

The Acid Catalyzed Polycondensation of Furfuryl Alcohol

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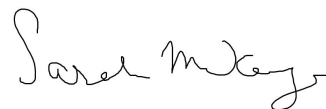
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April 22nd, 2019



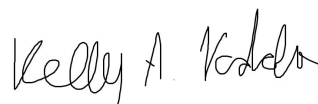
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ABSTRACT

Inspired by a chemical explosion involving a drum of furfuryl alcohol at a local chemical plant, the team investigated the acid-catalyzed polycondensation of furfuryl alcohol through COMSOL multi-physics modeling and a series of lab experiments. To investigate the explosion, furfuryl alcohol was reacted in stainless steel vessels with methanesulfonic and hydrochloric acid contaminants to observe the changes in temperature and pressure throughout the reaction. The maximum temperature recorded in the experiments was 170.5 °C, and pressures greater than 75 psi were generated. The reaction proved to be both volatile and unpredictable. The timeline of this reaction ultimately allowed the team to develop improved process safety recommendations for the handling of furfuryl alcohol in industry.

ACKNOWLEDGEMENTS

The team would like to thank Professor Stephen Kmiolek of Worcester Polytechnic Institute (WPI) for the opportunity to work on this project. Professor Kmiolek provided never-ending guidance, support, and enthusiasm over the course of this past year.

The team would also like to thank Tom Partington, WPI's Goddard Hall Unit Operations Lab Manager. Tom built the reaction vessels needed to run experiments, and added various safety and design features in order to help the experiments run smoothly.

The team would also like to thank Avery Brown and Andrew Butler for their helpful contributions in the team's attempts to discover the composition of the resin formed in the reaction and exploring methods of breaking it down.

Finally, the team would like to thank Professor William Clark of WPI for his help and knowledge in COMSOL when the team was modeling the reaction.

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1.0 INTRODUCTION

The project team studied chemical explosion phenomena, specifically explosions resulting from acid catalyzed polymerization reactions. The team modeled reactions using COMSOL Multiphysics to increase their understanding of the reaction, compare theoretical data to experimentally determined data, and to gauge how successful the computer simulation was at modeling the actual reaction. The interest in this reaction stemmed from an incident that occurred at a local chemical company involving a drum of furfuryl alcohol contaminated with acid that led to an overpressurization of the drum, and a subsequent explosion. No personnel were harmed in the incident, but this event identified gaps in the chemical industry's knowledge of the reactivity of furfuryl alcohol, and proved the need for more research to prevent these types of incidents from happening in the future.

In an attempt to model the incident, the main chemical the team studied was furfuryl alcohol, in the presence of different acid contaminants. Specifically, the team investigated the use of methanesulfonic acid and hydrochloric acid as potential contaminants that could cause acid-catalyzed polycondensation reaction to occur. The goal of this research was to gain a stronger understanding of the thermodynamics and kinetics of these reactions that would ultimately allow the team to develop improved process safety design recommendations and prevent similar explosions from occurring in industry.

2.0 BACKGROUND

2.1 Chemical Explosions Prevalence, Definitions, and Incidents

According to the NFPA report, “Between 2011 and 2015, municipal fire departments in the U.S. responded to an estimated average of 37,910 fires at industrial or manufacturing properties each year, with annual losses from these fires estimated at 16 civilian deaths, 273 civilian injures and \$1.2 billion in direct property damage” (NFPA, 2018). While not all of those fires are due to chemical plant explosions, explosions impact personnel and the surrounding area quite significantly and negatively.

There are two different types of explosions: detonating and deflagrating. A detonating explosion involves the rapid decomposition of a substance at high pressure. Subcategories of this type include primary and secondary detonation. Primary explosives will detonate by ignition from a source that produces a significant amount of energy in the form of heat, while secondary explosives demand a detonator. A deflagrating explosion requires fast burning at relatively low-pressure conditions. Examples of a deflagrating explosion are black and smokeless powders. (Britannica, 2018).

Immediate health concerns surrounding explosions are smoke inhalation, burns due to heat released, and debris. Longer-term effects include eye and lung damage due to severe irritants. Toxins present in the smoke have the ability to form free radicals, which can directly cause airway inflammation. Chemical explosions exacerbate immediate and long-term effects due to the hazardous nature of the chemicals. Specific safety data sheets (SDS) of the chemicals used for the purpose of this study can be found in Appendix A.

Chemical explosions can have detrimental long-term effects on the environment due to contamination of the water, air, and nature. The toxins negatively influence the ecosystem and also propose adversity to humans through eventual inhalation or consumption. (Public Health England, 2018).

The project was motivated by an incident that occurred at a local chemical company. On December 14th, 2010, in the facility located in Marlborough, MA, a 55-gallon HDPE drum, partially filled with furfuryl alcohol became overpressurized. The drum deformed from heat, and due to the combination of heat and pressure, a hole was blown out (Figures 1 - 2).

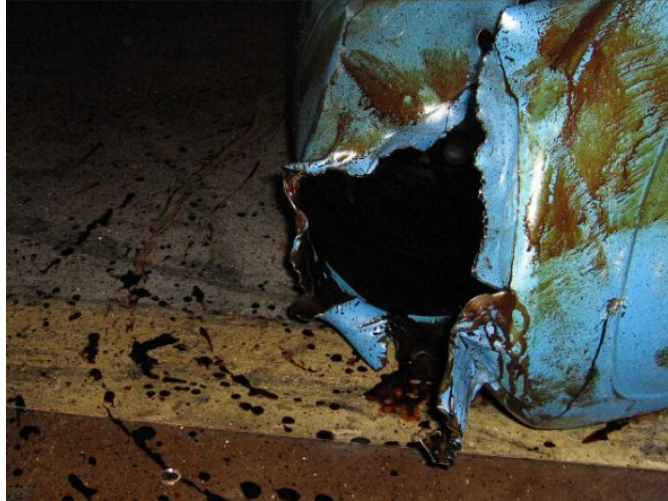


Figure 1. Overpressurized and overheated drum which resulted in a hole being blown out



Figure 2. Overpressurized and overheated drum aftermath

At the time of the rupture, the drum was propelled 35 feet in the air, hitting the roof and falling back down, spraying a sticky black resin. The drum was in the staging area and no people were located in the immediate vicinity. The facility was evacuated immediately afterward and a later investigation determined that a pump transfer line was contaminated with trace amounts of an acid. The work conducted in this project sought to better understand the unintended reactions that occurred, including the heat and pressure release, and to develop a safety timeline to help guide future safety efforts.

Another example of a more detrimental chemical explosion was in the Chinese city of Tianjin. There was illegal storage of 49,000 tons of sodium cyanide when the warehouse was supposed to only store 24 tons. The explosion killed 173, most of which were firefighters and police officers,

and injured 798. The release of sodium cyanide was concerning in terms of the potentially devastating environmental consequences. Sodium cyanide poisons the respiratory system and creates a poisonous acid upon contact with water. Cyanide also created mass panic due to potential inhalation of toxic gases, which called for an evacuation within a 3-kilometer radius (Bleiker, 2015).

Investigators later found that stocks of nitrocellulose, a flammable compound used as a binding agent, became too dry within the heat of the day and burst into flames. These flames spread to the illegal storage of combustible fertilizer ammonium nitrate, which destroyed an adjacent lot and caused considerable damage. The plant warehouse was also illegally built too close to the apartment buildings. The incident contaminated air, water, and soil, but luckily did not have an effect on the ocean water quality near Tianjin. (Associated Press, 2016). Proper precautions and personnel following stricter procedures could have prevented this tragedy.

An example of a polycondensation reaction explosion involved ethylene oxide stored in steel cylinders. There were two explosions in 1946 and 1947, where a 200 lb capacity container exploded due to overpressurization. The cylinders had been tested to withstand 1200 psi, meaning considerable pressure buildup had occurred before the explosion and release of contents. In both incidents, the ethylene oxide contained trace amounts of alkali and water. The residue from the second case, observed as a polycondensate of ethylene oxide, was dark brown viscous and water-miscible liquid. After several studies with the contaminants involved, the catalyst, responsible for the initiation of the reaction, was determined to be alkali (Gupta, 1949).

Another incident involved benzyl chloride being introduced to a factory in Harima, Hyogo, Japan, without a proper safety evaluation. This introduction led to a polycondensation reaction with rust, which resulted in an explosion of the receiver vessel. The investigation determined that benzyl chloride went into gaps in the iron rust and when the polycondensation reaction occurred the hydrogen chloride gas was generated, causing the receiver vessel to explode due to the increased pressure. (ARAI, Mitsuru, TAMURA, Masamitsu, Yokohama National University, 1997).

2.2 Existing Safety Precautions and Regulations for Preventing Chemical Explosions

In order to minimize the hazardous situations that surround chemical explosions, many government agencies have implemented codes and standards that companies must follow. These codes and standards provide guidelines for the handling of chemicals throughout the entirety of a production process and into the storage and shipping. In addition, there are regulations in place that focus on minimizing negative environmental impacts.

