volume. The initial volume is recorded when we insert the acid. The final volume is when the rate of change of the volume returns to what it was prior to the acid insertion (start of the third phase of the graph).

$$0.64\ mL - (-0.095\ mL) = 0.735mL$$

The change in water level in the pipette through the course of the experiment is equal to 0.735mL. From there, we have everything necessary to calculate the heat of reaction. To calculate the heat of reaction, the following equation is used:

$$-\left|\frac{\Delta \mathrm{V} \times \ \delta_i \ / \ (\delta_w - \delta_i) \times L_F}{V_{FA} \ \times \ \delta_{FA}}\right| = The\ heat\ of\ reaction\ of\ FA$$

Figure C-1 shows the calculation within our Google Spreadsheet.



```
=-abs(C11-B11)*0.917/(1-0.917)*333/(D11*1.13)
```

A	B	C	D	E
Trial	Pipette volume 1 (mL)	Pipette volume 2 (mL)	FA volume (mL)	Heat of reaction [unadjusted] (J/g)
2-2 FA Reaction IC	-0.08	0.75	5	-540
2-3 FA Reaction IC	0.19	0.75	5	-365
2-4 FA Reaction IC	0.31	0.602	5	-190
2-9 FA Reaction IC Right	0.56	1.4	5	-547
2-9 FA Reaction IC Left	0.35	0.92	5	-371
2-10 FA Reaction IC Rig	0.05	1.5	5	-944
2-10 FA Reaction IC Lef	0.208	1.17	5	-626
2-11 FA Reaction IC Rig	0.16	0.965	5	-524
2-11 FA Reaction IC Lef	-0.095	0.64	5	-479

Figure C-1. Heat of reaction calculation in Google Spreadsheet.

This equation uses three known densities (density of ice, water, and FA), the heat of fusion of ice, the total volume of FA, and the change in water level in the pipette.

$$-\left|\frac{0.735\ \mathrm{mL}\times\ 0.917\ mL\ /\ (1-.0.917\ mL)*333\,\frac{J}{g}}{5\ mL\ \times\ 1.13\,\frac{g}{mL}}\right| =\ -479J/g$$

For Trial 8 we got an experimental heat of reaction of -479J/g.
This equation does not account for any heat loss to the surroundings. A heat loss factor of 30% accounted for in the final answer.

$$\frac{\left(-479\,\frac{J}{g}\right)}{(1-.3)} =\ -684J/g$$

The new adjusted heat of reaction for Trial 8 is -684J/g.

Appendix D. Sample Calculations to Determine Heat Capacity

For Trial 6

Constants:
The Density of Water = 1.000g/cm^3 = δ_w
The Density of Ice = 0.917g/cm^3 = δ_i
(Densities are at 0°C)
The Heat of Fusion of Ice = 333.000J/g = L_F
Known Values:
Initial Temperature of the PFA = 100°C
Final Temperature of the PFA = 0°C
The mass of the PFA sample = 3.619grams
Need to Know
The change in water level in the pipette = $\Delta V(mL)$
The heat capacity of PFA = C_p(J/g °C)
Experimentally Determined Values
The initial water level in the pipette = 0.0017mL
The final water level in the pipette = 0.0673mL

We first needed to identify the change in water volume in the pipette due to the addition of the heated sample. During the experiment, we logged the volume of water within the pipette against time. We took note of the slopes before and after the sample was added. Three distinct slopes can be seen in Figure D-1.

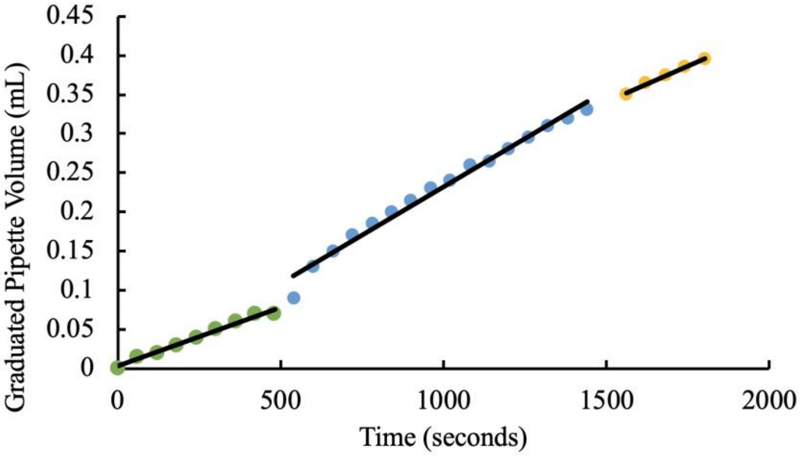


Figure D-1. Trial 6 temperature vs. time graph.

The first slope is due to the gradual change in volume within the pipette. This is caused by the experimental setup. The second slope is after the addition of the heated sample. The addition of the heated sample melts ice, causing the volume within the pipette to change at a faster rate. It is important to note that there is still a gradual volume change due to the experimental setup. The third slope takes place after the sample has cooled, and the slope returns to its gradual increase. We used these slopes to find the y-intercepts and get the final and initial volumes within the pipette during the experiment. The initial volume, found from the y-int of the green section, of the was found to be 0.0017mL. The final volume was 0.0673mL, found from the y-int of the yellow section. The change is volume is equal to the final minus initial volume.

$$0.0673mLs - 0.0017mLs = 0.735mLs$$

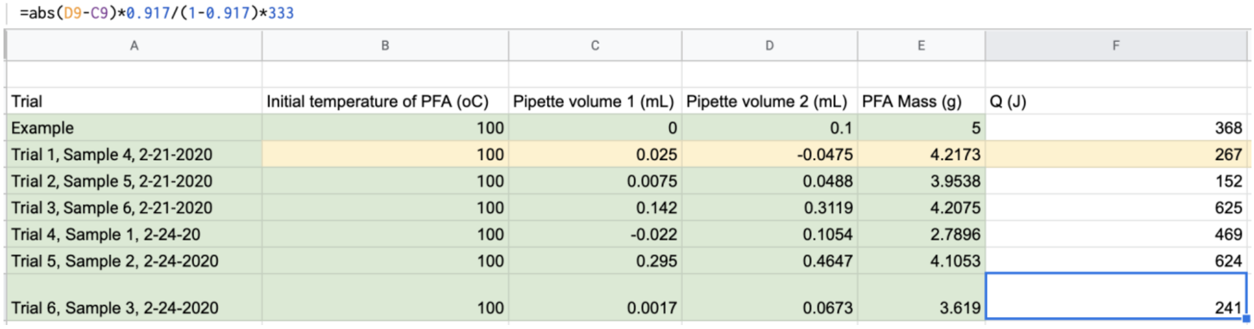
In order to find the heat capacity for PFA, we needed to determine how much heat was produced by the PFA sample. To do this we used the following equation:

$$Q = |\Delta V\left(\frac{\delta_i}{1-\delta_i}\right)L_F|$$

Heat is given in Joules. The calculation for Trial 6 is demonstrated below.

$$|(0.0673\text{mL} - 0.0017\text{mL})\left(\frac{0.917\frac{g}{mL}}{1-0.917\frac{g}{mL}}\right)\left(333\frac{J}{g}\right)| = 241J$$

These calculations were completed within a Google Spreadsheet, shown in Figure D-2.



`=abs(D9-C9)*0.917/(1-0.917)*333`

A	B	C	D	E	F
Trial	Initial temperature of PFA (oC)	Pipette volume 1 (mL)	Pipette volume 2 (mL)	PFA Mass (g)	Q (J)
Example	100	0	0.1	5	368
Trial 1, Sample 4, 2-21-2020	100	0.025	-0.0475	4.2173	267
Trial 2, Sample 5, 2-21-2020	100	0.0075	0.0488	3.9538	152
Trial 3, Sample 6, 2-21-2020	100	0.142	0.3119	4.2075	625
Trial 4, Sample 1, 2-24-20	100	-0.022	0.1054	2.7896	469
Trial 5, Sample 2, 2-24-2020	100	0.295	0.4647	4.1053	624
Trial 6, Sample 3, 2-24-2020	100	0.0017	0.0673	3.619	241

Figure D-2. Heat calculation within Google Spreadsheets.

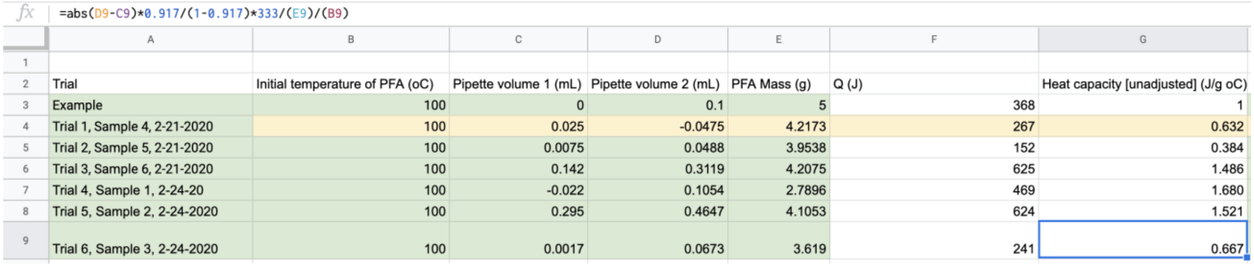
Now that we have our Q value, we calculated the heat capacity of the sample. Using the known temperature difference and mass of the PFA sample, we determined the experimental heat capacity. We used a rearranged heat equation, solved for heat capacity.

$$Cp = \frac{Q}{m\,\Delta \text{T}}$$

Next, we inputted our Trial 6 variables and solve.

$$(241J)/(3.619g)(100°\text{C} - 0°\text{C}) = 0.667J/g°\text{C}$$

These calculations were also completed in the same google spreadsheet, as demonstrated in Figure D-3.



`=abs(D9-C9)*0.917/(1-0.917)*333/(E9)/(B9)`

	A	B	C	D	E	F	G
1							
2	Trial	Initial temperature of PFA (oC)	Pipette volume 1 (mL)	Pipette volume 2 (mL)	PFA Mass (g)	Q (J)	Heat capacity [unadjusted] (J/g oC)
3	Example	100	0	0.1	5	368	1
4	Trial 1, Sample 4, 2-21-2020	100	0.025	-0.0475	4.2173	267	0.632
5	Trial 2, Sample 5, 2-21-2020	100	0.0075	0.0488	3.9538	152	0.384
6	Trial 3, Sample 6, 2-21-2020	100	0.142	0.3119	4.2075	625	1.486
7	Trial 4, Sample 1, 2-24-20	100	-0.022	0.1054	2.7896	469	1.680
8	Trial 5, Sample 2, 2-24-2020	100	0.295	0.4647	4.1053	624	1.521
9	Trial 6, Sample 3, 2-24-2020	100	0.0017	0.0673	3.619	241	0.667

Figure D-3. Heat capacity calculation within google spreadsheets

For Trial 6 we calculated an experimental heat capacity of 0.667 J/g °C. This equation does not account for any heat loss to the surroundings. A heat loss factor of 10% accounted for in the final answer.

$$\frac{\left(0.667\frac{J}{g}\,°\mathrm{C}\right)}{(1-.1)} = 0.741 J/g°\mathrm{C}$$

The adjusted heat of reaction for Trial 6 is 0.741J/g °C .

Appendix E. Overall Heat Transfer Coefficient Data

Some trials were recorded more than the time shown. For the sake of being concise, the beginning of those tests are shown.

20 mL Beaker, All Trials

Time (s)	Temp. (C)	Temp. (K)	Time (s)	Temp. (C)	Temp. (K)	Time (s)	Temp. (C)	Temp. (K)
0	80.6	353.75	0	78.4	351.55	0	84.7	357.85
10	79.6	352.75	10	77.9	351.05	10	83.5	356.65
20	78.6	351.75	20	76.8	349.95	20	82.3	81
30	77.4	350.55	30	75.8	348.95	30	81	352.65
40	76.1	349.25	40	74.7	347.85	40	79.5	351.65
50	75.1	348.25	50	73.6	346.75	50	78.5	350.25
60	74.1	347.25	60	72.6	345.75	60	77.1	349.15
70	73	346.15	70	71.5	344.65	70	76	348.15
80	72.1	345.25	80	70.4	343.55	80	75	346.95
90	71.2	344.35	90	69.4	342.55	90	73.8	345.95
100	70.2	343.35	100	68.6	341.75	100	72.8	345.05
110	69.5	342.65	110	67.7	340.85	110	71.9	345.05
120	68.5	341.65	120	66.9	340.05	120	70.8	343.95
130	67.7	340.85	130	65.9	339.05	130	69.9	343.05
140	67	340.15	140	65.2	338.35	140	69	342.15
150	66.1	339.25	150	64.3	337.45	150	68.2	341.35
160	65.3	338.45	160	63.6	336.75	160	67.3	340.45
170	64.5	337.65	170	62.8	335.95	170	66.5	339.65
180	63.9	337.05	180	62.2	335.35	180	65.6	338.75
190	63.1	336.25	190	61.4	334.55	190	64.9	338.05
200	62.4	335.55	200	60.7	333.85	200	64.1	337.25
210	61.8	334.95	210	60	333.15	210	63.5	336.65
220	61.1	334.25	220	59.3	332.45	220	62.7	335.85
230	60.5	333.65	230	58.6	331.75	230	62	335.15
240	59.8	332.95	240	58.1	331.25	240	61.4	334.55
250	59.2	332.35	250	57.4	330.55	250	60.7	333.85
260	58.6	331.75	260	56.9	330.05	260	60.1	333.25
270	58	331.15	270	56.4	329.55	270	59.2	332.35
280	57.5	330.65	280	55.8	328.95	280	58.7	331.85
290	57	330.15	290	55.2	328.35	290	58.1	331.25
300	56.4	329.55	300	54.7	327.85	300	57.5	330.65
310	55.8	328.95	310	54.1	327.25	310	57	330.15
320	55.2	328.35	320	53.6	326.75	320	56.4	329.55

330	54.7	327.85	330	53.1	326.25	330	55.9	329.05
340	54.2	327.35	340	52.7	325.85	340	55.3	328.45
350	53.7	326.85	350	52.2	325.35	350	54.7	327.85
360	53.2	326.35	360	51.7	324.85	360	54.2	327.35
370	52.7	325.85	370	51.3	324.45	370	53.7	326.85
380	52.3	325.45	380	50.8	323.95	380	53.2	326.35
390	51.9	325.05	390	50.3	323.45	390	52.7	325.85
400	51.4	324.55	400	49.9	323.05	400	52.3	325.45
410	51	324.15	410	49.5	322.65	410	51.9	325.05
420	50.5	323.65	420	49.1	322.25	420	51.4	324.55
430	50	323.15	430	48.6	321.75	430	50.9	324.05
440	49.6	322.75	440	48.3	321.45	440	50.4	323.55
450	49.2	322.35	450	47.9	321.05	450	50	323.15
460	48.8	321.95	460	47.5	320.65	460	49.5	322.65
470	48.4	321.55	470	47.1	320.25	470	49.1	322.25
480	48	321.15	480	46.8	319.95	480	48.7	321.85
490	47.7	320.85	490	46.4	319.55	490	48.3	321.45
500	47.3	320.45	500	46.1	319.25	500	48	321.15
510	47	320.15	510	45.7	318.85	510	47.6	320.75
520	46.6	319.75	520	45.3	318.45	520	47.2	320.35
530	46.3	319.45	530	45	318.15	530	46.9	320.05
540	45.9	319.05	540	44.6	317.75	540	46.5	319.65
550	45.5	318.65	550	44.3	317.45	550	46.1	319.25
560	45.2	318.35	560	44	317.15	560	45.7	318.85
570	44.9	318.05	570	43.7	316.85	570	45.4	318.55
580	44.5	317.65	580	43.4	316.55	580	45.1	318.25
590	44.2	317.35	590	43.1	316.25	590	44.7	317.85
600	43.9	317.05	600	42.8	315.95	600	44.4	317.55
610	43.6	316.75	610	42.5	315.65	610	44.1	317.25
620	43.3	316.45	620	42.2	315.35	620	43.8	316.95
630	43	316.15	630	41.9	315.05	630	43.5	316.65
640	42.8	315.95	640	41.6	314.75	640	43.2	316.35
650	42.5	315.65	650	41.3	314.45	650	42.9	316.05
660	42.2	315.35	660	41	314.15	660	42.6	315.75
670	41.9	315.05	670	40.8	313.95	670	42.3	315.45
680	41.6	314.75	680	40.5	313.65	680	42	315.15
690	41.3	314.45	690	40.3	313.45	690	41.7	314.85
700	41.1	314.25	700	40	313.15	700	41.5	314.65
710	40.8	313.95	710	39.7	312.85	710	40.9	314.05
720	40.5	313.65	720	39.6	312.75	720	40.7	313.85
730	40.3	313.45	730	39.3	312.45	730	40.4	313.55

740	40	313.15	740	39.1	312.25	740	40.1	313.25
750	39.8	312.95	750	38.9	312.05	750	39.9	313.05
760	39.5	312.65	760	38.7	311.85	760	39.6	312.75
770	39.3	312.45	770	38.4	311.55	770	39.4	312.55
780	39.1	312.25	780	38.1	311.25	780	39.2	312.35
790	38.9	312.05				790	39	312.15
800	38.7	311.85				800	38.8	311.95
810	38.4	311.55				810	38.5	311.65
820	38.2	311.35				820	38.3	311.45
830	38	311.15				830	38.1	311.25
840	37.8	310.95				840	37.9	311.05
850	37.5	310.65						
860	37.3	310.45						
870	37.1	310.25						
880	36.9	310.05						
890	36.7	309.85						
900	36.5	309.65						
910	36.4	309.55						
920	36.2	309.35						
930	36	309.15						
940	35.8	308.95						
950	35.7	308.85						
960	35.5	308.65						
970	35.3	308.45						
980	35.1	308.25						
990	35	308.15						
1000	34.9	308.05						
1010	34.7	307.85						
1020	34.5	307.65						
1030	34.4	307.55						
1040	34.2	307.35						
1050	34.1	307.25						
1060	33.9	307.05						

50mL Beaker, All Trials

Time (s)	Temp. (C)	Temp. (K)	Time (s)	Temp. (C)	Temp. (K)	Time (s)	Temp. (C)	Temp. (K)
0	100.4	373.55	0	122.2	395.35	0	103.7	376.85
10	99.1	372.25	10	120.5	393.65	10	102.2	375.35
20	97.9	371.05	20	118.8	391.95	20	100.9	374.05
30	96.9	370.05	30	117.3	390.45	30	99.6	372.75
40	95.9	369.05	40	115.6	388.75	40	98.6	371.75
50	94.6	367.75	50	114.1	387.25	50	97.4	370.55
60	93.1	366.25	60	112.7	385.85	60	96.2	369.35
70	92.5	365.65	70	111.5	384.65	70	95.1	368.25
80	91.6	364.75	80	110.1	383.25	80	94	367.15
90	90.6	363.75	90	108.9	382.05	90	92.9	366.05
100	89.9	363.05	100	107.5	380.65	100	91.9	365.05
110	88.8	361.95	110	106.3	379.45	110	90.8	363.95
120	87.9	361.05	120	105.2	378.35	120	89.8	362.95
130	87	360.15	130	104	377.15	130	88.8	361.95
140	86.2	359.35	140	103	376.15	140	88	361.15
150	85.5	358.65	150	101.9	375.05	150	86.9	360.05
160	84.6	357.75	160	100.8	373.95	160	86.1	359.25
170		273.15	170	99.6	372.75	170	85.2	358.35
180	83.2	356.35	180	99.8	372.95	180	84.6	357.75
190	82.5	355.65	190	97.8	370.95	190	83.9	357.05
200	71.7	344.85	200	97	370.15	200	83.2	356.35
210		273.15	210	96.1	369.25	210	82.5	355.65
220	71.6	344.75	220	95	368.15	220	69.9	343.05
230	70	343.15	230	94.2	367.35	230	69.3	342.45
240	69.5	342.65	240	93.5	366.65	240	68.8	341.95
250	69	342.15	250	92.6	365.75	250	68.3	341.45
260	68.5	341.65	260	91.9	365.05	260	67.7	340.85
270	68	341.15	270	91	364.15	270	67.2	340.35
280	67.6	340.75	280	90.2	363.35	280	66.7	339.85
290	67	340.15	290	88.6	361.75	290	66.2	339.35
300	66.5	339.65	300	87.8	360.95	300	65.7	338.85
310	66	339.15	310	87.1	360.25	310	65.3	338.45
320	65.5	338.65	320	86.5	359.65	320	64.8	337.95
330	65.1	338.25	330	85.8	358.95	330	64.3	337.45
340	64.7	337.85	340	85.1	358.25	340	64	337.15
350	64.3	337.45	350	84.4	357.55	350	63.5	336.65
360	63.7	336.85	360	83.7	356.85	360	63	336.15
370	63.2	336.35	370	83.1	356.25	370	62.7	335.85

380	62.8	335.95	380	82.5	355.65	380	62.3	335.45
390	62.4	335.55	390	70.6	343.75	390	62	335.15
400	62	335.15	400	70.1	343.25	400	61.5	334.65
410	61.6	334.75	410	69.6	342.75	410	61.1	334.25
420	61.2	334.35	420	69.1	342.25	420	60.7	333.85
430	60.8	333.95	430	68.6	341.75	430	60.2	333.35
440	60.4	333.55	440	68.2	341.35	440	59.8	332.95
450	60	333.15	450	67.7	340.85	450	59.4	332.55
460	59.6	332.75	460	67.2	340.35	460	59.1	332.25
470	59.2	332.35	470	66.9	340.05	470	58.8	331.95
480	58.9	332.05	480	66.3	339.45	480	58.4	331.55
490	58.3	331.45	490	65.9	339.05	490	58	331.15
500	58.1	331.25	500	65.3	338.45	500	57.6	330.75
510	57.7	330.85	510	65	338.15	510	57.3	330.45
520	57.3	330.45	520	64.6	337.75	520	57	330.15
530	57	330.15	530	64	337.15	530	56.6	329.75
540	56.7	329.85	540	63.7	336.85	540	56.3	329.45
550	56.4	329.55	550	63.3	336.45	550		273.15
560	56	329.15	560	62.8	335.95	560	55.6	328.75
570	55.6	328.75	570	62.5	335.65	570	55.3	328.45
580	55.3	328.45	580	62.1	335.25	580	54.9	328.05
590	54.9	328.05	590	61.7	334.85	590	54.6	327.75
600	54.6	327.75	600	61.3	334.45	600	54.3	327.45
610	54.3	327.45	610	60.9	334.05	610	54	327.15
620	53.9	327.05	620	60.5	333.65	620	53.6	326.75
630	53.7	326.85	630	60.1	333.25	630	53.2	326.35
640	53.3	326.45	640	59.7	332.85	640	52.9	326.05
650	53	326.15	650	59.3	332.45	650	52.6	325.75
660	52.7	325.85	660	58.9	332.05	660	52.3	325.45
670	52.5	325.65	670	58.7	331.85	670	52	325.15
680	52.2	325.35	680	58.3	331.45	680	51.8	324.95
690	51.9	325.05	690	57.9	331.05	690	51.5	324.65
700	51.6	324.75	700	57.5	330.65	700	51.2	324.35
710	51.3	324.45	710	57.3	330.45	710	50.9	324.05
720	51.1	324.25	720	57	330.15	720	50.6	323.75
730	50.8	323.95	730	56.6	329.75	730	50.3	323.45
740	50.5	323.65	740	56.2	329.35	740	50.1	323.25
750	50.2	323.35	750	55.9	329.05	750	49.7	322.85
760	50	323.15	760	55.6	328.75	760	49.5	322.65
770	49.7	322.85	770	55.3	328.45	770	49.2	322.35

100mL Beaker, All Trials

Time (s)	Temp. (C)	Temp. (K)	Time - degrees C	Time (hh:mm:ss)	Time from start (seconds)	temp (oC)	Time - degrees C	Time from start (seconds)	Temp (C)
			14:31:00.596 -> 82.76	14:31:00.596	0.0	82.76	15:07:21.496 -> 85.78	0	85.78
0	109.2	382.35	14:31:01.108 -> 82.76	14:31:01.108	0.5	82.76	15:07:22.004 -> 85.78	0.5	85.78
10	108.6	381.75	14:31:01.616 -> 82.76	14:31:01.616	1.0	82.76	15:07:22.509 -> 85.78	1	85.78
20	107.8	380.95	14:31:02.125 -> 82.76	14:31:02.125	1.5	82.76	15:07:23.018 -> 85.78	1.5	85.78
30	107.1	380.25	14:31:02.600 -> 82.76	14:31:02.600	2.0	82.76	15:07:23.524 -> 85.78	2	85.78
40	106.2	379.35	14:31:03.108 -> 82.76	14:31:03.108	2.5	82.76	15:07:24.002 -> 85.78	2.5	85.78
50	105.4	378.55	14:31:03.619 -> 83.77	14:31:03.619	3.0	83.77	15:07:24.508 -> 85.78	3	85.78
60	104.6	377.75	14:31:04.101 -> 82.76	14:31:04.101	3.5	82.76	15:07:25.017 -> 85.78	3.5	85.78
70	103.7	376.85	14:31:04.612 -> 82.76	14:31:04.612	4.0	82.76	15:07:25.492 -> 85.78	4	85.78
80	102.9	376.05	14:31:05.132 -> 83.77	14:31:05.132	4.5	83.77	15:07:25.998 -> 85.78	4.5	85.78
90	102	375.15	14:31:05.604 -> 83.77	14:31:05.604	5.0	83.77	15:07:26.504 -> 85.78	5	85.78
100	101.2	374.35	14:31:06.120 -> 83.77	14:31:06.120	5.5	83.77	15:07:27.015 -> 85.78	5.5	85.78
110	100.4	373.55	14:31:06.628 -> 83.77	14:31:06.628	6.0	83.77	15:07:27.522 -> 85.78	6	85.78
120	99.7	372.85	14:31:07.102 -> 83.77	14:31:07.102	6.5	83.77	15:07:28.000 -> 85.78	6.5	85.78
130	99	372.15	14:31:07.608 -> 83.77	14:31:07.608	7.0	83.77	15:07:28.508 -> 84.77	7	84.77
140	98.3	371.45	14:31:08.117 -> 83.77	14:31:08.117	7.5	83.77	15:07:29.018 -> 85.78	7.5	85.78
150	97.6	370.75	14:31:08.626 -> 83.77	14:31:08.626	8.0	83.77	15:07:29.525 -> 85.78	8	85.78
160	96.8	369.95	14:31:09.131 -> 83.77	14:31:09.131	8.5	83.77	15:07:30.001 -> 85.78	8.5	85.78

170	96.2	369.35	14:31:09.609 -> 83.77	14:31:09.609	9.0	83.77	15:07:30.510 -> 85.78	9	85.78
180	95.5	368.65	14:31:10.115 -> 83.77	14:31:10.115	9.5	83.77	15:07:31.018 -> 85.78	9.5	85.78
190	94.8	367.95	14:31:10.618 -> 83.77	14:31:10.618	10.0	83.77	15:07:31.527 -> 84.77	10	84.77
200	94.1	367.25	14:31:11.128 -> 83.77	14:31:11.128	10.5	83.77	15:07:31.999 -> 85.78	10.5	85.78
210	93.4	366.55	14:31:11.635 -> 83.77	14:31:11.635	11.0	83.77	15:07:32.508 -> 85.78	11	85.78
220	92.8	365.95	14:31:12.109 -> 82.76	14:31:12.109	11.5	82.76	15:07:33.016 -> 85.78	11.5	85.78
230	92.2	365.35	14:31:12.618 -> 83.77	14:31:12.618	12.0	83.77	15:07:33.524 -> 85.78	12	85.78
240	91.6	364.75	14:31:13.127 -> 82.76	14:31:13.127	12.5	82.76	15:07:34.031 -> 84.77	12.5	84.77
250	90.9	364.05	14:31:13.637 -> 82.76	14:31:13.637	13.0	82.76	15:07:34.504 -> 85.78	13	85.78
260	90.3	363.45	14:31:14.112 -> 82.76	14:31:14.112	13.5	82.76	15:07:35.012 -> 85.78	13.5	85.78
270	89.7	362.85	14:31:14.618 -> 82.76	14:31:14.618	14.0	82.76	15:07:35.524 -> 85.78	14	85.78
280	89.1	362.25	14:31:15.128 -> 82.76	14:31:15.128	14.5	82.76	15:07:36.030 -> 85.78	14.5	85.78
290	88.4	361.55	14:31:15.632 -> 82.76	14:31:15.632	15.0	82.76	15:07:36.503 -> 85.78	15	85.78
300	88	361.15	14:31:16.142 -> 82.76	14:31:16.142	15.5	82.76	15:07:37.009 -> 85.78	15.5	85.78
310	87.5	360.65	14:31:16.616 -> 82.76	14:31:16.616	16.0	82.76	15:07:37.515 -> 84.77	16	84.77
320	86.9	360.05	14:31:17.124 -> 82.76	14:31:17.124	16.5	82.76	15:07:38.022 -> 84.77	16.5	84.77
330	86.4	359.55	14:31:17.628 -> 82.76	14:31:17.628	17.0	82.76	15:07:38.528 -> 84.77	17	84.77
340	85.8	358.95	14:31:18.134 -> 82.76	14:31:18.134	17.5	82.76	15:07:39.036 -> 84.77	17.5	84.77
350	85.3	358.45	14:31:18.642 -> 82.76	14:31:18.642	18.0	82.76	15:07:39.541 -> 85.78	18	85.78
360	84.7	357.85	14:31:19.116 -> 82.76	14:31:19.116	18.5	82.76	15:07:40.016 -> 84.77	18.5	84.77
370	84.3	357.45	14:31:19.622 -> 82.76	14:31:19.622	19.0	82.76	15:07:40.525 -> 84.77	19	84.77