One agency, the National Fire Protection Agency (NFPA) has published more than 300 codes and standards that are recognized and utilized worldwide. These codes cover most industries and mainly focus on minimizing the potential and consequences of fires. The existing safety precautions and regulations, focusing on chemicals and chemical explosions, are included in the following codes and standards:

- **NFPA 30. Flammable and Combustible Liquids Code**
- **NFPA 35. Standard for Manufacturing Organic coatings**
- **NFPA 45. Standard on Fire Protection for Laboratories Using Chemicals**
- **NFPA 69. Standard on Explosion Prevention Systems**
- **NFPA 400. Hazardous Materials Code**
- **NFPA 495. Explosive Materials Code**

Additionally, the Occupational Safety and Health Administration (OSHA) administers standards and rules that employers need to legally follow in order to protect their employees from potential dangers. Standard number 1910.132 covers the required Personal Protective Equipment (PPE) that employers must provide to their employees. The requirements for employers include performing a “hazard assessment” on the workplace, providing employees with proper PPE and the training on its use/care, maintaining the PPE, and continuously evaluating the effectiveness on the implemented PPE program. Additionally, the employee is expected to properly wear PPE, attend the provide PPE training classes, properly care and maintain their PPE, and inform a supervisor if PPE needs repair or replacement. Standard number 1910.144 details proper color identification for marking physical hazards. As a general reference, the color red denotes fire protection apparatus equipment, danger or stop, and the color yellow denotes caution. In terms of chemical dangers, any containers holding flammable liquids must be painted red with an additional marker, whether it is a yellow band on the can or the contents labeled in yellow on the can. Standard number 1910 Subpart L App A details regulations for the various fire protection techniques companies may have in place. These range from fire brigades, portable fire extinguishers and standpipe and hose systems to more automatic extinguishing systems.

In terms of transporting chemicals, the Department of Transportation (DOT) has its own set of unique rules that companies must follow. A subgroup of the Department of Transportation is the Pipeline and Hazardous Materials Safety Administration (PHMSA). This Administration has an operator qualification rule, adopted into the code of federal regulations under Subpart N in 49 CFR Part 192 and Subpart G in 49 CFR Part 195, under which each pipeline operator is responsible for developing an operator qualification program. This program entails defining the training and qualification requirements, having a written version of the plan, and ensuring their contractors and vendors comply with the requirements. Additionally, each pipeline operator must

establish a task list applicable to their system. Operators must adhere to the most current version of the Electronic Code of Federal Regulations, which details specifications for packing, tanks, maintenance, and general transportation rules. If certain types of hazmat incidents occur, they must be reported according to 49 CFR Parts 171-180. Incidents must be reported through PHMSA within 30 days of the incident, and a written report must be submitted within one year using the proper report form. The information on the report is analyzed by PHMSA and similar agencies to reduce risk and increase public safety. (USDOT, 2018).

The Environmental Protection Agency (EPA), a well-known and respected agency of the US government, has instituted acts for toxic substance controls and pollution prevention. Under their Toxic Substances Control Act (TSCA) the importation of chemicals that are not on the TSCA inventory, or are subject to exemptions, are prohibited. The chemicals not on the list are referred to as “new chemicals”, and manufacturers must submit a pre-manufacturing notification to EPA before manufacturing or importing new chemicals. Chemical Data Reporting (CDR) requires manufacturers to provide EPA with info regarding chemicals especially those in transport or in large quantities.

In terms of pollution prevention, the Pollution Prevention Act is aiming to reduce the amount of pollution through setting standards in production, operation, and raw material use. Source reductions are not common due to existing regulations, but compliance focuses on proper treatment and disposal. This act also includes practices that increase energy and water efficiency, and protect resources through conservation. (EPA, 2018).

Additionally, EPA provides information on the compatibility of certain chemicals in compatibility charts (Appendix B).

WPI also provides compatibility charts, from the CRC Laboratory handbook, to ensure safe operations (Appendix B). Alcohols are classified as group 6 and incompatible with inorganic acids. Some inorganic acid examples include hydrochloric acid and sulfuric acid.

2.3 Kinetics of Polycondensation Reactions

The reaction between an acid and furfuryl alcohol is classified as an acid catalyzed polycondensation reaction. The polymerization of the furfuryl alcohol occurs through two mechanisms: chain-growth polymerization and step-growth polymerization. Chain-growth polymerization is the process in which unsaturated monomer molecules add onto the active site of a growing polymer chain one at a time. Step-growth elimination involves the reaction of multi-functional monomers (monomers with more than one reactive group) forming dimers, trimers, and eventually oligomers.

This particular reaction is catalyzed by the presence of an acid. Choura et al. found that the hydrogen ions present from the acid primarily attack the alcohol group, causing the formation of a carbocation on the methylene branch of the furanic ring, forming methylene linkages in the polymer strand. It is also possible for the hydrogen ions to attack the oxygen atom in the furan ring, opening the possibility of an OH-OH condensation, resulting in the formation of a diketone structure. These two reactions form two different reaction intermediates as seen in the figure below.

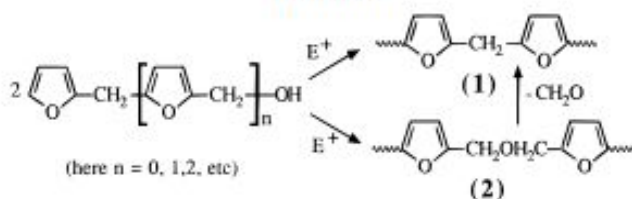


Figure 3. Primary Reaction Pathways for Polycondensation of Furfuryl Alcohol (Choura et al.)

The first of these two reaction mechanisms is more thermodynamically favored than the other and was considered as the primary means of reaction throughout this experiment (Kim et al.). Dunlop and Peters have also hypothesized a third reaction, involving the formation of dimethylene ether linkages through the methyl groups of two furan rings reacting together.



Figure 4. Condensation Reaction of Furfuryl Alcohol Resulting in the Formation of Dimethylene Ether Linkage (Bertarione et al.)

To this date, the reaction chemistry of this particular polycondensation reaction is still unclear due to the complexity of the reaction. These multiple reaction mechanisms propose the possibility of the formation of oligomer chains with different chain linkages, and the potential for conjugated species to form. This is also supported by the fact that this reaction produces a thick, black resin-like substance. If the reaction only occurred through one of the aforementioned mechanisms, a linear polymer chain would be produced, resulting in a colorless product due to the absence of chromophore (Bertarione et al.).

The kinetics of this reaction are complex and widely unknown due to the intensity of the reaction in most circumstances. One research group, Sun et al., studied the kinetics of the reaction in an aqueous solution which served as a controllable environment. The goal of their research was to

see if the oligomer products of this reaction could be controlled and eventually converted into long alkane chains (C₉-C₂₅) for preparing diesel precursors. It was determined by Sun et al. that this reaction is dependent on the strength and concentration of the acid, and temperature of the reaction. The reaction is a first order reaction described by the following equation:

$$r_A = -dC_A/dt = k' C_{H^+}^\alpha C_A^\beta \quad (1)$$

$$k = k' C_{H^+}^\alpha \quad (2)$$

$$r_A = k C_A^\beta \quad (3)$$

Where k' is the reaction rate constant, C_{H⁺} is the concentration of hydrogen ion in the system, C_A is the concentration of furfuryl alcohol, α is the reaction order of hydrogen ions, β is the reaction order of furfuryl alcohol, and t is the reaction time. Their research concluded that the reaction order of both the hydrogen ions and furfuryl alcohol are first order. This also concludes that the rate of the reaction is dependent on the strength of the acid due to the presence of readily available hydrogen ions. It was also determined that the conversion of the reaction increased with increasing temperature, and further influencing the length of the polymer chains created in the reaction. Higher temperatures favored the production of smaller oligomer chains, while lower temperatures promoted the production of longer, high molecular weight chains through step-growth polymerization. Ultimately it was determined that the rate of reaction for a 100g aqueous solution containing 25g of furfuryl alcohol and 1.25g of sulfuric acid can be described by the following equation:

$$r_A = -dC_A/dt = 4.89 * 10^9 e^{-7721/T} C_{H^+} C_A \quad (4)$$

This rate equation was used in the preliminary modeling of the experiment to construct a baseline model. There is still a great deal to be learned about the kinetics of this reaction, especially in uncontrolled environments.

2.4 Reaction Thermodynamics

The measured heat of reaction for the polycondensation of furfuryl alcohol is approximately 860 kJ/kg of furfuryl alcohol (Kmiotek, personal communication November 10, 2018). Based on these numbers, had an entire drum of furfuryl alcohol reacted, over 36.8 MW of energy could have been produced.

2.5 COMSOL Overview

COMSOL Multiphysics® is simulation software for modeling all fields of scientific research, engineering, and manufacturing. This is done by allowing the user the ability to build a 3D shape using specified materials. When this shape is created, the user may model to see how different flow rates and chemical reactions would take place within the designed shape. For the purposes of this experiment, the team modeled a chemical process by creating a 3D model of a drum, and inputting the physical properties of the different chemical species and selected the physics involved. For the model, the team chose to use the transport of diluted species and heat transfer as the multiphysics models (Comsol 2018).

3.0 METHODOLOGY

3.1 COMSOL Modeling

A COMSOL model was developed to serve as a predictive model for the acid-catalyzed polycondensation of furfuryl alcohol to analyze the rate of reaction and heat generated in the reaction. The model developed is a time dependent study that utilizes the transport of diluted species and heat transfer in fluids physics models within COMSOL to simulate the phenomena present in the reaction. The model space was set up as a rectangular cross section in 2-D axial mode that would resemble a cylinder when rotated 360 degrees around the z-axis. In this model it was assumed that the reaction would be symmetrical around the z-axis. The 2-D axial mode was used in this simulation to allow for faster calculations, and to simplify the physical location of each component in the reaction.

The physical properties of furfuryl alcohol were researched from verified sources online and manually input into the model. For the acid component of the reaction, the physical properties of sulfuric acid were input despite the fact that most of the experimentation conducted in this project involved the use of methanesulfonic and hydrochloric acid. This substitution of acids was due to primarily two reasons. The first is that information on the physical properties of methanesulfonic acid were not easily accessible. Secondly, the source of where the team obtained information on the kinetics of this polycondensation reaction used sulfuric acid in their study (Sun et al.).

The reaction kinetics were also manually input in the model through the “Reactions” subcategory under the Transport of Diluted Species physics model. The rate of reaction was defined as a variable dependent on the time, temperature, and initial concentrations of furfuryl alcohol and acid. In an attempt to simplify the reaction, it was assumed that the activation energy remained constant throughout the course of the reaction, meaning the reaction would only follow one reaction mechanism. The heat of reaction was specified as a heat source within the Heat Transfer in Fluids physics model.