380	83.8	356.95	14:31:20.134 -> 82.76	14:31:20.134	19.5	82.76	15:07:41.033 -> 84.77	19.5	84.77
390	83.3	356.45	14:31:20.639 -> 82.76	14:31:20.639	20.0	82.76	15:07:41.539 -> 84.77	20	84.77
400	82.8	355.95	14:31:21.146 -> 82.76	14:31:21.146	20.5	82.76	15:07:42.044 -> 84.77	20.5	84.77
410	82.3	355.45	14:31:21.617 -> 82.76	14:31:21.617	21.0	82.76	15:07:42.519 -> 84.77	21	84.77
420	69.9	343.05	14:31:22.125 -> 82.76	14:31:22.125	21.5	82.76	15:07:43.025 -> 84.77	21.5	84.77
430	69.5	342.65	14:31:22.631 -> 81.75	14:31:22.631	22.0	81.75	15:07:43.535 -> 84.77	22	84.77
440	69.1	342.25	14:31:23.136 -> 82.76	14:31:23.136	22.5	82.76	15:07:44.009 -> 83.77	22.5	83.77
450	68.9	342.05	14:31:23.644 -> 82.76	14:31:23.644	23.0	82.76	15:07:44.523 -> 84.77	23	84.77
460	68.5	341.65	14:31:24.152 -> 82.76	14:31:24.152	23.5	82.76	15:07:45.030 -> 84.77	23.5	84.77
470	68.2	341.35	14:31:24.623 -> 81.75	14:31:24.623	24.0	81.75	15:07:45.540 -> 84.77	24	84.77
480	67.8	340.95	14:31:25.131 -> 82.76	14:31:25.131	24.5	82.76	15:07:46.042 -> 83.77	24.5	83.77
490	67.5	340.65	14:31:25.638 -> 81.75	14:31:25.638	25.0	81.75	15:07:46.520 -> 84.77	25	84.77
500	67.2	340.35	14:31:26.144 -> 82.76	14:31:26.144	25.5	82.76	15:07:47.025 -> 83.77	25.5	83.77
510	66.8	339.95	14:31:26.651 -> 82.76	14:31:26.651	26.0	82.76	15:07:47.534 -> 84.77	26	84.77
520	66.5	339.65	14:31:27.156 -> 82.76	14:31:27.156	26.5	82.76	15:07:48.041 -> 84.77	26.5	84.77
530	66.1	339.25	14:31:27.628 -> 82.76	14:31:27.628	27.0	82.76	15:07:48.548 -> 84.77	27	84.77
540	65.8	338.95	14:31:28.135 -> 81.75	14:31:28.135	27.5	81.75	15:07:49.023 -> 84.77	27.5	84.77
550	65.5	338.65	14:31:28.645 -> 82.76	14:31:28.645	28.0	82.76	15:07:49.531 -> 83.77	28	83.77
560	65.1	338.25	14:31:29.147 -> 82.76	14:31:29.147	28.5	82.76	15:07:50.044 -> 83.77	28.5	83.77
570	64.8	337.95	14:31:29.653 -> 81.75	14:31:29.653	29.0	81.75	15:07:50.548 -> 83.77	29	83.77
580	64.5	337.65	14:31:30.159 -> 81.75	14:31:30.159	29.5	81.75	15:07:51.019 -> 84.77	29.5	84.77

590	64.2	337.35	14:31:30.630 -> 82.76	14:31:30.630	30.0	82.76	15:07:51.526 -> 84.77	30	84.77
600	63.9	337.05	14:31:31.137 -> 81.75	14:31:31.137	30.5	81.75	15:07:52.033 -> 83.77	30.5	83.77
610	63.6	336.75	14:31:31.643 -> 81.75	14:31:31.643	31.0	81.75	15:07:52.544 -> 83.77	31	83.77
620	63.3	336.45	14:31:32.149 -> 81.75	14:31:32.149	31.5	81.75	15:07:53.021 -> 83.77	31.5	83.77
630	63	336.15	14:31:32.655 -> 80.74	14:31:32.655	32.0	80.74	15:07:53.528 -> 84.77	32	84.77
640	62.7	335.85	14:31:33.136 -> 81.75	14:31:33.136	32.5	81.75	15:07:54.039 -> 83.77	32.5	83.77
650	62.5	335.65	14:31:33.646 -> 81.75	14:31:33.646	33.0	81.75	15:07:54.552 -> 83.77	33	83.77
660	62.2	335.35	14:31:34.154 -> 81.75	14:31:34.154	33.5	81.75	15:07:55.028 -> 83.77	33.5	83.77
670	61.9	335.05	14:31:34.662 -> 81.75	14:31:34.662	34.0	81.75	15:07:55.534 -> 83.77	34	83.77
680	61.6	334.75	14:31:35.140 -> 81.75	14:31:35.140	34.5	81.75	15:07:56.043 -> 83.77	34.5	83.77
690	61.3	334.45	14:31:35.653 -> 81.75	14:31:35.653	35.0	81.75	15:07:56.547 -> 83.77	35	83.77
700	61	334.15	14:31:36.160 -> 81.75	14:31:36.160	35.5	81.75	15:07:57.058 -> 83.77	35.5	83.77
710	60.7	333.85	14:31:36.638 -> 81.75	14:31:36.638	36.0	81.75	15:07:57.528 -> 82.76	36	82.76
720	60.4	333.55	14:31:37.145 -> 81.75	14:31:37.145	36.5	81.75	15:07:58.040 -> 83.77	36.5	83.77
730	60.1	333.25	14:31:37.653 -> 81.75	14:31:37.653	37.0	81.75	15:07:58.546 -> 83.77	37	83.77
740	59.9	333.05	14:31:38.161 -> 80.74	14:31:38.161	37.5	80.74	15:07:59.051 -> 83.77	37.5	83.77
750	59.6	332.75	14:31:38.664 -> 81.75	14:31:38.664	38.0	81.75	15:07:59.559 -> 82.76	38	82.76
760	59.3	332.45	14:31:39.171 -> 80.74	14:31:39.171	38.5	80.74	15:08:00.035 -> 83.77	38.5	83.77
770	59.1	332.25	14:31:39.643 -> 81.75	14:31:39.643	39.0	81.75	15:08:00.548 -> 83.77	39	83.77
780	58.8	331.95	14:31:40.149 -> 81.75	14:31:40.149	39.5	81.75	15:08:01.056 -> 83.77	39.5	83.77
790	58.5	331.65	14:31:40.660 -> 81.75	14:31:40.660	40.0	81.75	15:08:01.537 -> 82.76	40	82.76

250mL Beaker, All Trials

Time - degrees C	Time from start (s)	Temp (oC)	Time - degrees C	Time from start (s)	Temp (C)	Time - degrees C	Time from start (s)	Temp (C)
15:52:36.400 -> 83.77	0	83.77	16:32:58.269 -> 83.77	0	83.77	13:32:39.254 -> 90.82	0	90.82
15:52:36.907 -> 83.77	0.5006495	83.77	16:33:00.273 -> 83.77	2	83.77	13:32:41.250 -> 90.82	2	90.82
15:52:37.385 -> 83.77	1.001299	83.77	16:33:02.266 -> 84.77	4	84.77	13:32:43.246 -> 90.82	4	90.82
15:52:37.892 -> 83.77	1.5019485	83.77	16:33:04.272 -> 84.77	6	84.77	13:32:45.243 -> 89.81	6	89.81
15:52:38.394 -> 83.77	2.002598	83.77	16:33:06.243 -> 84.77	8	84.77	13:32:47.235 -> 89.81	8	89.81
15:52:38.901 -> 83.77	2.5032475	83.77	16:33:08.270 -> 83.77	10	83.77	13:32:49.235 -> 89.81	10	89.81
15:52:39.407 -> 83.77	3.003897	83.77	16:33:10.263 -> 83.77	12	83.77	13:32:51.248 -> 89.81	12	89.81
15:52:39.911 -> 83.77	3.5045465	83.77	16:33:12.260 -> 83.77	14	83.77	13:32:53.247 -> 88.81	14	88.81
15:52:40.417 -> 83.77	4.005196	83.77	16:33:14.263 -> 83.77	16	83.77	13:32:55.245 -> 89.81	16	89.81
15:52:40.891 -> 82.76	4.5058455	82.76	16:33:16.269 -> 83.77	18	83.77	13:32:57.255 -> 89.81	18	89.81
15:52:41.399 -> 83.77	5.006495	83.77	16:33:18.270 -> 84.77	20	84.77	13:32:59.252 -> 89.81	20	89.81
15:52:41.906 -> 83.77	5.5071445	83.77	16:33:20.268 -> 83.77	22	83.77	13:33:01.264 -> 88.81	22	88.81
15:52:42.417 -> 83.77	6.007794	83.77	16:33:22.266 -> 83.77	24	83.77	13:33:03.241 -> 88.81	24	88.81
15:52:42.891 -> 83.77	6.5084435	83.77	16:33:24.260 -> 83.77	26	83.77	13:33:05.245 -> 89.81	26	89.81
15:52:43.399 -> 83.77	7.009093	83.77	16:33:26.264 -> 83.77	28	83.77	13:33:07.252 -> 89.81	28	89.81
15:52:43.904 -> 83.77	7.5097425	83.77	16:33:28.270 -> 82.76	30	82.76	13:33:09.254 -> 88.81	30	88.81
15:52:44.417 -> 83.77	8.010392	83.77	16:33:30.288 -> 82.76	32	82.76	13:33:11.260 -> 88.81	32	88.81
15:52:44.891 -> 83.77	8.5110415	83.77	16:33:32.265 -> 83.77	34	83.77	13:33:13.258 -> 88.81	34	88.81
15:52:45.400 -> 83.77	9.011691	83.77	16:33:34.276 -> 83.77	36	83.77	13:33:15.253 -> 88.81	36	88.81

15:52:45.907 -> 83.77	9.5123405	83.77	16:33:36.278 -> 83.77	38	83.77	13:33:17.258 -> 88.81	38	88.81
15:52:46.415 -> 82.76	10.01299	82.76	16:33:38.276 -> 82.76	40	82.76	13:33:19.265 -> 88.81	40	88.81
15:52:46.923 -> 83.77	10.5136395	83.77	16:33:40.268 -> 82.76	42	82.76	13:33:21.273 -> 87.80	42	87.80
15:52:47.395 -> 83.77	11.014289	83.77	16:33:42.267 -> 82.76	44	82.76	13:33:23.261 -> 87.80	44	87.80
15:52:47.906 -> 83.77	11.5149385	83.77	16:33:44.268 -> 82.76	46	82.76	13:33:25.261 -> 87.80	46	87.80
15:52:48.412 -> 83.77	12.015588	83.77	16:33:46.276 -> 82.76	48	82.76	13:33:27.260 -> 87.80	48	87.80
15:52:48.919 -> 83.77	12.5162375	83.77	16:33:48.272 -> 82.76	50	82.76	13:33:29.274 -> 87.80	50	87.80
15:52:49.397 -> 83.77	13.016887	83.77	16:33:50.267 -> 82.76	52	82.76	13:33:31.262 -> 87.80	52	87.80
15:52:49.904 -> 83.77	13.5175365	83.77	16:33:52.262 -> 82.76	54	82.76	13:33:33.274 -> 86.79	54	86.79
15:52:50.415 -> 82.76	14.018186	82.76	16:33:54.267 -> 81.75	56	81.75	13:33:35.249 -> 87.80	56	87.80
15:52:50.920 -> 82.76	14.5188355	82.76	16:33:56.263 -> 82.76	58	82.76	13:33:37.263 -> 87.80	58	87.80
15:52:51.425 -> 82.76	15.019485	82.76	16:33:58.289 -> 81.75	60	81.75	13:33:39.275 -> 86.79	60	86.79
15:52:51.903 -> 83.77	15.5201345	83.77	16:34:00.288 -> 81.75	62	81.75	13:33:41.255 -> 86.79	62	86.79
15:52:52.409 -> 83.77	16.020784	83.77	16:34:02.288 -> 81.75	64	81.75	13:33:43.259 -> 86.79	64	86.79
15:52:52.920 -> 82.76	16.5214335	82.76	16:34:04.292 -> 80.74	66	80.74	13:33:45.253 -> 86.79	66	86.79
15:52:53.425 -> 82.76	17.022083	82.76	16:34:06.300 -> 80.74	68	80.74	13:33:47.258 -> 86.79	68	86.79
15:52:53.936 -> 82.76	17.5227325	82.76	16:34:08.268 -> 80.74	70	80.74	13:33:49.256 -> 86.79	70	86.79
15:52:54.411 -> 82.76	18.023382	82.76	16:34:10.270 -> 81.75	72	81.75	13:33:51.264 -> 85.78	72	85.78
15:52:54.924 -> 82.76	18.5240315	82.76	16:34:12.275 -> 81.75	74	81.75	13:33:53.287 -> 85.78	74	85.78
15:52:55.426 -> 82.76	19.024681	82.76	16:34:14.273 -> 81.75	76	81.75	13:33:55.258 -> 86.79	76	86.79
15:52:55.933 -> 82.76	19.5253305	82.76	16:34:16.298 -> 80.74	78	80.74	13:33:57.263 -> 85.78	78	85.78