Within the model space, two domain probes were set up. One domain probe output the concentration across the domain at any given time, while the other gave the temperature gradients. These probes allowed the team to track the course of the reaction through the change in concentration of furfuryl alcohol, and changes in temperature.

In order to gain a deeper understanding of what was calculated in the model, the team looked into each of the physics models and the equations that it was solving for in the time dependent

study. The Transport of Diluted Species physics model was used to observe the concentration gradients, diffusion of components, and the mechanics of the reaction. For a dilute species (eg. the small amount of acid contaminant) the equations below were considered when computing the diffusion of one species into the other.

$$N_i = -D_i \nabla c_i \quad (5)$$

$$\frac{\delta C_i}{\delta t} + \nabla \cdot N_i = R_i \quad (6)$$

The diffusion coefficients for each species were defined as the default for liquids in COMSOL at $1 \times 10^{-9} \text{ m}^2/\text{s}$. The rate of the reaction was defined for each species, with the rate of reaction for the acid equal to 0, because this species is self-propagating and assumed to be constant. The rate of reaction of the furfuryl alcohol was defined as a second order reaction dependent on the concentration of furfuryl alcohol and acid.

The Heat transfer in Fluids physics model allowed the team to study energy transport, viscous effects of fluid flow, and the effect of temperature and pressure on the system. The transient heat equation, used to effectively calculate temperature field in a fluid is below.

$$Q = \rho C_p \frac{\delta T}{\delta t} + \rho C_p u \cdot \nabla T + \nabla \cdot (-k \nabla T) \quad (7)$$

Within this physics model, the thermal conductivity value for furfuryl alcohol was input as $0.1799 \text{ W/m} \cdot \text{K}$ (Cameo Chemicals). The initial temperature was defined as 273.15 K , and the heat of the reaction was set up as a heat source defined as the reaction rate multiplied by the reaction heat.

The study observed was time dependent, and the time frame was set at 30 minutes to mimic a real world scenario. The 30 minute time frame was determined based on the prior knowledge that this reaction could happen spontaneously, hours after a possible contamination. The computational grid for this simulation was adjusted through the physics-controlled mesh settings. The element size was set as extremely fine, which allowed Comsol to compute the physics of the model at the highest number of points on the grid.

A summary of all the settings and inputs to COMSOL can be found in Appendix C.

3.2 Initial Experimentation

3.2.1 Open Beaker Experiments with Methanesulfonic Acid

In order to gain a better understanding of the reaction before attempting larger scale experiments, the team performed small-scale experiments with the furfuryl alcohol and methanesulfonic acid inside 50 mL glass beakers within a fume hood. These experiments were conducted with an ice bath on the side, since the team knew this reaction would likely be extremely exothermic. In the first experiment, an initial amount of 10 μ L of methanesulfonic acid, which was clear and colorless, was added to 22 mL of furfuryl alcohol, which was also clear but yellow in color. This experiment would be observed for 90 min, and if no reaction occurred within this time period the experiment would be repeated without the ice bath. For safety purposes, the experiment could not be disposed of before the reaction had completed. To ensure the reaction would go to completion, additional acid was to be added.

3.2.2 Testing Acid Limit to Propagate Reactions

In order to discover the limit to propagate these reactions the team conducted trials with varying amounts of methanesulfonic acid, added all at once, into 20 mL of furfuryl alcohol. Observations were made about temperature, boiling, total time of reaction, and physical characteristics of the mixture.

3.2.3 Insulating the Beaker and Creating a Closed System

In order to more accurately simulate the final testing conditions for the experiment, the team began introducing modifications to the small scale set-up. The first change the team made was to insulate the glass beaker. This was done by wrapping the 50 mL glass beaker in several layers of aluminum foil. Once the base and walls were covered, 20 mL of furfuryl alcohol was added to the beaker. The beaker was then sealed with an additional aluminum foil cover, which had two holes - one to insert the thermometer and the other to introduce the 0.5 mL of acid. It should be noted that since the beaker was insulated with aluminum foil, the team could not observe any physical changes to the solution. However, the temperature of the system over time was observed.

To test the reaction in a closed vessel, a 250 mL narrow mouth HDPE bottle was used. A rubber stopper was inserted into the mouth of the bottle to act as both a seal and pressure relief system. The furfuryl alcohol was added to the bottle first, followed by the acid, and then the rubber stopper was inserted. The rubber stopper was inserted enough as so it would not topple over and it could withstand some pressure build-up. It should be noted that the team was unable to observe

the temperature and physical changes of the reaction over time due to the physical constraints of the system.

3.2.4 Testing of Stronger Acids

The team was curious to see how the reaction would respond to acids stronger than methanesulfonic acid. The acid that was selected was concentrated hydrochloric acid (12 M) due to its availability, and prevalence in industry. The same procedures were followed as before and the team began testing with the same volumes as the team had done with the methanesulfonic acid. Due to the observations made during the initial experimentation with the hydrochloric acid, the team decided to take further precautionary measures to ensure the safety of the team, while allowing for a more in depth analysis of the reaction.

3.2.5 Breaking down the resin

Research was performed in order to determine what could break down the resin after it had cured in order to clean the reaction vessels. Once a couple of possibilities were determined, pieces of the cured resin from the previous experiment were broken off and set aside for experimentation. Some potential options for removing the resin from the vessel included heat, physical force, and exploring chemical mediums that could potentially help loosen the solid resin.

3.3 Final Experimentations

3.3.1 Small Scale

The small scale reaction vessel could hold 100 mL volume and consisted of three thermocouples at various heights, a pressure gauge, a pressure relief valve with a max pressure rating of 75 psi, and screws to open the top with ease after formation of the resin solid. The thermocouples were Type K thermocouples supplied by McMaster Carr, and were connected to a PC with two National Instruments 1-Channel Temperature Input Devices (USB-TC01). These devices recorded the temperature of the reaction over time through their built-in Temperature Logger software. Videos were taken of the pressure gauge to effectively study pressure as a function of time. Images of this vessel and dimensions can be found in Appendix D.

The small scale experimentation in the 100 mL stainless steel vessel began with trials of 20 mL of furfuryl alcohol, and 0.5 mL of HCl. The team completed 4 trials under these conditions to establish a baseline of expected temperatures and pressures for further experimentation. The acid was added to the reaction vessel through a long glass pipette inserted into the pressure relief valve port before being quickly removed to allow the pressure relief valve to be screwed on. Between each trial, the teflon tape wrapped around the pressure relief valve was replaced to maintain the air-tight seal.

The team then varied the amount of furfuryl alcohol from 20 mL to 30 mL, which was still at a conservative liquid level within the vessel, and completed a total of 3 trials under these conditions.

Lastly, the team conducted two experimental trials with methanesulfonic acid as the reaction catalyst. The team added 1 mL of methanesulfonic acid to 20 mL of furfuryl alcohol. These experiments were conducted in an attempt to understand the differences in the results of the reaction when the acid catalyst was changed.

3.3.2 Large Scale

The large scale reaction experiments involved the use of a 1000 mL stainless steel reaction vessel. The 1000 mL vessel was designed to be a scaled up version of the smaller 100 mL vessel, consisting of three thermocouples at various heights, a pressure gauge, a pressure relief valve, and screws to open the top with ease after formation of the resin solid. The same equipment was used from the previous experiments to record the temperature of the reaction throughout the experiments. Images of this vessel and dimensions can be found in Appendix E.

The first large scale experiments were completed with 100 mL of furfuryl alcohol, and 1 mL of HCl. These experiments were repeated three times before the initial amount of furfuryl alcohol was increased to 200 mL, and the team added 2 mL of HCl. The increase in furfuryl alcohol was performed in an attempt to observe how scaling up the reaction affected the temperature, pressure, and resin formation.

3.3.3 Analysis of Resin Composition

In attempt to run an NMR analysis the team first dissolved the resin in acetone and dimethyl sulfoxide (DMSO). Mass of the sample was taken before and after the dissolving period and observations of physical changes were noted.

4.0 RESULTS AND DISCUSSION

4.1 COMSOL Modeling

According to the COMSOL modeling, the reaction takes off almost as soon as the model begins running along the boundary of the acid. The max temperature reached by the reaction itself is 525 K (252°C) and this was achieved at 0.3 minutes into the simulation. The relative concentration gradients changed minimally as the diffusion coefficient assumed for the liquids was $1.0 \times 10^{-9} \text{ m}^2/\text{s}$; however, the concentrations of both the acid and furfuryl alcohol decreased along the line of the reaction.

One of the most important aspects of this simulation was to gain a better understanding of the temperatures produced in this exothermic reaction. As previously explained, a temperature probe was built into the reaction model to plot the temperature over time. The following figure displays the temperature of the reaction at 0.3 min (~20 seconds) after the addition of the acid.

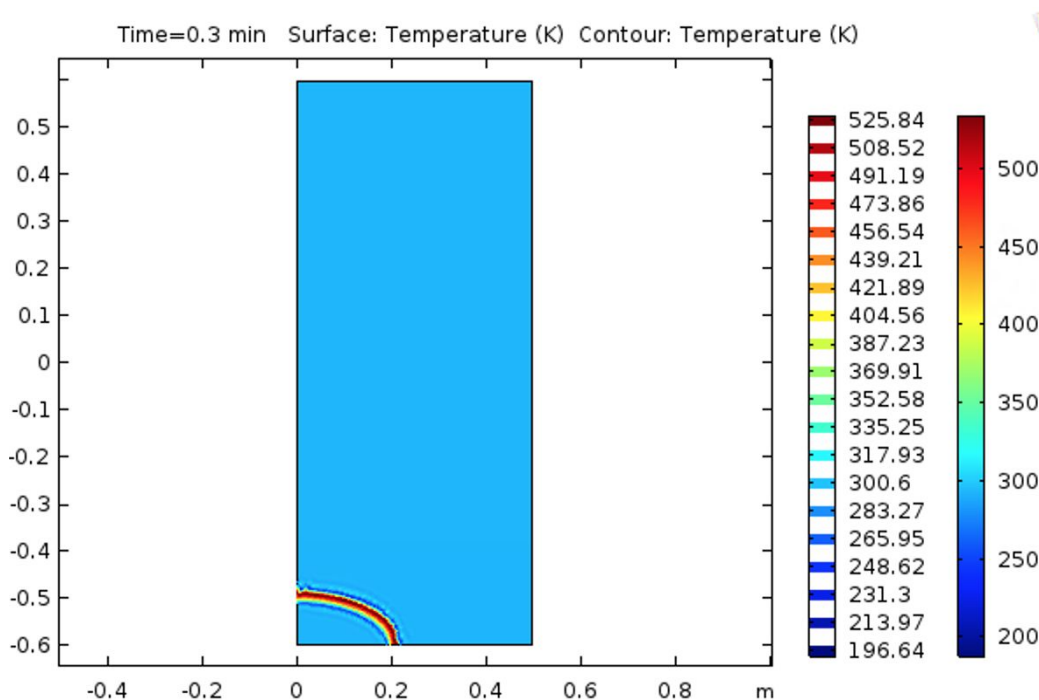


Figure 5. 2-D Temperature Gradient at 0.3 mins into Reaction Simulation

As one can see from the figure above, there is a large temperature gradient with temperatures ranging from approximately 250 K to 525 K. Based on observations made throughout later experimentation, the extreme temperatures along the surface between the acid and furfuryl alcohol made sense. The reaction generates a great deal of heat, and similar temperatures were

observed throughout experimentation. This was an extremely important take-away from this simulation because it allowed the team to predict the maximum temperatures they expected to see while conducting their experiments, and allowed them to take the appropriate safety measures while working with the products of this reaction.

However, the model does have some inconsistencies that should be noted. In the figure above, there is a boundary layer of temperatures around 200 K, which is quite unrealistic as these are sub-zero temperatures on the Celsius scale. This is most likely the result of the activation energy of the reaction and the model gathering the required energy from the immediate surroundings at the interface between the acid and alcohol. Realistically, the heat generated in this reaction would dissipate through convection into the surroundings and raise the temperature of surrounding alcohol, but this phenomena is deterred in the reaction model due to the way the activation energy component of the reaction is modeled.

The other main objective of this model was to understand how the concentration of reactants changed over time. The figure below illustrates the concentration gradient of the acid in the reaction at the end of the model simulation.

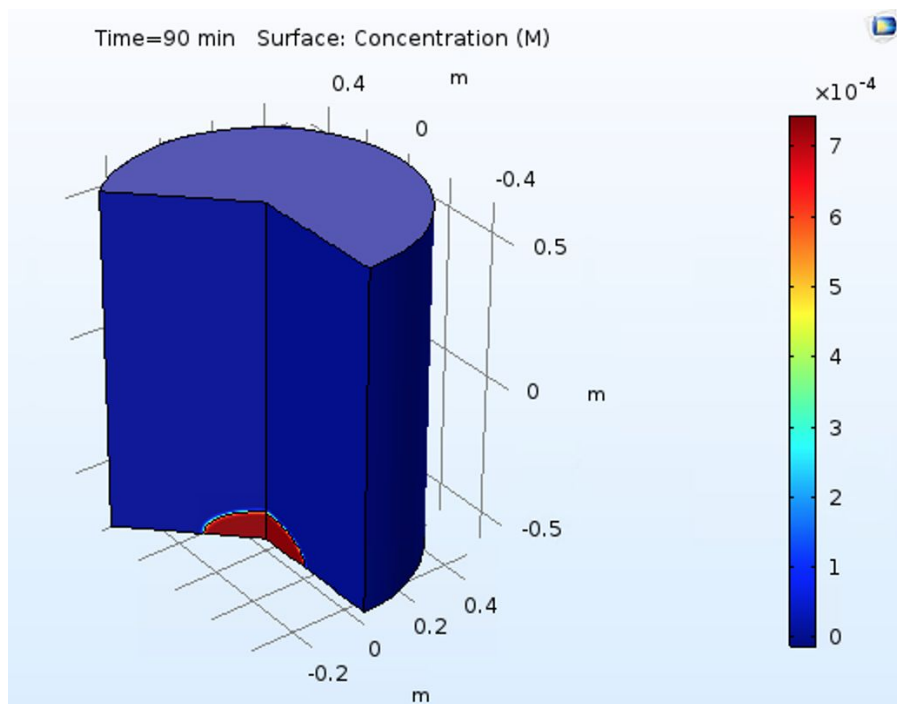


Figure 6. Surface Concentration Gradient of Acid at the End of the Model Simulation

As one can see in the figure above, the acid is clumped entirely at the bottom of the reaction vessel. Initially the team was surprised by these results because they anticipated that the acid would diffuse into the furfuryl alcohol during the reaction. Later experimentation would prove

that this phenomena of the acid not diffusing into the surrounding alcohol was accurate when methanesulfonic acid was used, and the acid clumped at the bottom of the vessel when the resin was formed. This was also the result of the acid being more dense than the alcohol, sinking to the bottom of the mixture.

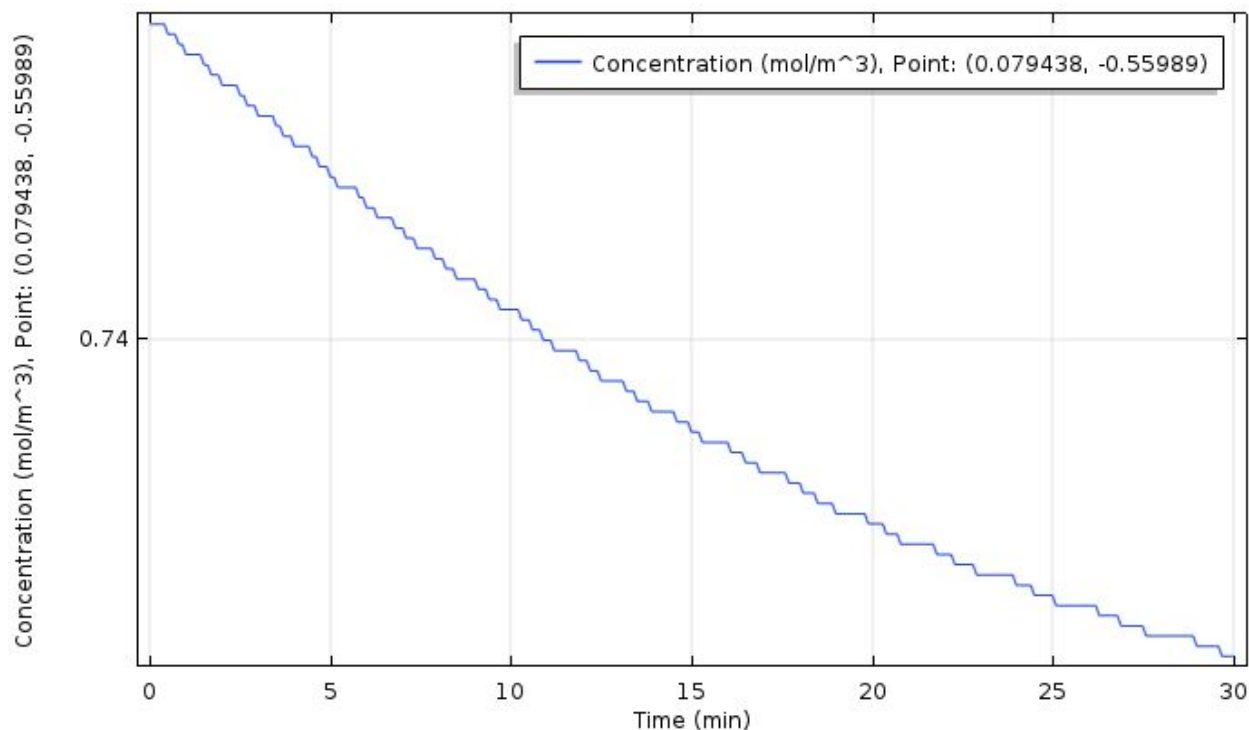


Figure 7: Furfuryl Alcohol concentration over time

COMSOL was used to generate the graph above, which shows the decrease in concentration of furfuryl alcohol over time. While the team expected this trend to hold true, they did not expect the concentration to decrease linearly. Since the reaction is exothermic, the increase in temperature as a result of the reaction also increases the rate of reaction. Limitations in the modeling prevented the team from being able to model this phenomena effectively.

4.2 Initial Experimentation

4.2.1 Open Beaker Experiment Results

When the methanesulfonic acid was introduced into the furfuryl alcohol (in both the ice bath and room temperature environment), it immediately formed a black resin and sunk to the bottom of the 50 mL glass beaker. The temperature of the system was unaffected as it only changed approximately 1-2 °C over the course of 90 minutes. Additionally, the black “blob” of resin did not increase in size considerably over that time period. Approximately 30 minutes into the

experiment the team attempted to stir the beaker in an attempt to swirl the acid around, which resulted in a brown cloud forming around the resin, but no further reaction.

After waiting 90 minutes and observing no change in the experiment, the team made the assumption that there was not enough heat generated to cause the furfuryl alcohol to polymerize. The minimal heat generation could be attributed to both the cooling effects of the ice bath and open container environment. In order to understand how the reaction would occur and what the final product would look like the team needed the reaction to go to completion. To do this, an additional ~0.9 mL of acid was added to the beaker.