15:52:56.438 -> 82.76	20.02598	82.76	16:34:18.303 -> 80.74	80	80.74	13:33:59.262 -> 85.78	80	85.78
15:52:56.910 -> 82.76	20.5266295	82.76	16:34:20.294 -> 80.74	82	80.74	13:34:01.268 -> 85.78	82	85.78
15:52:57.419 -> 82.76	21.027279	82.76	16:34:22.287 -> 81.75	84	81.75	13:34:03.275 -> 85.78	84	85.78
15:52:57.925 -> 82.76	21.5279285	82.76	16:34:24.298 -> 80.74	86	80.74	13:34:05.274 -> 85.78	86	85.78
15:52:58.434 -> 83.77	22.028578	83.77	16:34:26.303 -> 80.74	88	80.74	13:34:07.289 -> 85.78	88	85.78
15:52:58.911 -> 82.76	22.5292275	82.76	16:34:28.296 -> 79.73	90	79.73	13:34:09.296 -> 84.77	90	84.77
15:52:59.418 -> 82.76	23.029877	82.76	16:34:30.289 -> 80.74	92	80.74	13:34:11.264 -> 84.77	92	84.77
15:52:59.932 -> 82.76	23.5305265	82.76	16:34:32.284 -> 79.73	94	79.73	13:34:13.286 -> 85.78	94	85.78
15:53:00.439 -> 82.76	24.031176	82.76	16:34:34.298 -> 79.73	96	79.73	13:34:15.281 -> 84.77	96	84.77
15:53:00.914 -> 83.77	24.5318255	83.77	16:34:36.282 -> 80.74	98	80.74	13:34:17.287 -> 84.77	98	84.77
15:53:01.425 -> 82.76	25.032475	82.76	16:34:38.286 -> 79.73	100	79.73	13:34:19.281 -> 84.77	100	84.77
15:53:01.935 -> 82.76	25.5331245	82.76	16:34:40.309 -> 79.73	102	79.73	13:34:21.289 -> 84.77	102	84.77
15:53:02.442 -> 82.76	26.033774	82.76	16:34:42.305 -> 79.73	104	79.73	13:34:23.284 -> 84.77	104	84.77
15:53:02.920 -> 82.76	26.5344235	82.76	16:34:44.305 -> 80.74	106	80.74	13:34:25.281 -> 83.77	106	83.77
15:53:03.430 -> 82.76	27.035073	82.76	16:34:46.311 -> 79.73	108	79.73	13:34:27.283 -> 83.77	108	83.77
15:53:03.935 -> 82.76	27.5357225	82.76	16:34:48.306 -> 78.72	110	78.72	13:34:29.281 -> 84.77	110	84.77
15:53:04.442 -> 82.76	28.036372	82.76	16:34:50.301 -> 79.73	112	79.73	13:34:31.282 -> 83.77	112	83.77
15:53:04.916 -> 82.76	28.5370215	82.76	16:34:52.294 -> 79.73	114	79.73	13:34:33.278 -> 83.77	114	83.77
15:53:05.421 -> 82.76	29.037671	82.76	16:34:54.294 -> 79.73	116	79.73	13:34:35.275 -> 83.77	116	83.77
15:53:05.931 -> 81.75	29.5383205	81.75	16:34:56.319 -> 78.72	118	78.72	13:34:37.306 -> 83.77	118	83.77
15:53:06.434 -> 81.75	30.03897	81.75	16:34:58.320 -> 78.72	120	78.72	13:34:39.275 -> 82.76	120	82.76

15:53:06.942 -> 81.75	30.5396195	81.75	16:35:00.319 -> 79.73	122	79.73	13:34:41.284 -> 83.77	122	83.77
15:53:07.449 -> 81.75	31.040269	81.75	16:35:02.317 -> 78.72	124	78.72	13:34:43.273 -> 82.76	124	82.76
15:53:07.925 -> 81.75	31.5409185	81.75	16:35:04.313 -> 78.72	126	78.72	13:34:45.286 -> 82.76	126	82.76
15:53:08.435 -> 81.75	32.041568	81.75	16:35:06.308 -> 78.72	128	78.72	13:34:47.291 -> 82.76	128	82.76
15:53:08.941 -> 82.76	32.5422175	82.76	16:35:08.304 -> 78.72	130	78.72	13:34:49.289 -> 82.76	130	82.76

250mL Plastic Bottle

Time - degrees C	Time from start (s)	Temp (oC)	Time - degrees C	Time from start (s)	Temp (oC)	Time - degrees C	Time from start (s)	Temp (oC)
14:24:01.586 -> 65.62	0	65.62	14:58:42.797 -> 80.74	0	80.74	15:34:45.263 -> 75.70		75.70
14:24:03.581 -> 65.62	2	65.62	14:58:44.790 -> 80.74	2	80.74	15:34:47.257 -> 75.70		75.70
14:24:05.582 -> 64.61	4	64.61	14:58:46.809 -> 80.74	4	80.74	15:34:49.252 -> 75.70		75.70
14:24:07.584 -> 65.62	6	65.62	14:58:48.811 -> 80.74	6	80.74	15:34:51.254 -> 76.71	0	76.71
14:24:09.561 -> 65.62	8	65.62	14:58:50.815 -> 80.74	8	80.74	15:34:53.269 -> 75.70	2	75.70
14:24:11.570 -> 64.61	10	64.61	14:58:52.794 -> 80.74	10	80.74	15:34:55.272 -> 76.71	4	76.71
14:24:13.572 -> 64.61	12	64.61	14:58:54.797 -> 79.73	12	79.73	15:34:57.275 -> 75.70	6	75.70
14:24:15.562 -> 64.61	14	64.61	14:58:56.799 -> 80.74	14	80.74	15:34:59.273 -> 75.70	8	75.70
14:24:17.560 -> 64.61	16	64.61	14:58:58.810 -> 79.73	16	79.73	15:35:01.283 -> 74.69	10	74.69
14:24:19.570 -> 64.61	18	64.61	14:59:00.814 -> 80.74	18	80.74	15:35:03.264 -> 74.69	12	74.69
14:24:21.576 -> 63.60	20	63.60	14:59:02.797 -> 79.73	20	79.73	15:35:05.260 -> 75.70	14	75.70
14:24:23.582 -> 64.61	22	64.61	14:59:04.803 -> 79.73	22	79.73	15:35:07.267 -> 75.70	16	75.70
14:24:25.580 -> 63.60	24	63.60	14:59:06.801 -> 79.73	24	79.73	15:35:09.268 -> 74.69	18	74.69
14:24:27.583 -> 64.61	26	64.61	14:59:08.799 -> 79.73	26	79.73	15:35:11.294 -> 75.70	20	75.70
14:24:29.586 -> 64.61	28	64.61	14:59:10.825 -> 79.73	28	79.73	15:35:13.278 -> 74.69	22	74.69
14:24:31.601 -> 64.61	30	64.61	14:59:12.823 -> 79.73	30	79.73	15:35:15.265 -> 75.70	24	75.70
14:24:33.574 -> 64.61	32	64.61	14:59:14.818 -> 79.73	32	79.73	15:35:17.272 -> 74.69	26	74.69
14:24:35.594 -> 64.61	34	64.61	14:59:16.828 -> 79.73	34	79.73	15:35:19.272 -> 75.70	28	75.70
14:24:37.594 -> 63.60	36	63.60	14:59:18.826 -> 79.73	36	79.73	15:35:21.273 -> 74.69	30	74.69

14:24:39.575 -> 64.61	38	64.61	14:59:20.824 -> 78.72	38	78.72	15:35:23.285 -> 75.70	32	75.70
14:24:41.602 -> 64.61	40	64.61	14:59:22.829 -> 78.72	40	78.72	15:35:25.268 -> 74.69	34	74.69
14:24:43.580 -> 63.60	42	63.60	14:59:24.829 -> 78.72	42	78.72	15:35:27.298 -> 74.69	36	74.69
14:24:45.594 -> 63.60	44	63.60	14:59:26.829 -> 78.72	44	78.72	15:35:29.269 -> 74.69	38	74.69
14:24:47.594 -> 63.60	46	63.60	14:59:28.830 -> 78.72	46	78.72	15:35:31.271 -> 73.68	40	73.68
14:24:49.605 -> 63.60	48	63.60	14:59:30.828 -> 79.73	48	79.73	15:35:33.275 -> 74.69	42	74.69
14:24:51.584 -> 63.60	50	63.60	14:59:32.825 -> 78.72	50	78.72	15:35:35.304 -> 73.68	44	73.68
14:24:53.599 -> 63.60	52	63.60	14:59:34.824 -> 78.72	52	78.72	15:35:37.306 -> 74.69	46	74.69
14:24:55.587 -> 63.60	54	63.60	14:59:36.818 -> 78.72	54	78.72	15:35:39.277 -> 73.68	48	73.68
14:24:57.610 -> 63.60	56	63.60	14:59:38.827 -> 78.72	56	78.72	15:35:41.286 -> 74.69	50	74.69
14:24:59.579 -> 63.60	58	63.60	14:59:40.819 -> 77.72	58	77.72	15:35:43.285 -> 73.68	52	73.68
14:25:01.597 -> 63.60	60	63.60	14:59:42.827 -> 77.72	60	77.72	15:35:45.280 -> 73.68	54	73.68
14:25:03.604 -> 63.60	62	63.60	14:59:44.824 -> 77.72	62	77.72	15:35:47.281 -> 73.68	56	73.68
14:25:05.613 -> 63.60	64	63.60	14:59:46.835 -> 77.72	64	77.72	15:35:49.285 -> 73.68	58	73.68
14:25:07.587 -> 63.60	66	63.60	14:59:48.837 -> 77.72	66	77.72	15:35:51.294 -> 73.68	60	73.68
14:25:09.602 -> 63.60	68	63.60	14:59:50.837 -> 77.72	68	77.72	15:35:53.298 -> 72.68	62	72.68
14:25:11.607 -> 63.60	70	63.60	14:59:52.848 -> 77.72	70	77.72	15:35:55.301 -> 73.68	64	73.68
14:25:13.604 -> 63.60	72	63.60	14:59:54.843 -> 77.72	72	77.72	15:35:57.292 -> 73.68	66	73.68
14:25:15.597 -> 63.60	74	63.60	14:59:56.836 -> 77.72	74	77.72	15:35:59.286 -> 72.68	68	72.68
14:25:17.590 -> 62.60	76	62.60	14:59:58.833 -> 77.72	76	77.72	15:36:01.297 -> 73.68	70	73.68
14:25:19.587 -> 62.60	78	62.60	15:00:00.827 -> 76.71	78	76.71	15:36:03.315 -> 73.68	72	73.68

14:25:21.603 -> 62.60	80	62.60	15:00:02.836 -> 76.71	80	76.71	15:36:05.309 -> 72.68	74	72.68
14:25:23.609 -> 62.60	82	62.60	15:00:04.842 -> 76.71	82	76.71	15:36:07.316 -> 73.68	76	73.68
14:25:25.600 -> 62.60	84	62.60	15:00:06.840 -> 76.71	84	76.71	15:36:09.318 -> 72.68	78	72.68
14:25:27.609 -> 62.60	86	62.60	15:00:08.845 -> 76.71	86	76.71	15:36:11.314 -> 72.68	80	72.68
14:25:29.614 -> 62.60	88	62.60	15:00:10.823 -> 76.71	88	76.71	15:36:13.289 -> 73.68	82	73.68
14:25:31.598 -> 62.60	90	62.60	15:00:12.842 -> 76.71	90	76.71	15:36:15.297 -> 72.68	84	72.68
14:25:33.594 -> 62.60	92	62.60	15:00:14.846 -> 76.71	92	76.71	15:36:17.298 -> 72.68	86	72.68
14:25:35.595 -> 62.60	94	62.60	15:00:16.844 -> 76.71	94	76.71	15:36:19.307 -> 72.68	88	72.68
14:25:37.619 -> 62.60	96	62.60	15:00:18.852 -> 76.71	96	76.71	15:36:21.312 -> 71.67	90	71.67
14:25:39.610 -> 62.60	98	62.60	15:00:20.829 -> 76.71	98	76.71	15:36:23.293 -> 72.68	92	72.68
14:25:41.617 -> 62.60	100	62.60	15:00:22.837 -> 75.70	100	75.70	15:36:25.322 -> 72.68	94	72.68
14:25:43.610 -> 62.60	102	62.60	15:00:24.833 -> 76.71	102	76.71	15:36:27.326 -> 72.68	96	72.68
14:25:45.619 -> 62.60	104	62.60	15:00:26.828 -> 76.71	104	76.71	15:36:29.326 -> 72.68	98	72.68
14:25:47.609 -> 61.59	106	61.59	15:00:28.861 -> 75.70	106	75.70	15:36:31.322 -> 71.67	100	71.67
14:25:49.609 -> 61.59	108	61.59	15:00:30.836 -> 75.70	108	75.70	15:36:33.329 -> 71.67	102	71.67
14:25:51.612 -> 61.59	110	61.59	15:00:32.849 -> 75.70	110	75.70	15:36:35.299 -> 71.67	104	71.67
14:25:53.611 -> 62.60	112	62.60	15:00:34.864 -> 75.70	112	75.70	15:36:37.331 -> 71.67	106	71.67
14:25:55.619 -> 62.60	114	62.60	15:00:36.853 -> 75.70	114	75.70	15:36:39.326 -> 71.67	108	71.67
14:25:57.617 -> 61.59	116	61.59	15:00:38.860 -> 74.69	116	74.69	15:36:41.319 -> 71.67	110	71.67
14:25:59.635 -> 62.60	118	62.60	15:00:40.861 -> 75.70	118	75.70	15:36:43.326 -> 71.67	112	71.67
14:26:01.622 -> 61.59	120	61.59	15:00:42.838 -> 75.70	120	75.70	15:36:45.331 -> 71.67	114	71.67