As the additional acid was added in increments, the resin began to grow and the solution began to heat up. The yellow color of the furfuryl alcohol quickly became a dark brown/black liquid with a visible increase in viscosity. At approximately 70°C the solution began to boil and the reaction proceeded without the need of additional acid. During the course of the reaction, fumes were released and the temperature exceeded the max temperature of the thermometer (150 °C), and the final product had doubled in volume. This initial trial allowed the team to make important observations on the temperatures they should expect to see in future experimentation, the behavior of the reaction, and how the resin formed. Figure 8 below shows the solution mid experiment.



Figure 8. Mid-experiment. The solution is boiling, releasing fumes, and has exceeded 120°C.

Once the reaction appeared to finish, the entire beaker was moved into the ice bath to cool. After the temperature of the resin cooled to approximately 30 °C the team attempted to remove the resin from the beaker. On the first trial, the resin could not be removed from the beaker so it was

disposed of in the trash. For the second trial, the resin was eventually removed and examined (Figure 9).



Figure 9. End Product of the trial experiments. The resin retained the shape of the container it was in.

While these initial trials did not provide the team with any useful data points, they played a critical role in guiding later experiments. The team learned that the resin significantly increased in volume as the reaction proceeded. Due to this information, for future experiments the team only filled the vessel with 25% to 50% of furfuryl alcohol to mitigate the chance of resin entering any of the pressure gauges and pressure release valves. Additionally, the team learned that the final resin was not as sticky or soft as they initially expected. The resulting resin was solid, brittle, black, and porous.

Prior to testing on the small and large scale reaction vessels, the team needed to conduct further experimentation on the final product to understand the best way to remove and clean it. It was essential that the team found a way to clean the vessel without damaging it so that it could be reused.

4.2.2 Discovering Initial Acid Limitations to Propagate Reaction

In order to discover the limit to propagate reactions by adding a larger amount of acid initially, as opposed to in increments over time, the team ran two additional trials.

In the first trial, the team added 0.5 mL of methanesulfonic acid to 20 mL of furfuryl alcohol. The fluid turned very dark instantaneously. Around 8 minutes the team observed the state of the fluid, which was slightly viscous and contained a few solid chunks at the bottom of the flask. Around 35 minutes the team dislodged the chunks of resin at the bottom of the flask with the

thermometer and insulated the outside of the glass container with their hands. After a few minutes, the temperature steadily rose to 53.5 °C and at that point the temperature started increasing at a much faster rate. At 68 °C the fluid in the beaker started boiling and the reaction went to completion. The final resin took up approximately 75% of the volume of the beaker.

In the second trial the team added 0.6 mL of methanesulfonic acid to 20 mL of furfuryl alcohol. Around 12 minutes the team disrupted the mixture by probing the chunks and again insulating the system. The reaction started heating up, and after 15 minutes it reached completion. This time the solid resin rose to slightly over the top of the beaker.

With the lower amount of acid the team noted that the solid formed was less rigid, and more pliable than with the resin that formed with the greater amount of acid. The team hypothesized that the differences in physical properties are due to the amount of heat that was generated by the reaction, with higher temperatures further casting the resin, resulting in the formation of a more rigid polymer.

4.2.3 Insulating the Beaker and creating a closed system

In order to prevent heat from escaping the 50 mL glass beaker and to better simulate the reaction vessels, aluminum foil was placed around the beaker to help with insulation. The beaker had aluminum foil around the sides and the top, with two holes for the thermometer and pipet to add acid.

For the first trial, 0.4 mL of methanesulfonic acid was added to 20 mL of furfuryl alcohol, and while the initial temperature seemed to remain higher for a longer period of time, the heat dissipated eventually after the initial addition of acid. The temperature reached 30.6 °C and started to drop after about 6 minutes. As such after about 30 minutes had passed, the mixture was probed with the thermometer until eventually it was forced to completion. A washer had been placed at the bottom of the beaker before the reaction took place to test how the resin stuck to stainless steel, and the washer came clean upon washing.

For the second trial, 20 mL of furfuryl alcohol was added again but this time the acid was split between two pipets with 200 µL and 300 µL respectively. Once the acid was added, another sheet of aluminum foil was added for extra insulation. The initial temperature reached was higher at 45 °C, however, this was probably due to the extra acid that was included in the mixture. The temperature started to decline after about 10 minutes. After 90 minutes passed, the reaction still had not completed and prodding it resulted in no reactivity, which lead to the addition of 250 µL of methanesulfonic acid to the beaker. After an additional amount of time and stirring, the reaction still did not go to completion. In order to achieve the reaction the team

placed the mixture on a hot plate until the contents reached 45 °C with constant mixing, at which point the team transferred the beaker back to the hood, where the reaction went to completion.

For additional closed system experiments, the team completed trials using 0.5mL of methanesulfonic acid with 30 mL and 40 mL of furfuryl alcohol in 250 mL HDPE bottles. If the system was not agitated the reaction did not propagate with this acid amount. The team waited over 60 minutes and observed no change in consistency. The team tried agitating the contents of the bottle by shaking the container 2 times right after the acid addition. Two out of the five trials proceeded to react within the 8-11.5 min time range, and the rest were unchanged after 60 minutes.

4.2.4 Breaking down the resin

In order to run multiple experiments in the stainless steel reaction vessels, the team needed to develop a method of cleaning out the resin in a safe manner. Having determined that heat was likely the safest method to breakdown the resin in order to get it out of the reaction vessel, the team tested hardened pieces of resin.

The first experiment used the furnaces found on the top floor of the UO Lab in Goddard Hall. A small amount of resin was placed in a crucible and allowed to reach the max temperature of the furnace about 210 °C. At this point it was observed that the resin became harder through this process, as it reached a heat where the resin ‘cured’. A melting temperature was estimated to be around 600 °C from this trial.

In order to test this theory the team placed the sample in a higher power furnace and gradually increased the temperature. The resin sample of approximately 1.143 grams was heated up until 750 °C and the state of the solid remained unchanged after an hour. The team did not pursue experimentation at higher temperatures in the furnace.

Next, the team used a propane torch in attempt to melt down the resin. Again, a small amount of resin was placed in a crucible within a fume hood. Upon contact with the propane torch, the resin immediately caught on fire. It was assumed that the heat applied to the resin was enough to gasify the sample, causing it to combust. Upon examination, the resin had not softened, and there was no change in the physical state after applying direct heat through the torch. The torch was also applied to the wall of the crucible in which the sample was placed in to see if the resin melted through indirect contact with the heat source. The resin did not respond to the heat that was applied through the wall of the crucible. From this experiment it was determined that using a direct heat source such as a propane torch was not a feasible means of removing the hardened resin from the reaction vessel.

After multiple failed attempts of removing the resin through applying heat sources, it was determined that physical means of removal was the safest and most applicable option. The team determined that chiseling the resin out and scrubbing the reaction vessel with acetone and a wire brush was the most effective way of removing it. The hardened solid could be broken apart and disposed of, and the goopier resin could be scrubbed away with acetone.

4.3.1 Swapping Methanesulfonic Acid for Hydrochloric Acid to Propagate Reaction

The team investigated utilizing 0.5 mL of 12 molar hydrochloric acid, a stronger acid, in place of methanesulfonic acid to propagate a reaction with 30 mL of furfuryl alcohol. The mixture was added to a 250 mL plastic bottle, first the furfuryl alcohol, and then the hydrochloric acid, and the cap was closed. At 3 minutes and 30 seconds the reaction rapidly propagated, resulting in an immense pressure buildup and a subsequent explosion of the 250 mL HDPE bottle. At the time of the explosion a loud popping sound could be heard as the contents escaped the bottle at two different exit points, the top of the bottle (breaking the cap) and along the seam towards the bottom of the bottle (Figure 10). Liquid level remained constant before the explosion and the bottle expanded before breaking. The pressure build up occurred within an estimated 2 seconds, making it impossible for one of the team members to manually relieve the pressure by unscrewing the cap. Additional images of the aftermath of this reaction can be found in Appendix F.



Figure 10. Overpressurized 250 mL HDPE bottle aftermath.

As a result of this initial experiment with the hydrochloric acid, the team determined several unique characteristics of this specific reaction when compared to the methanesulfonic reaction. Firstly, when the hydrochloric acid came into contact with the furfuryl alcohol, there was not a

glaring indicator of contamination. Instead of resin forming, gases being released and a hissing sound, the two chemicals simply mixed. There was a color change (yellow to black) that occurred gradually over time. In addition, there was also no indication of gasses being released over the course of the observed reaction. In the case of the methanesulfonic reaction, the team knew that when the liquid started to boil, the pressure increase would occur rapidly and the HDPE bottle would begin to fail. However, with the hydrochloric acid, the team did not observe any boiling of the liquid. Finally, the end product of this reaction resulted in a black liquid rather than a brittle solid.

In order to verify the initial observations and further investigate the hydrochloric acid reaction in a safer manner, the team completed additional trials using a rubber stopper to seal the system. In the first verification trial, the team mixed 30 mL of furfuryl alcohol and 0.15 mL of 12M HCl in the 250mL HDPE bottle. This reaction remained dormant for approximately an hour before more HCl was added in increments of 0.1, 0.2, and 0.3 mL. After a total of 0.75 mL was added, around the 2 hour mark, the reaction took about 90 seconds to propagate. The team observed that the bottle became a little foggy prior to when the pressure build-up removed the rubber stopper. After the stopper blew, the liquid began to boil rapidly, spit chemical droplets out of bottle and release excessive amounts of gas. The final product was a solidified black resin.

For the second verification trial, the team mixed 30 mL of furfuryl alcohol with 0.2 mL of 12M HCl in the 250 mL HDPE bottle. Similarly to the previous trial, the initial HCl volume did not cause the reaction to propagate. Thus, additional HCl was added in increments of 1.0 mL. After a total of 6.0 mL of HCl were added, the reaction began to propagate and run through completion. Again similarly to the previous trial, the pressure buildup in the bottle caused the rubber stopper to blow first, and then the liquid boiled. The liquid boiled aggressively, and the end product was a solidified black resin.

These additional two trials provided the team with further insight into the furfuryl alcohol and hydrochloric acid reaction. One important observation was the amount of acid required to propagate the reaction. In the first trial the team used 0.75 mL and in the second trial the team used 0.60 mL. Thus, the team determined that an acid volume of 0.4 mL would be a safe amount to propagate the reaction in a timely manner for future ~30 mL furfuryl alcohol trials in an insulated stainless steel vessel. Secondly, the team observed that if the contents of the reaction will boil if there is not an overpressurization of the reaction vessel. However, the team observed that the boiling point occurs after a significant amount of pressure build up, so in the case of the initial exploding trial, the bottle ruptured prior to the boiling point. Along with this, the team also observed that the final product of the reaction is dependent on the level of completion of the reaction and the temperatures achieved in the reaction. For instance, if the liquid is dispersed prior to reaching boiling, the final product is a liquid. However, after boiling, the final product is

a solid. Thus, the team assumed that the end product was temperature driven. Additionally, the experiments suggested that the strength of the acid catalyst can significantly alter the characteristics of the propagation.

4.3 Final Experimentation

4.3.1 Small Scale Reactions - 100 mL Stainless Steel Vessel

The team originally added 0.4 mL of HCl to 20 mL of furfuryl alcohol. The temperature increased slightly at a steady rate and then started to decline around 20 minutes after peaking at 28.6 °C for the liquid temperature. The team added an additional 0.2 mL and the reaction occurred rapidly. Since the team had not reached the threshold to propagate the reaction without additional acid this data was inconclusive and the team decided to start with a greater initial acid amount.

The team added 0.5 mL of HCl initially to 20mL of furfuryl alcohol. This amount was sufficient to propagate the reaction. The team conducted four total runs with the same acid amount to verify consistency of the reaction in terms of pressure and temperature. For the first run the maximum pressure reached on the pressure gauge was approximately 20 psi and the maximum liquid temperature recorded was about 140 °C.

The second trial reached a maximum temperature of about 160 °C and a maximum pressure of approximately 12 psi. The third trial reached a maximum temperature of approximately 130 °C and a maximum pressure of approximately 16 psi. The fourth trial reached 125 °C at its peak and a pressure of 14 psi. All four of the liquid level temperature logs for these trials can be seen in the figure below.

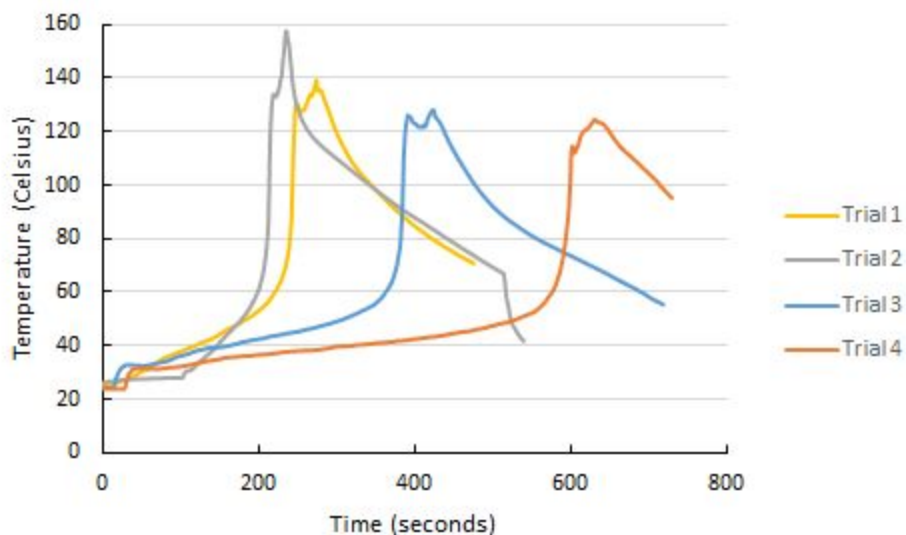


Figure 11. Small Vessel Comparison of Liquid Graphs - (20 mL FA, 0.5 mL HCl)

The timing of these temperature peaks occur between 4-10.5 minutes after the acid addition. The resins created from these reactions were observed to be sticky, squishy, and odorous, and could be removed using acetone and physical force. Images of these resins can be found in Appendix G. One of these samples was left out overnight and the resin had noticeably hardened and was no longer sticky, although it was still slightly compressible if pressed with sufficient force.

The following four figures illustrate the liquid and gas level temperatures over time within the reaction vessel for each of the four individual trials.

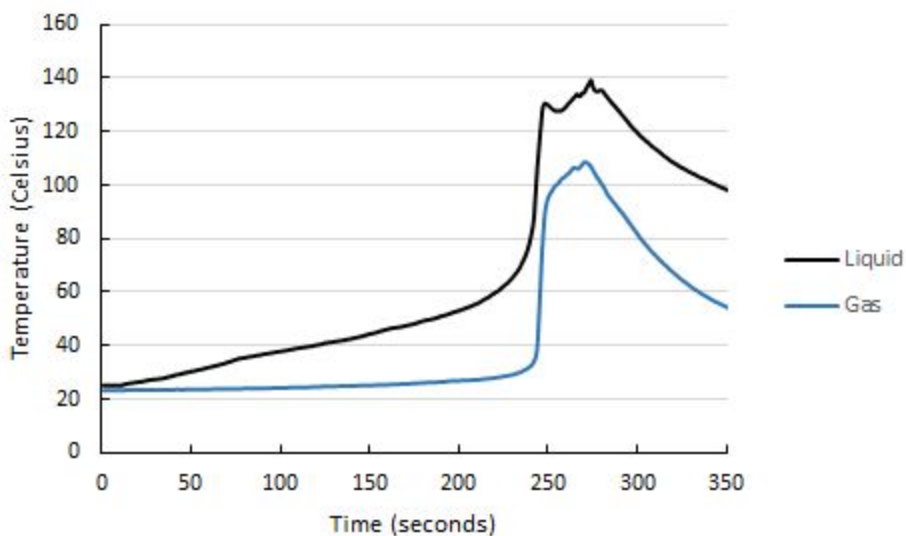


Figure 12. Small Vessel Trial 1 - (20 mL FA, 0.5 mL HCl)

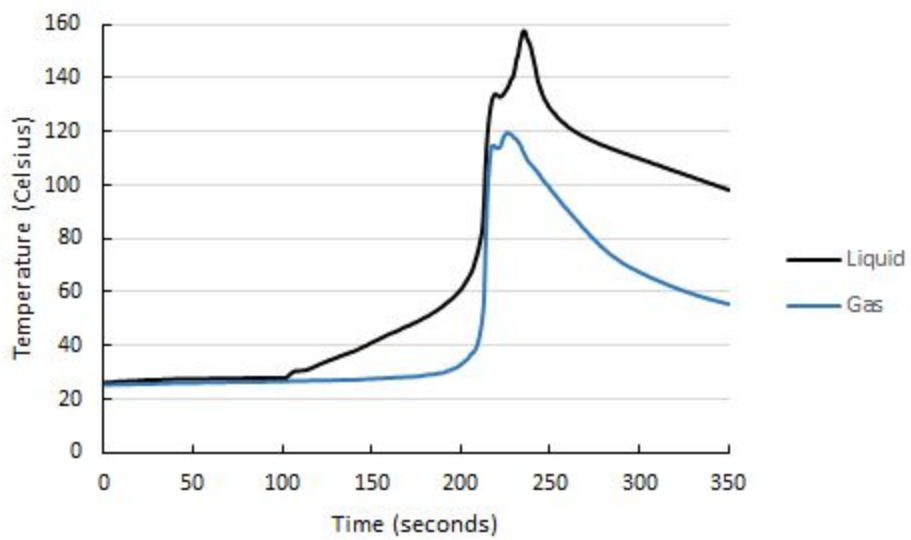


Figure 13. Small Vessel Trial 2 - (20 mL FA, 0.5 mL HCl)

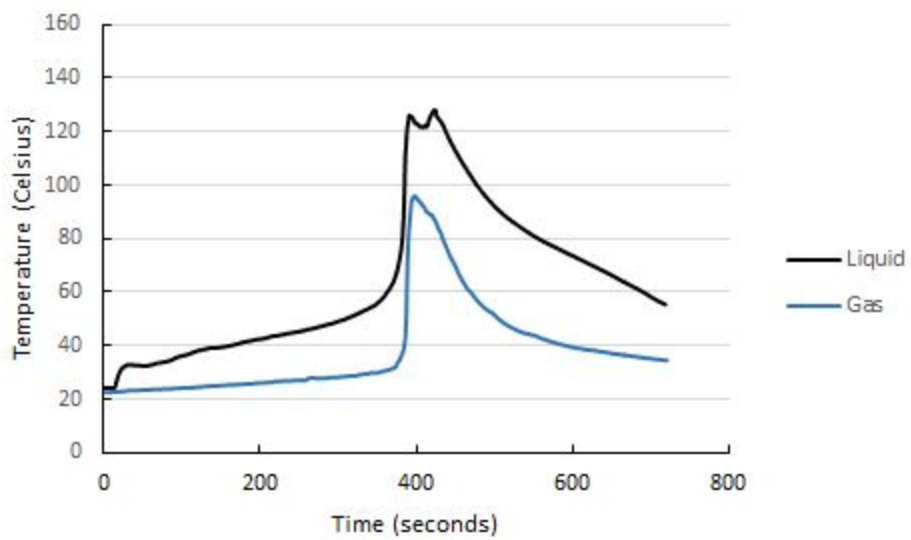


Figure 14. Small Vessel Trial 3 - (20 mL FA, 0.5 mL HCl)