14:26:03.621 -> 62.60	122	62.60	15:00:44.867 -> 75.70	122	75.70	15:36:47.333 -> 71.67	116	71.67
14:26:05.632 -> 61.59	124	61.59	15:00:46.868 -> 75.70	124	75.70	15:36:49.330 -> 71.67	118	71.67
14:26:07.637 -> 62.60	126	62.60	15:00:48.862 -> 75.70	126	75.70	15:36:51.320 -> 70.66	120	70.66
14:26:09.613 -> 61.59	128	61.59	15:00:50.862 -> 75.70	128	75.70	15:36:53.318 -> 71.67	122	71.67
14:26:11.627 -> 61.59	130	61.59	15:00:52.849 -> 74.69	130	74.69	15:36:55.323 -> 71.67	124	71.67

Appendix F. Sample Calculations for Determining the Overall Heat Transfer Coefficient

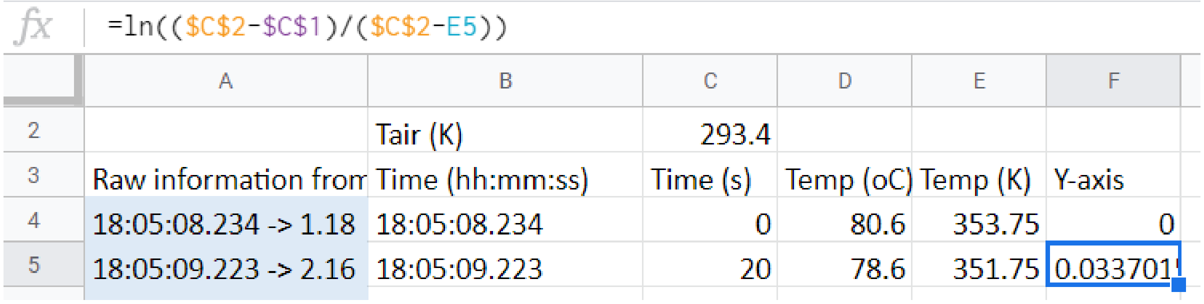
For Trial 1, 20mL Beaker

Constants:
Specific Heat of FA (C) = 2.1 J/(g*K)
Density of FA= 1.13g/mL
Data Needed:
Volume (V) of FA Added = 15mL
Diameter of Vessel (D) = 31.23mm
Height of Vessel (H) = 23mm
Temperature vs Time data of the constant cooling or heating of FA

These calculations should be in excel or google sheets. First, we calculated for the y-axis of the graph. The equation for this axis is

$$\text{y: axis} = \ln\left(\frac{T_{air} - T_o}{T_{air} - T}\right)$$

T_{air} is the ambient temperature (293.15K), T_o is the initial temperature of the FA (353.75K), and T is the temperature of the cooling FA in K. This value should be set up as a column that corresponds with time. A snip of the excel sheet we used is below.

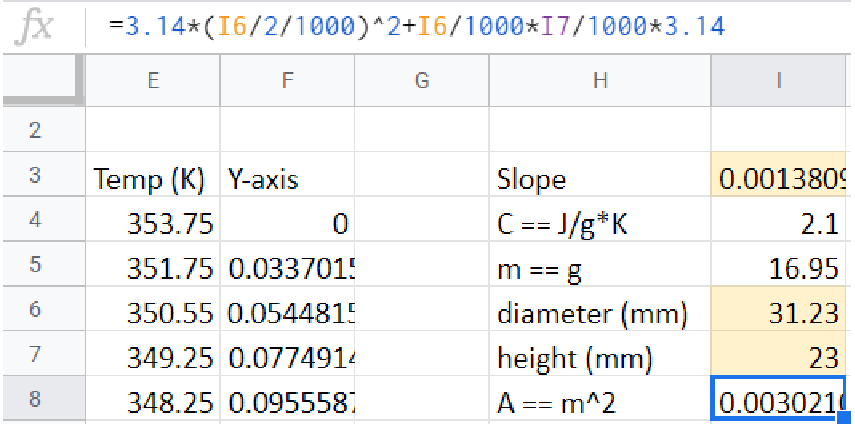


=ln((C2-C1)/(C2-E5))

	A	B	C	D	E	F
2		Tair (K)	293.4			
3	Raw information fror	Time (hh:mm:ss)	Time (s)	Temp (oC)	Temp (K)	Y-axis
4	18:05:08.234 -> 1.18	18:05:08.234	0	80.6	353.75	0
5	18:05:09.223 -> 2.16	18:05:09.223	20	78.6	351.75	0.033701

Figure F-1. Screenshot of Google Sheet, with equations, used to calculate U

Second, we calculated the slope of the y-axis) vs time (x-axis) data. This was done in excel simply by using the = slope (y-values, x-values). Third, we calculated the mass (m) of FA by multiplying volume and density. Fourth, we calculated the area (A) of heat transfer. We assumed that the beaker and the bottle are cylinders with heat transferring out of the sides and the top; no heat transfer is occurring through the bottom. Be careful to use meters in this calculation rather than millimeters which is how the data is recorded. A snip of that is included below.



```
=3.14*(I6/2/1000)^2+I6/1000*I7/1000*3.14
```

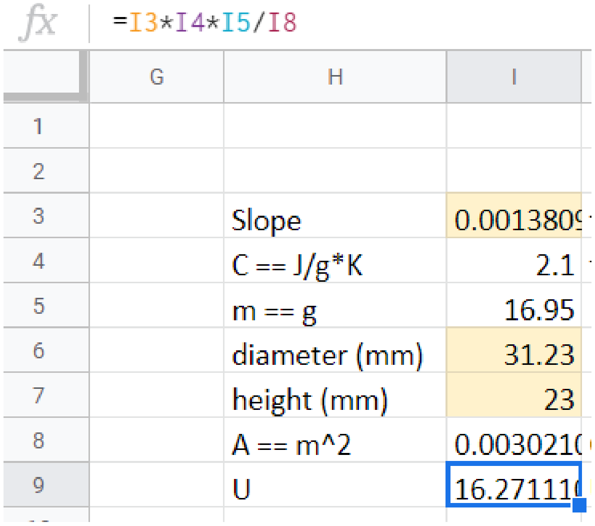
	E	F	G	H	I
2					
3	Temp (K)	Y-axis		Slope	0.0013809
4	353.75	0		C == J/g*K	2.1
5	351.75	0.0337015		m == g	16.95
6	350.55	0.0544815		diameter (mm)	31.23
7	349.25	0.077491		height (mm)	23
8	348.25	0.095558		A == m^2	0.003021

Figure F-2. Area of heat transfer snip

Lastly, to calculate U in units of W/(m^{2}K), we used the following equation.

$$U = slope * C * m/A$$

A snip is included below to show this calculation.



```
=I3*I4*I5/I8
```

	G	H	I
1			
2			
3		Slope	0.0013809
4		C == J/g*K	2.1
5		m == g	16.95
6		diameter (mm)	31.23
7		height (mm)	23
8		A == m^2	0.003021
9		U	16.27111

Figure F-3. Calculation of U snip

To conclude, we used excel to find standard deviation once we have completed our three experiments using the =stdev(results of U) function.

Appendix G: Mathcad Models and their Informing Experiments

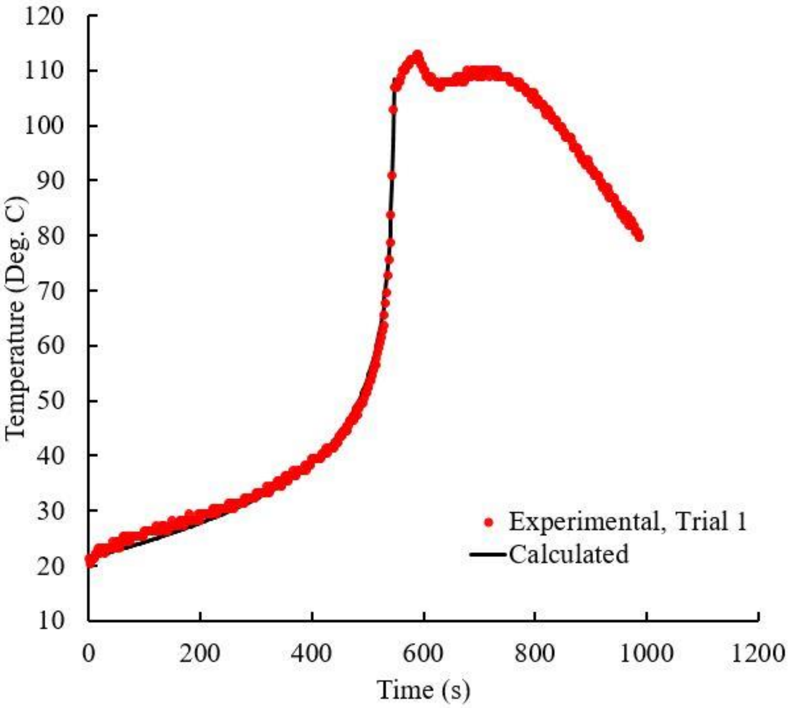


Figure G-1. Experimental and calculated fit temperature profile for the following conditions: 20mL beaker, 10mL recycled FA, 0.2mL of HCl.

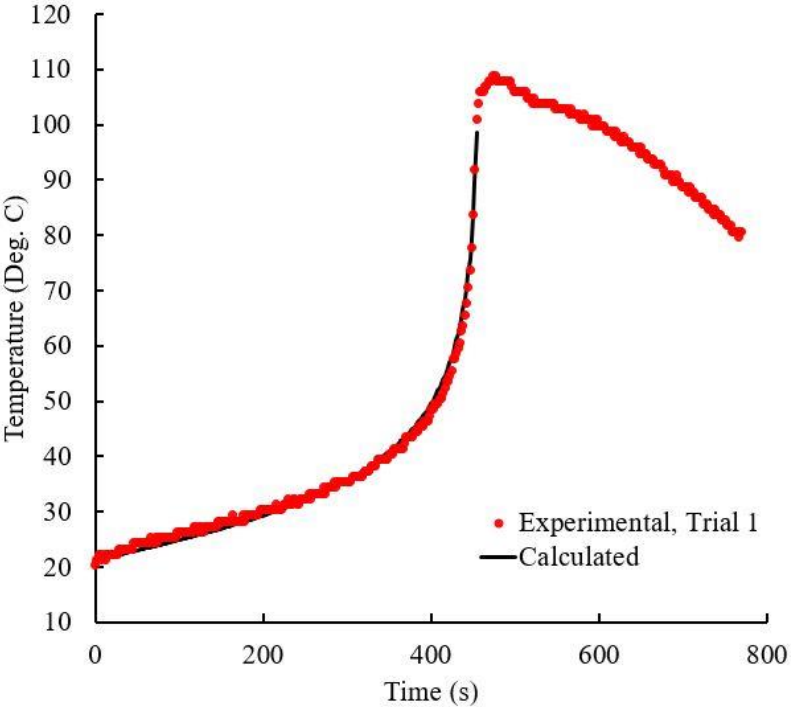


Figure G-2. Experimental and calculated fit temperature profile for the following conditions: 20mL beaker, 10mL FA, 0.2mL of HCl.

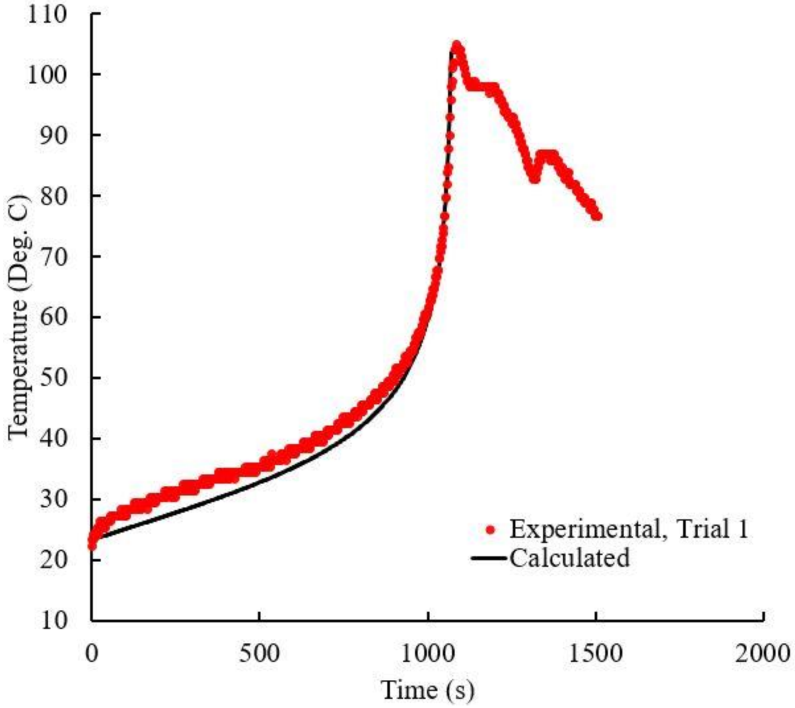


Figure G-3. Experimental and calculated fit temperature profile for the following conditions: 20mL beaker, 10mL FA, 0.1mL of HCl.

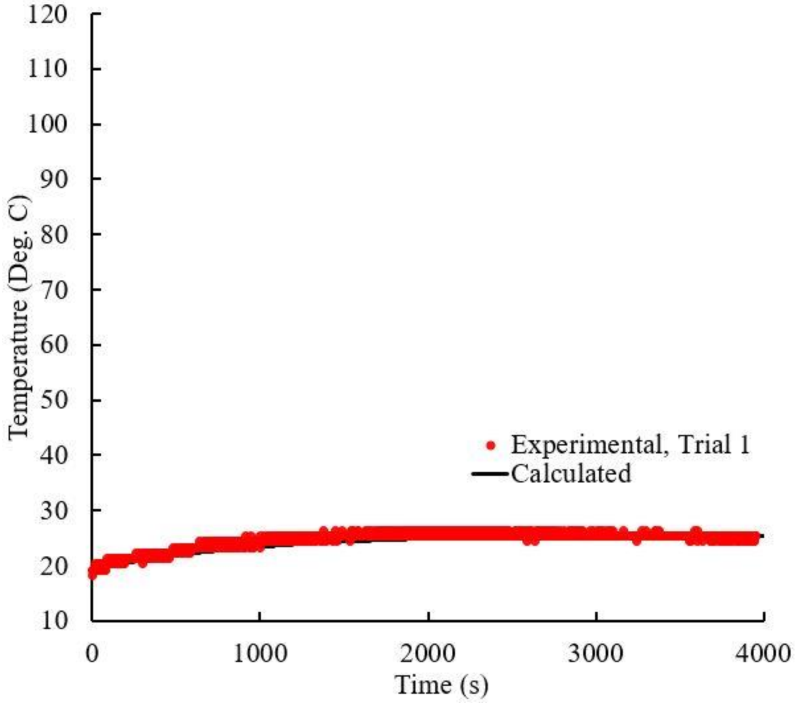


Figure G-4. Experimental and calculated fit temperature profile for the following conditions: 20mL beaker, 10mL FA, 0.05mL HCl.