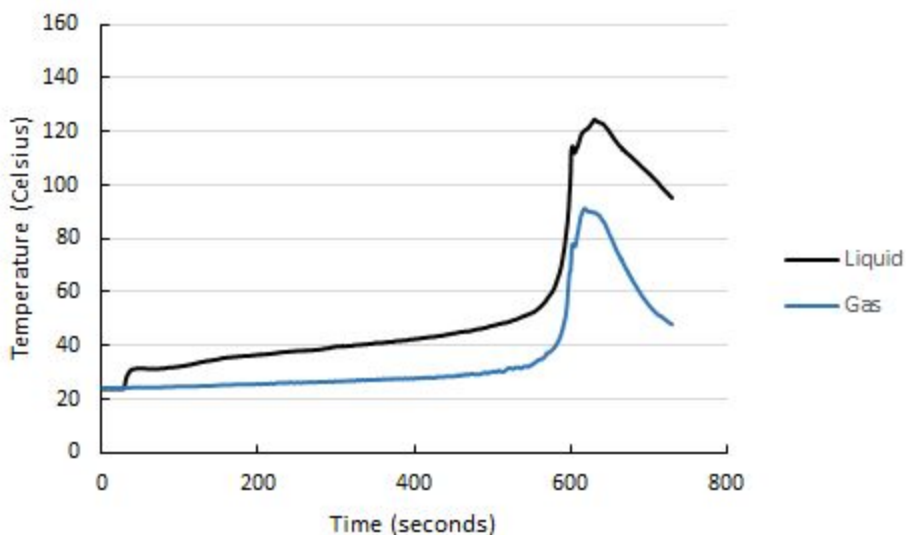


Figure 15. *Small Vessel Trial 4 - (20 mL FA, 0.5 mL HCl)*

After reviewing each of the graphs above, the team had three major takeaways. There are varying incubation times, two temperature peaks, and an inflection point of liquid temperature lines. The incubation period was measured by the team as the time between the introduction of the acid catalyst and the moment at which the liquid temperature began to rise exponentially (inflection point). The moment at which the acid was introduced to the furfuryl alcohol can be denoted by the initial bump in the liquid temperature line. The team observed that the incubation period varied between 100-400 seconds. One possible explanation for this phenomena could be the temperature of the reaction vessel itself. Throughout these experiments the team attempted to keep as many variables constant as possible in each of the trials, especially the starting temperature of the liquid level. However, the actual temperature of the stainless steel reaction vessel could have been warmer or cooler than the liquid level measured by the thermocouple inside. The team also observed that a starting liquid temperature difference of 1 °C had a significant effect on the incubation period and maximum temperature attained.

In each of the four initial trials the team observed a strange two peaked temperature curve where the temperature would reach an initial peak, cool off, and then spike back up. Kinetically, there is no explanation as to why the team observed this phenomena. One possible explanation for such occurrences could be the contact between the thermocouple and the changing height of the solid resin forming in reaction vessel. However, since the team could not see into the reaction vessel during the reaction, there was no way to prove this. Another possible explanation for this phenomena could be the condensation of the hot gases within the reaction vessel coming back down into contact with the thermocouple. The team made note of the observation and looked for similar phenomena in later trials.

Lastly, the team took special note of the inflection point in each of the temperature plots above. The team observed that once the reaction reached 50 °C, the rate of the reaction began to increase greatly, and the reaction would be guaranteed to go towards completion if it reached 60 °C. This became an important benchmark for the team to achieve in each of the experiments, otherwise, the team could not guarantee that the reaction would go towards completion leaving the team with unreacted furfuryl alcohol. This is also an incredibly important indicator in the timeline of a potential explosion, meaning that a contaminated drum could explode within seconds if the furfuryl alcohol inside reaches 60 °C.

Next the team decided to increase the amount of furfuryl alcohol in the reaction vessel from 20 mL to 30 mL. This change was an attempt to study the effects of increasing the volume of furfuryl alcohol, particularly on the rate of reaction and maximum temperatures and pressures achieved within the vessel. The team conducted four trials and the maximum temperature peaks occurred slightly below 120 °C, with the pressure gauge reading 10 psi at this time (Figures 16-20)

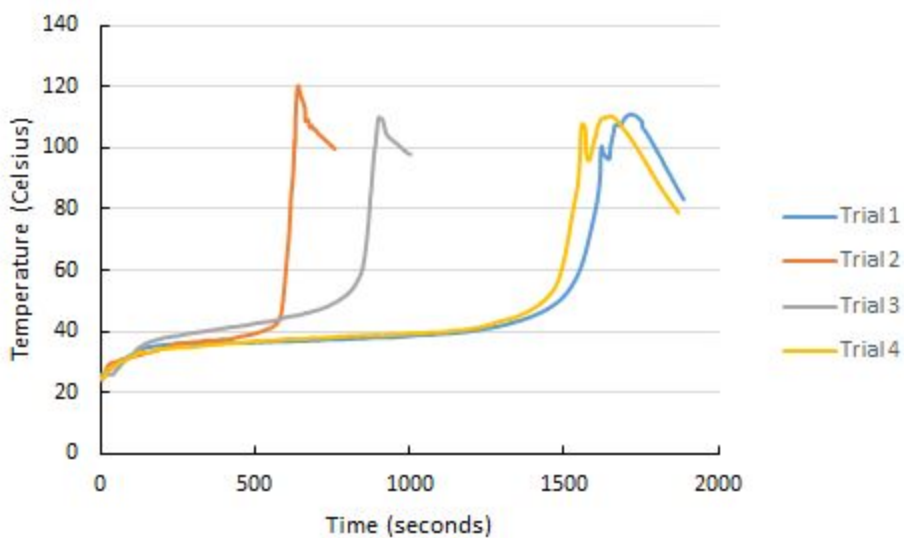


Figure 16. Small Vessel Comparison of Liquid Graphs - (30 mL FA, 0.5 mL HCl)

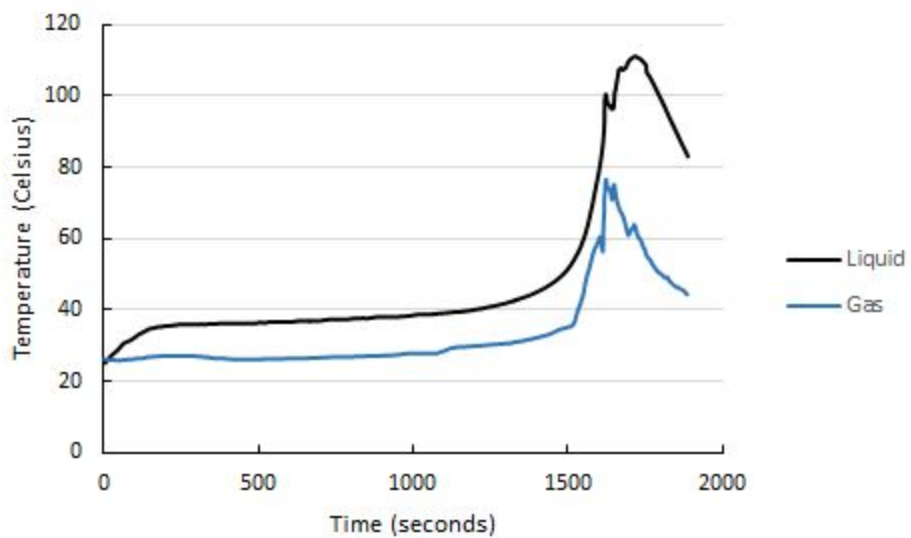


Figure 17. Small Vessel Trial 1 - (30 mL FA, 0.5 mL HCl)

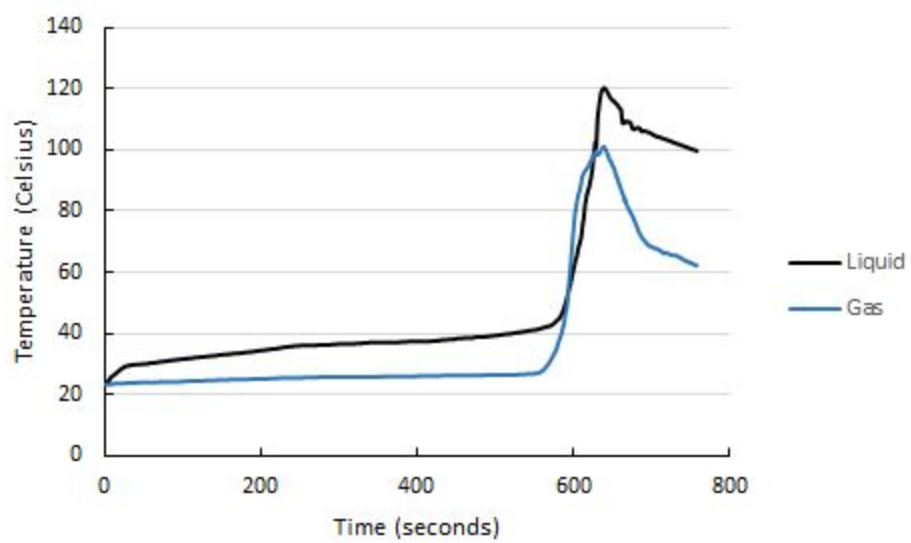


Figure 18. Small Vessel Trial 2 - (30 mL FA, 0.5 mL HCl)