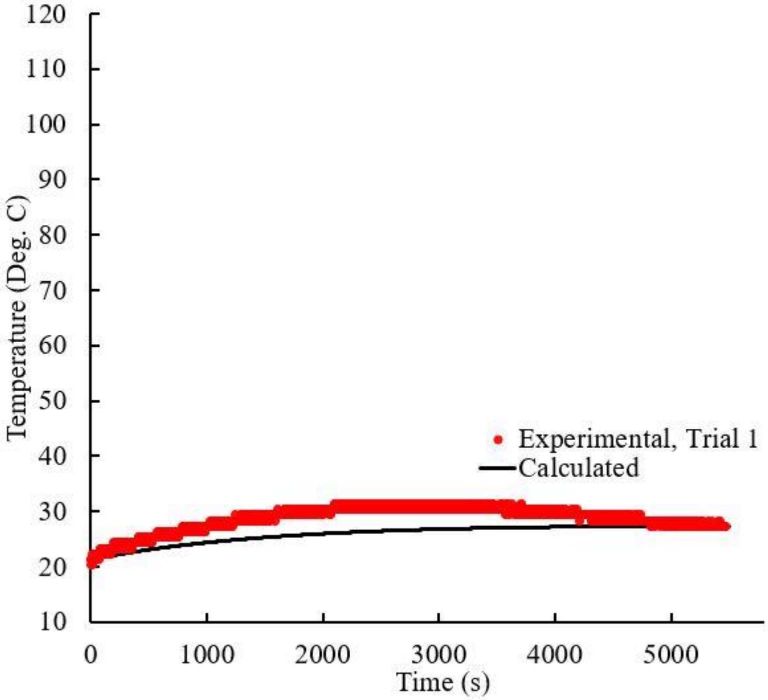


Figure G-5. Experimental and calculated fit temperature profile for the following conditions: 50mL beaker, 30mL FA, 0.1mL HCl.

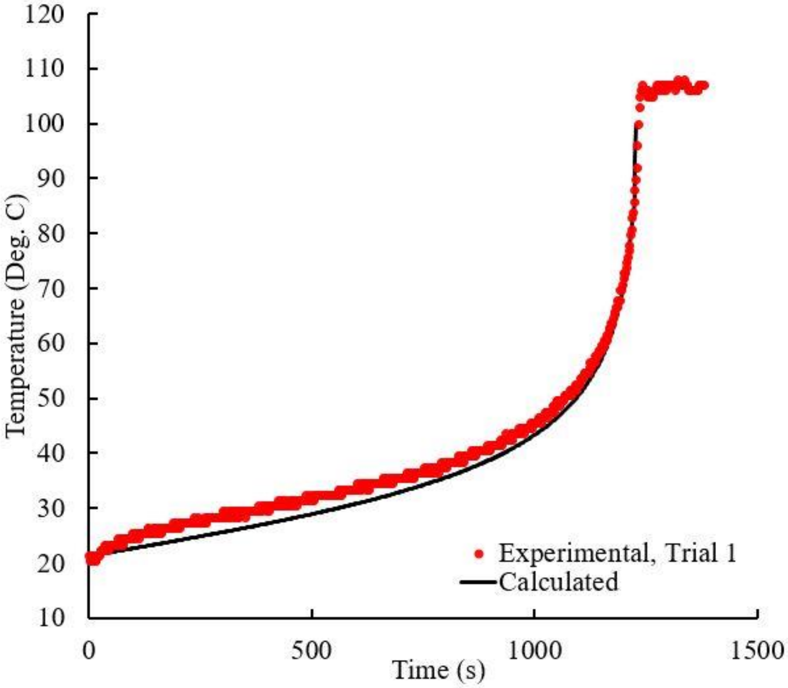


Figure G-6. Experimental and calculated fit temperature profile for the following conditions: 50mL beaker, 30mL FA, 0.2mL HCl.

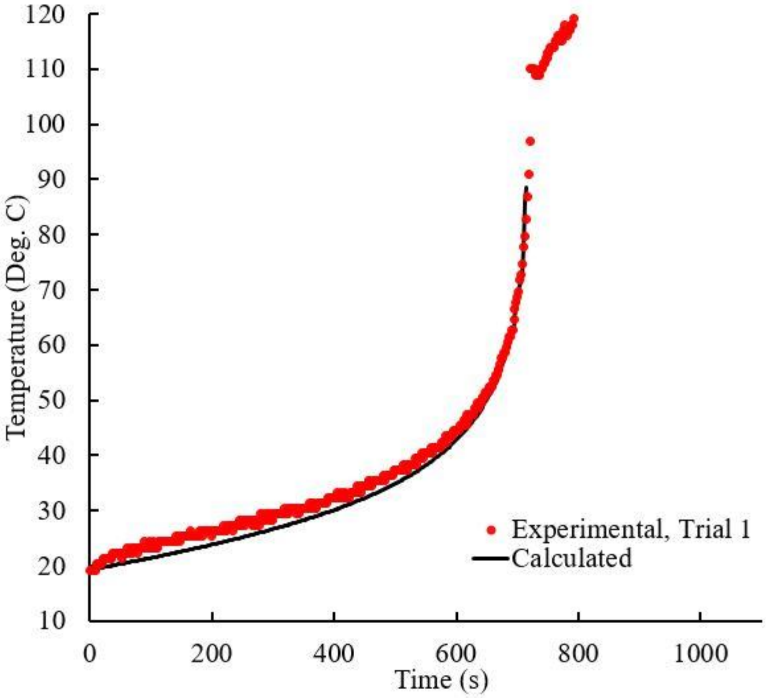


Figure G-7. Experimental and calculated fit temperature profile for the following conditions: 50mL beaker, 30mL FA, 0.3mL HCl.

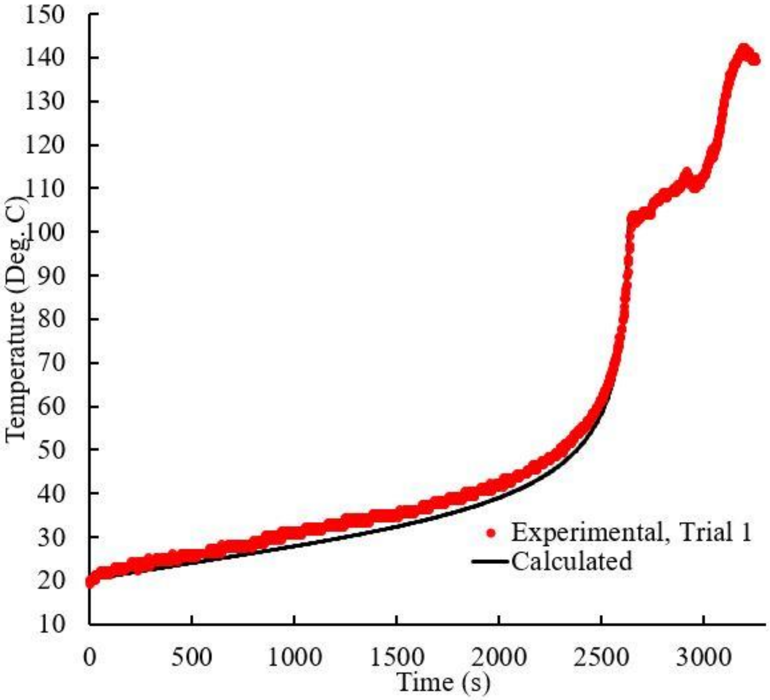


Figure G-8. Experimental and calculated fit temperature profile for the following conditions: 100mL beaker, 50mL, 0.2mL HCl.

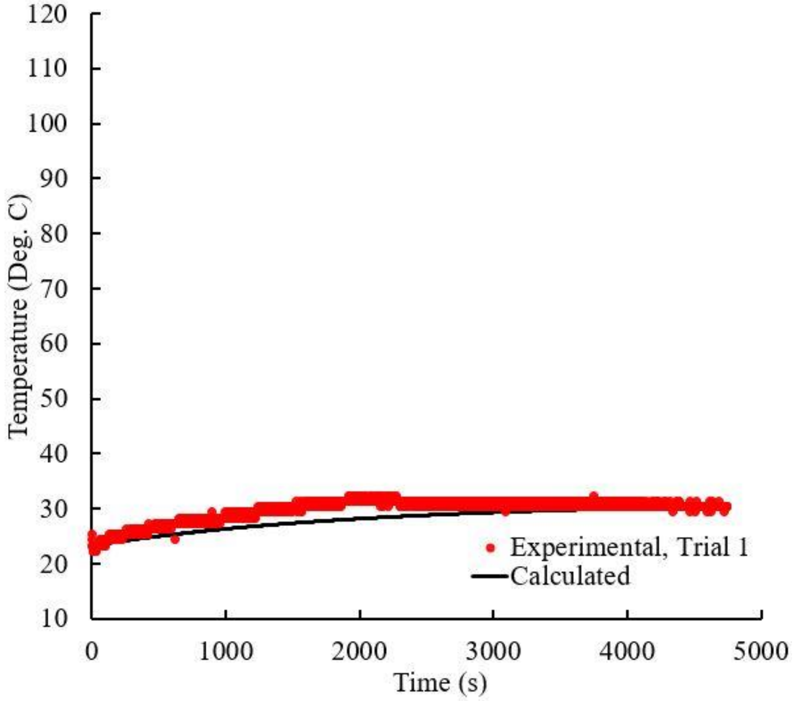


Figure G-9. Experimental and calculated fit temperature profile for the following conditions: 100mL beaker, 50mL, 0.15mL HCl.

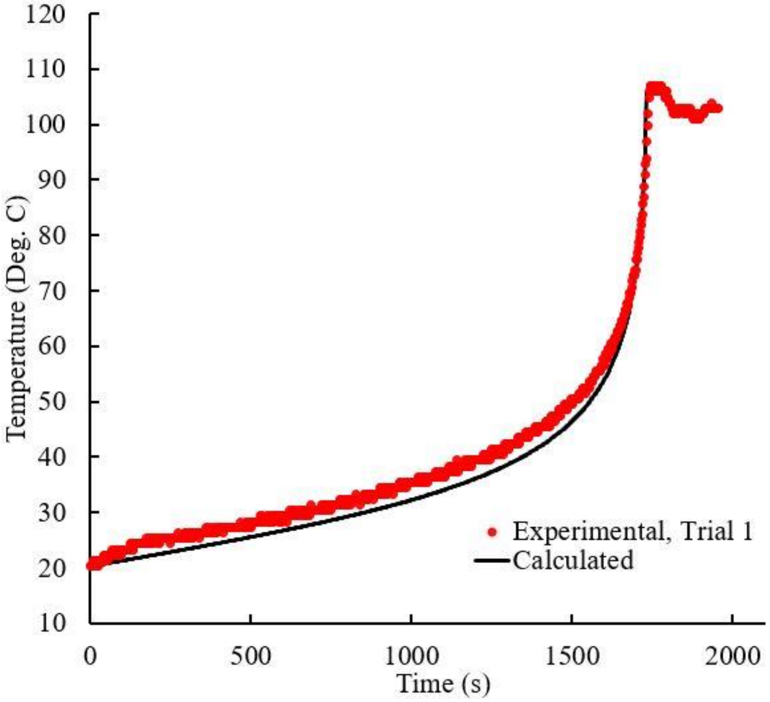


Figure G-10. Experimental and calculated fit temperature profile for the following conditions: 100mL beaker, 50mL, 0.3mL HCl.

Appendix H: Mathcad Predictions with Comparison Experiments

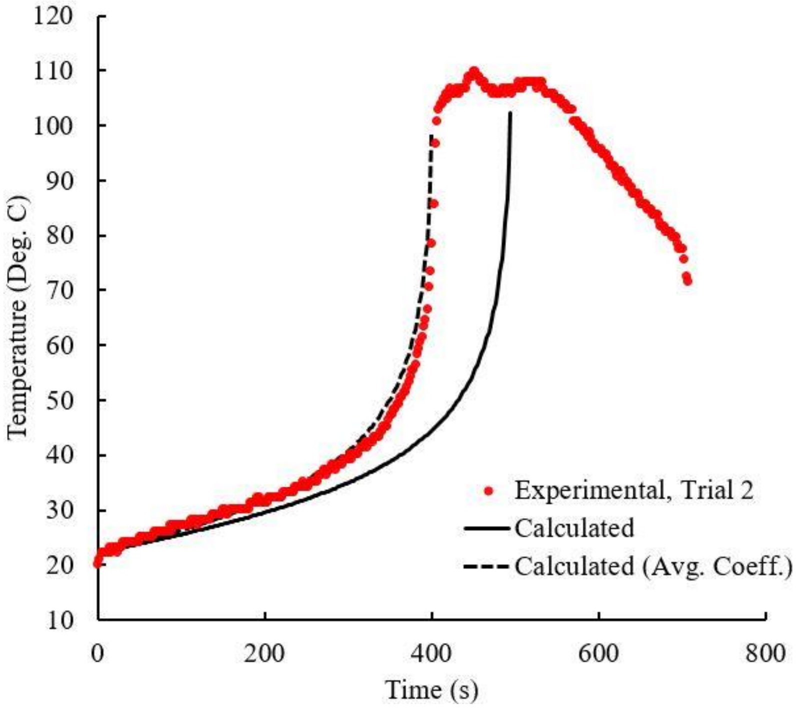


Figure H-1. Experimental and predicted temperature profile for the following conditions: 20mL beaker, 10mL recycled FA, 0.2mL of HCl.

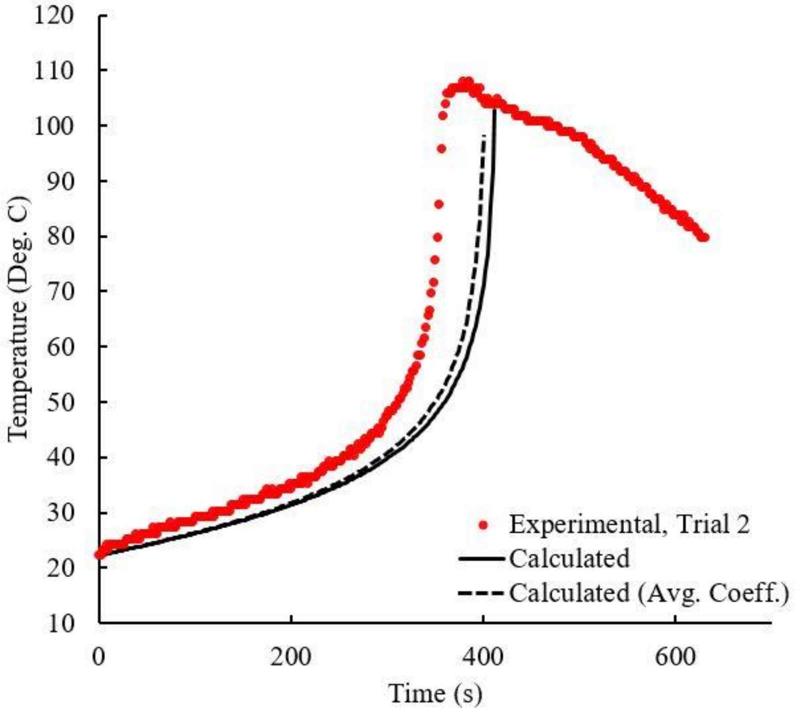


Figure H-2. Experimental and predicted temperature profile for the following conditions: 20mL beaker, 10mL FA, 0.2mL of HCl.

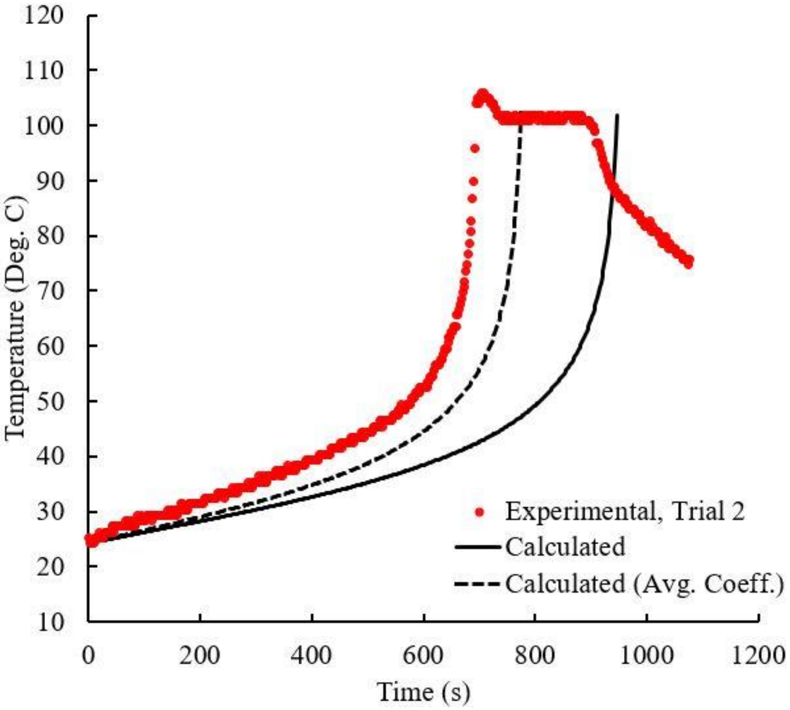


Figure H-3. Experimental and predicted temperature profile for the following conditions: 20mL beaker, 10mL FA, 0.1mL of HCl.

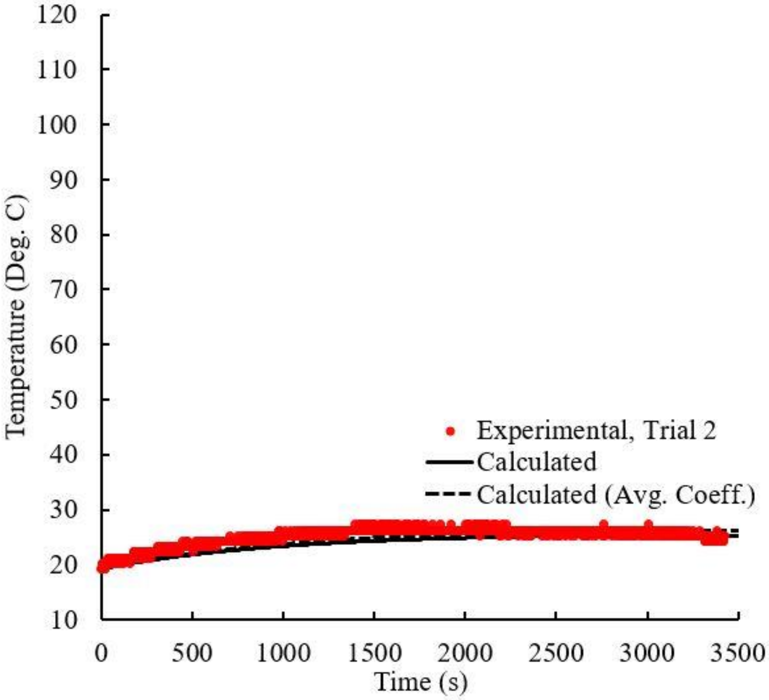


Figure H-4. Experimental and predicted temperature profile for the following conditions: 20mL beaker, 10mL FA, 0.05mL HCl.

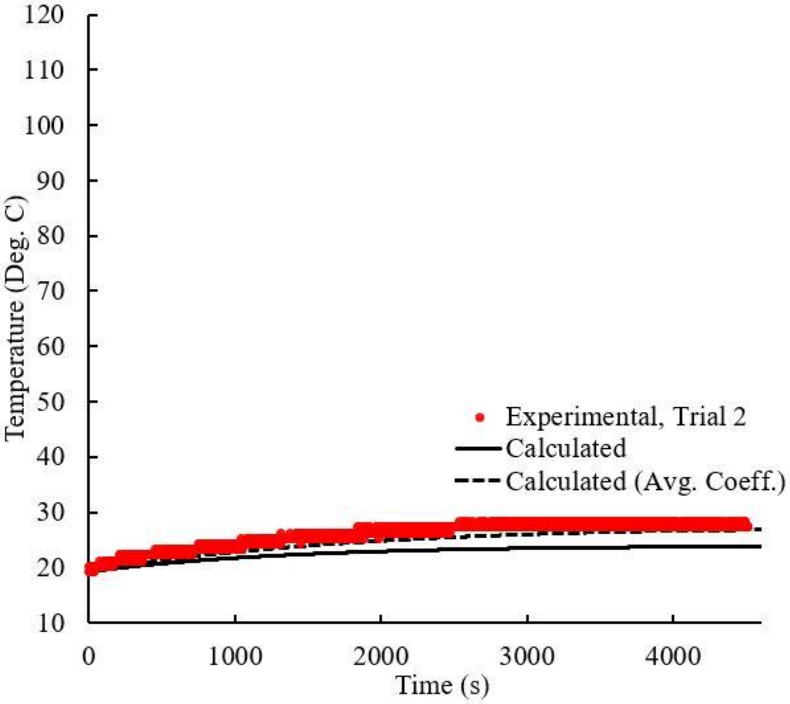


Figure H-5. Experimental and predicted temperature profile for the following conditions: 50mL beaker, 30mL FA, 0.1mL HCl.

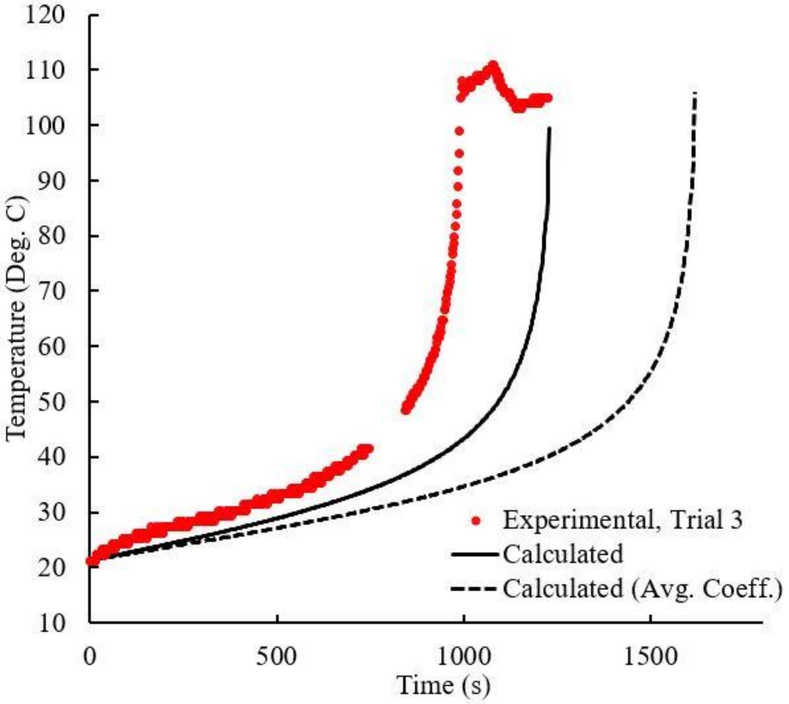


Figure H-6. Experimental and predicted temperature profile for the following conditions: 50mL beaker, 30mL FA, 0.2mL HCl.

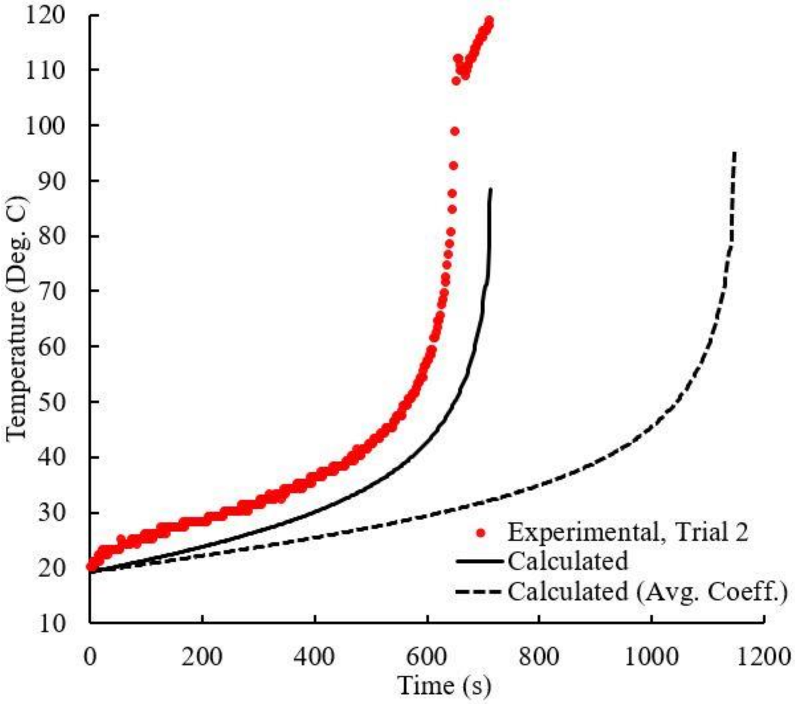


Figure H-7. Experimental and predicted temperature profile for the following conditions: 50mL beaker, 30mL FA, 0.3mL HCl.

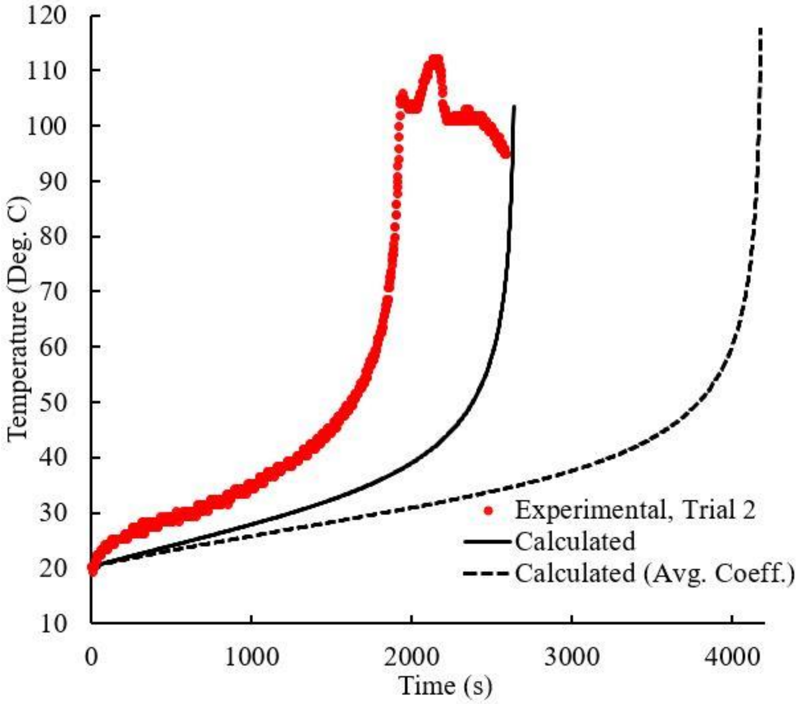


Figure H-8. Experimental and predicted temperature profile for the following conditions: 100mL beaker, 50mL, 0.2mL HCl.

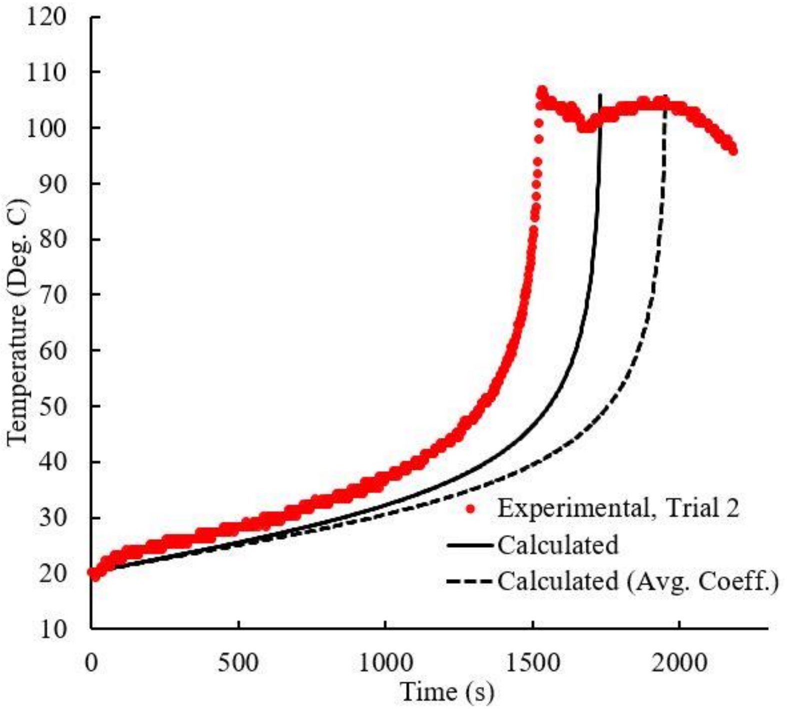
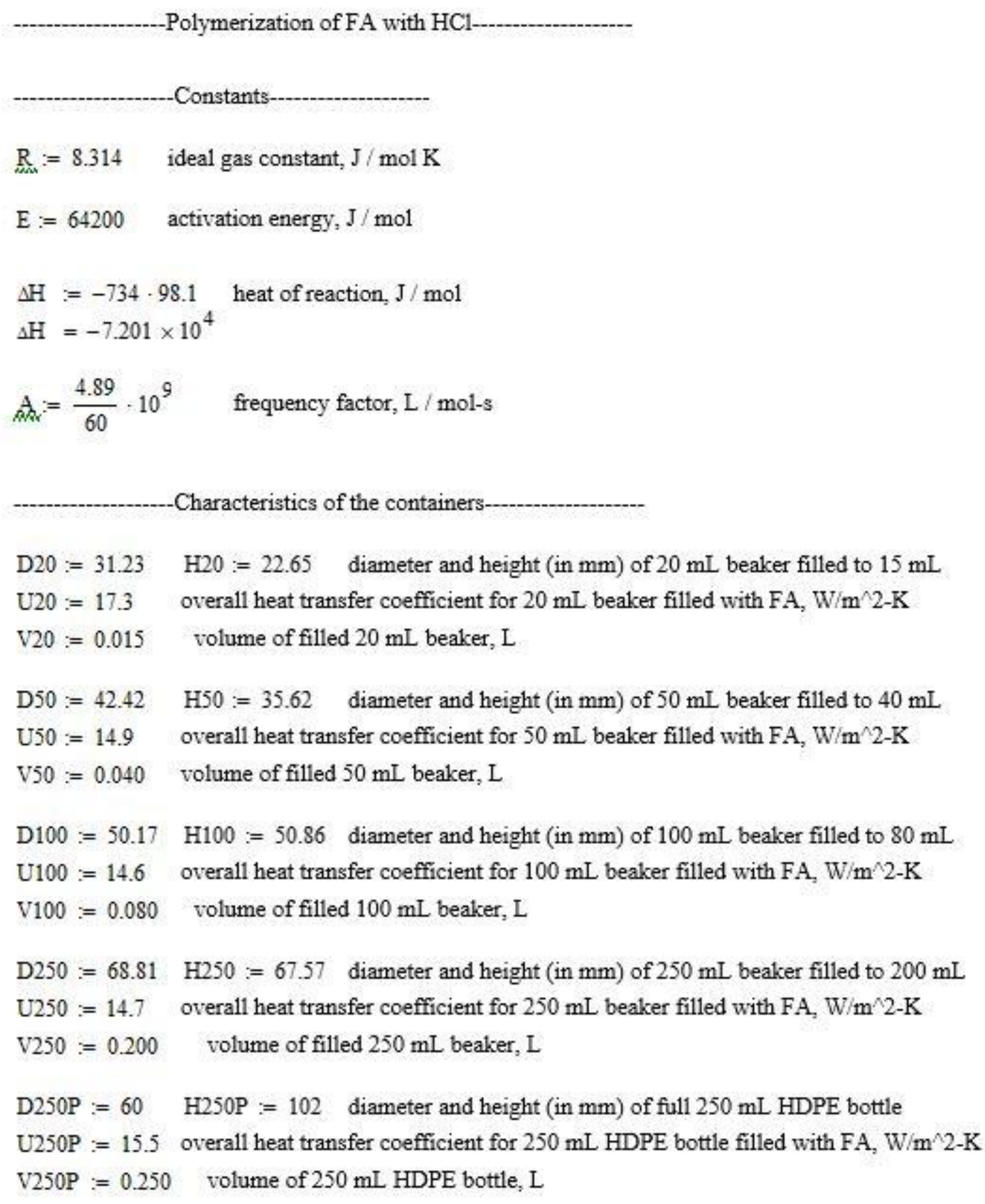


Figure H-9. Experimental and predicted temperature profile for the following conditions: 100mL beaker, 50mL, 0.3mL HCl.

Appendix I: Mathcad Model of Industrial Incident



-------------------Polymerization of FA with HCl-------------------

-------------------Constants-------------------

$R := 8.314$ ideal gas constant, J / mol K

$E := 64200$ activation energy, J / mol

$\Delta H := -734 \cdot 98.1$ heat of reaction, J / mol

$\Delta H = -7.201 \times 10^{4}$

$A := \frac{4.89}{60} \cdot 10^{9}$ frequency factor, L / mol-s

-------------------Characteristics of the containers-------------------

$D20 := 31.23$ $H20 := 22.65$ diameter and height (in mm) of 20 mL beaker filled to 15 mL

$U20 := 17.3$ overall heat transfer coefficient for 20 mL beaker filled with FA, W/m^2-K

$V20 := 0.015$ volume of filled 20 mL beaker, L

$D50 := 42.42$ $H50 := 35.62$ diameter and height (in mm) of 50 mL beaker filled to 40 mL

$U50 := 14.9$ overall heat transfer coefficient for 50 mL beaker filled with FA, W/m^2-K

$V50 := 0.040$ volume of filled 50 mL beaker, L

$D100 := 50.17$ $H100 := 50.86$ diameter and height (in mm) of 100 mL beaker filled to 80 mL

$U100 := 14.6$ overall heat transfer coefficient for 100 mL beaker filled with FA, W/m^2-K

$V100 := 0.080$ volume of filled 100 mL beaker, L

$D250 := 68.81$ $H250 := 67.57$ diameter and height (in mm) of 250 mL beaker filled to 200 mL

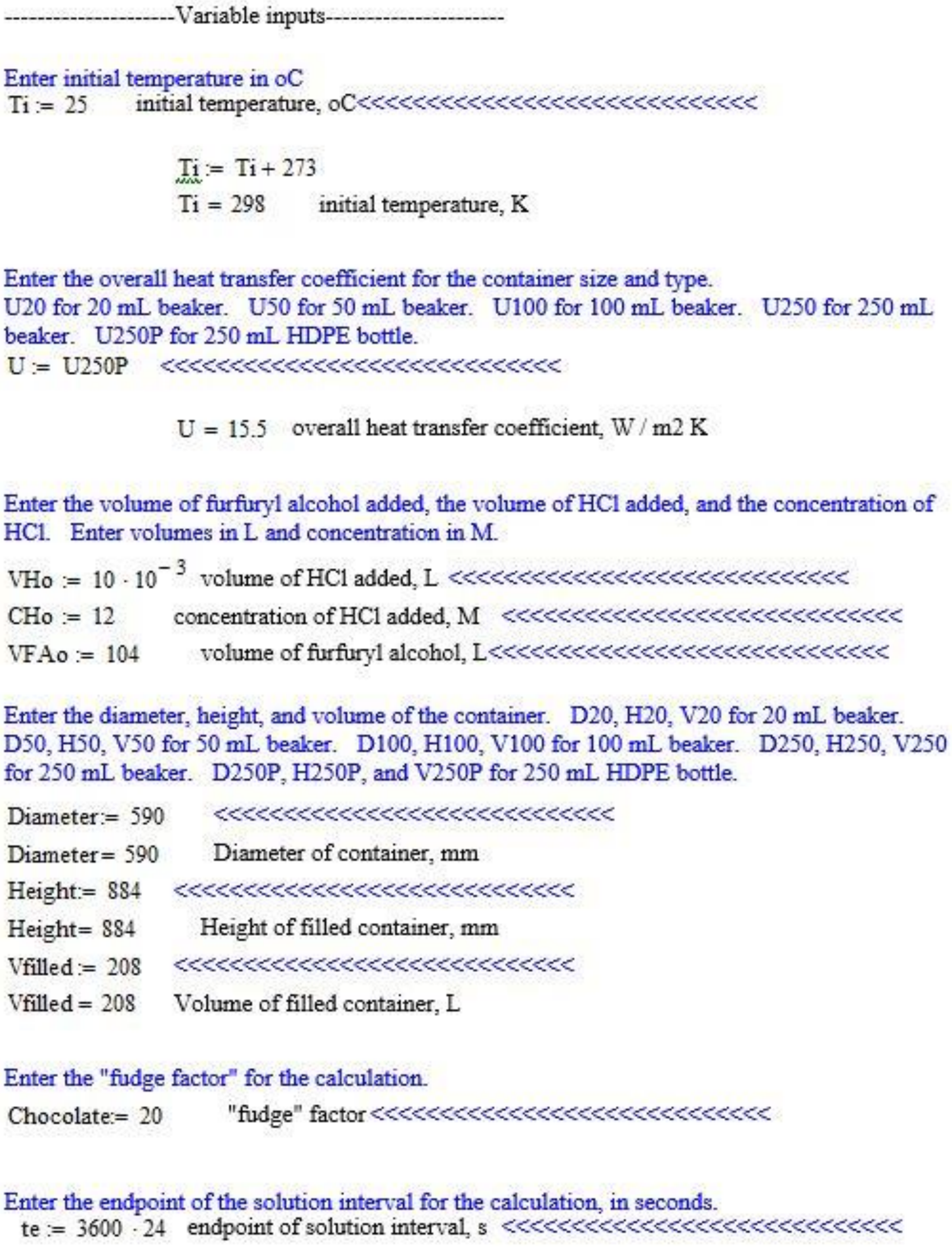
$U250 := 14.7$ overall heat transfer coefficient for 250 mL beaker filled with FA, W/m^2-K

$V250 := 0.200$ volume of filled 250 mL beaker, L

$D250P := 60$ $H250P := 102$ diameter and height (in mm) of full 250 mL HDPE bottle

$U250P := 15.5$ overall heat transfer coefficient for 250 mL HDPE bottle filled with FA, W/m^2-K

$V250P := 0.250$ volume of 250 mL HDPE bottle, L



---------------------Variable inputs----------------------

Enter initial temperature in oC

Ti := 25 initial temperature, oC<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Ti := Ti + 273

Ti = 298 initial temperature, K

Enter the overall heat transfer coefficient for the container size and type. U20 for 20 mL beaker. U50 for 50 mL beaker. U100 for 100 mL beaker. U250 for 250 mL beaker. U250P for 250 mL HDPE bottle.

U := U250P <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

U = 15.5 overall heat transfer coefficient, W / m2 K

Enter the volume of furfuryl alcohol added, the volume of HCl added, and the concentration of HCl. Enter volumes in L and concentration in M.

VHo := $10 \cdot 10^{-3}$ volume of HCl added, L <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

CHo := 12 concentration of HCl added, M <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

VFAo := 104 volume of furfuryl alcohol, L<<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Enter the diameter, height, and volume of the container. D20, H20, V20 for 20 mL beaker. D50, H50, V50 for 50 mL beaker. D100, H100, V100 for 100 mL beaker. D250, H250, V250 for 250 mL beaker. D250P, H250P, and V250P for 250 mL HDPE bottle.

Diameter := 590 <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Diameter = 590 Diameter of container, mm

Height := 884 <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Height = 884 Height of filled container, mm

Vfilled := 208 <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Vfilled = 208 Volume of filled container, L

Enter the "fudge factor" for the calculation.

Chocolate := 20 "fudge" factor <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

Enter the endpoint of the solution interval for the calculation, in seconds.

te := 3600 · 24 endpoint of solution interval, s <<<<<<<<<<<<<<<<<<<<<<<<<<<<<<

--------------------Algebra and estimations--------------------

$CH := \frac{CHo \cdot VHo}{VHo + VFAo}$ concentraion of H+ in solution, M

$CH = 1.154 \times 10^{-3}$

$C := 2$ J / g K

$m := VFAo \cdot 1000 \cdot 1.13 = 1.175 \times 10^{5}$ g

$Area := \left(Diameter \cdot Height \cdot \pi \cdot 10^{-6}\right) \cdot \frac{VFAo}{Vfilled} + Diameter^{2} \cdot \pi \cdot 0.25 \cdot 10^{-6}$ m2

$Area = 1.093$

--------------------Calculation--------------------

Giver

$$\frac{d}{dt}T(t) = \frac{VFA(t) \cdot -\Delta H \cdot \left(Chocolate \cdot A \cdot \exp\left(\frac{-E}{R \cdot T(t)}\right)\right) \cdot CH + U \cdot Area \cdot (Ti - T(t))}{C \cdot m}$$

$T(0) = Ti$

$$\frac{d}{dt}VFA(t) = VFA(t) \cdot \left(-A \cdot Chocolate \cdot \exp\left(\frac{-E}{R \cdot T(t)}\right)\right) \cdot CH \cdot \frac{98.10}{1.13 \cdot 1000}$$

$VFA(0) = VFAc$

$$\begin{pmatrix} T \\ VFA \end{pmatrix} := Odesolve\left[\begin{pmatrix} T \\ VFA \end{pmatrix}, t, te, 1 \times 10^{3}\right] \qquad t := 0, 2 .. te$$

$Tc(t) := T(t) - 273$