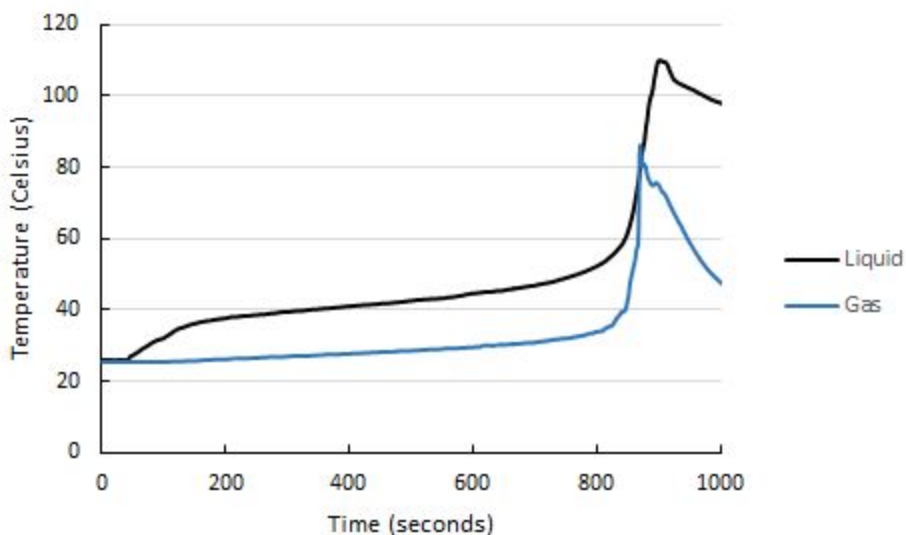


Figure 19. *Small Vessel Trial 3 - (30 mL FA, 0.5 mL HCl)*

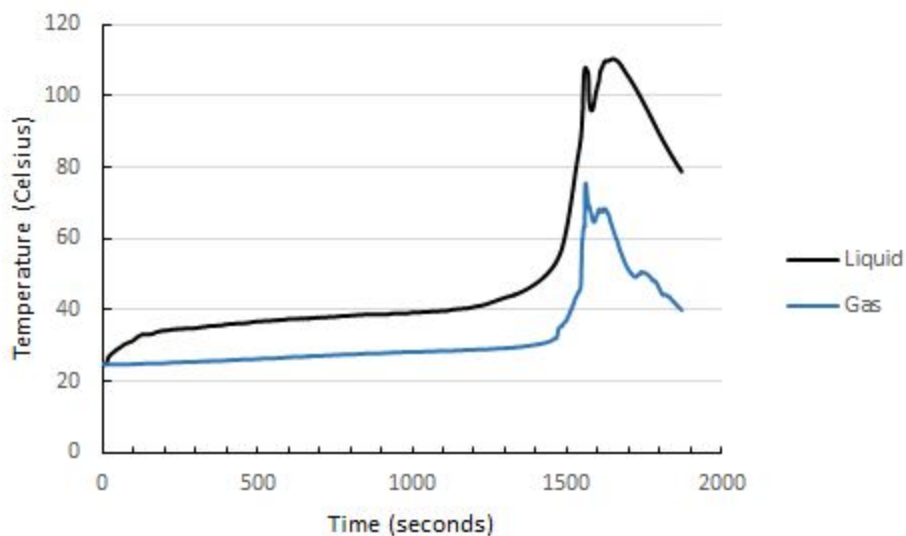


Figure 20. *Small Vessel Trial 4 - (30 mL FA, 0.5 mL HCl)*

The 30 mL trials proved to be fairly similar to the 20 mL trials. Both sets of reaction trials had similar maximum temperatures, and variable incubation periods. Originally the team anticipated that the 30 mL trials would result in greater temperatures because of the greater amount of furfuryl alcohol available to react. The team hypothesized that higher temperatures may have been achieved in the 30 mL reaction vessel, but the point of contact between the thermocouple and the solid resin formed would have been the same in all of the trials, and the 10 extra mL of furfuryl alcohol in the 30 mL trials was meaningless if the tip the of the thermocouple had

already been encased by resin. The gas level temperature readings throughout the 30 mL trials were also similar to the 20 mL trials. Overall, the team was unable to come to any meaningful conclusions by increasing the initial volume of furfuryl alcohol from 20 to 30 mL.

The team also decided to test methanesulfonic acid in the small reaction vessel to see how the reaction characteristics varied with different acid catalysts. In the first experiment with the methanesulfonic acid, the team added 1 mL of methane sulfonic acid to 20 mL of furfuryl alcohol, but the end of the pipet was accidentally plugged by resin forming in the tip, making it so only 0.7 mL was able to be effectively added. This trial resulted in a partially complete reaction with chunks of resin solid, and a large amount of dark liquid remaining. The maximum temperature reached was only 78.6 °C, which was achieved within 45 seconds of the acid being added to the reaction vessel. The resin formed was very brittle like in previous trials in the plastic bottles. Due to the rapid rate of reaction, no pressure change could be observed before the pressure relief valve was screwed in.

The second trial the team managed to add the full amount of 1 mL of methanesulfonic acid, but the reaction still did not reach completion. The temperature raised gradually to 62.7 °C, levelled off, and then decreased. Solid chunks of resin formed at the bottom of the reaction vessel, and the rest of the furfuryl alcohol remained black in color and in the liquid state. Throughout these two experiments with the methanesulfonic acid, the team was unable to make any meaningful conclusions other than the fact that the methanesulfonic acid is inconsistent. Due to these results the team decided to only investigate the addition of HCl in the larger reaction vessel.

While experiments with methanesulfonic were inconsistent, the observations made were important. In all of the experiments with the methanesulfonic the team noticed the acid immediately dropped to the bottom of the reaction vessel forming a black solid resin that remained dormant until disrupted. The team hypothesized that once the methanesulfonic acid was added to the furfuryl alcohol, the acid immediately became encased within the solid resin, preventing the reaction from propagating further. Alternatively, the team hypothesized that the acid was not strong enough to donate the free protons before the heat generated by the initial reaction had dissipated, and the reaction was unable to overcome the activation energy barrier present to continue the reaction.

Either of these explanations could be valid, but cannot be proven unless the reaction is analyzed on a molecular level. However, it is still unknown as to why the methanesulfonic immediately formed a black solid resin, while the hydrochloric acid gradually turned the furfuryl alcohol black, and eventually formed a the resin at a high enough temperature. Further experimentation should be conducted on a micro-scale to better understand how furfuryl alcohol reacts with different acids.

4.3.2 Large Scale Reactions - 1 L Stainless Steel Vessel

To begin the large vessel experimentation the team decided to conduct 3 trials by adding 1 mL of HCl to 100 mL of furfuryl alcohol in the large reaction vessel. In each trial the pressure reached a maximum of 20 psi, with maximum temperature peaks at 122.3 °C, 119.7 °C, and 143 °C, respectively. These peaks occurred between 10 and 37 minutes after the addition of HCl.

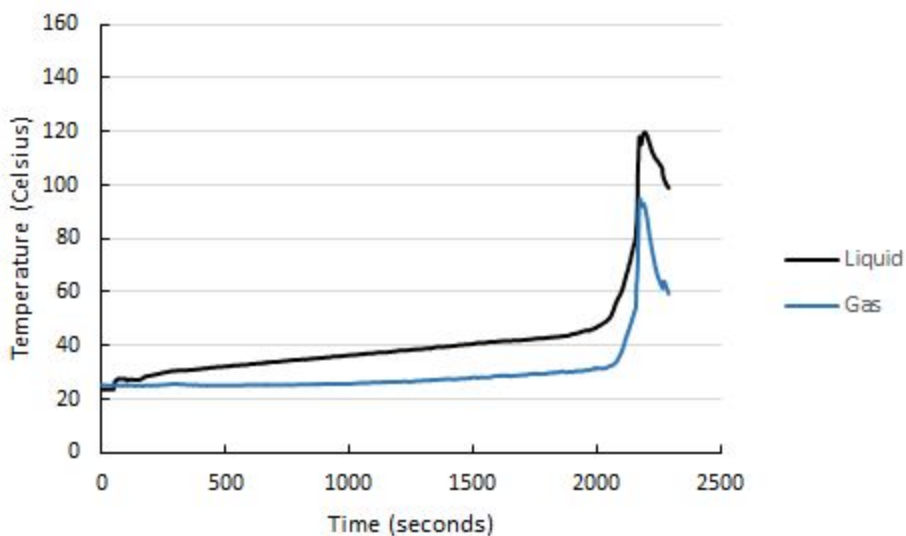


Figure 21. Large Vessel Trial 1 - (100 mL FA, 1 mL HCl)

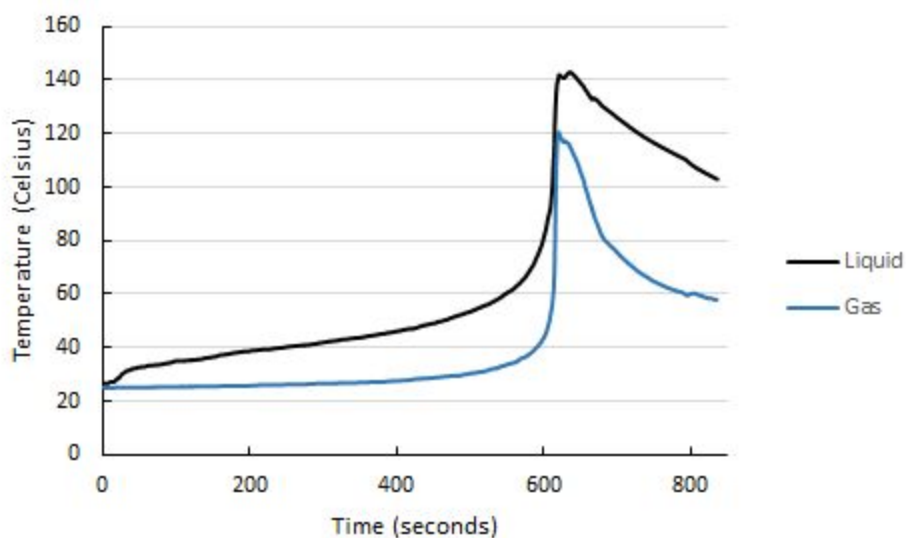


Figure 22. Large Vessel Trial 2 - (100 mL FA, 1 mL HCl)

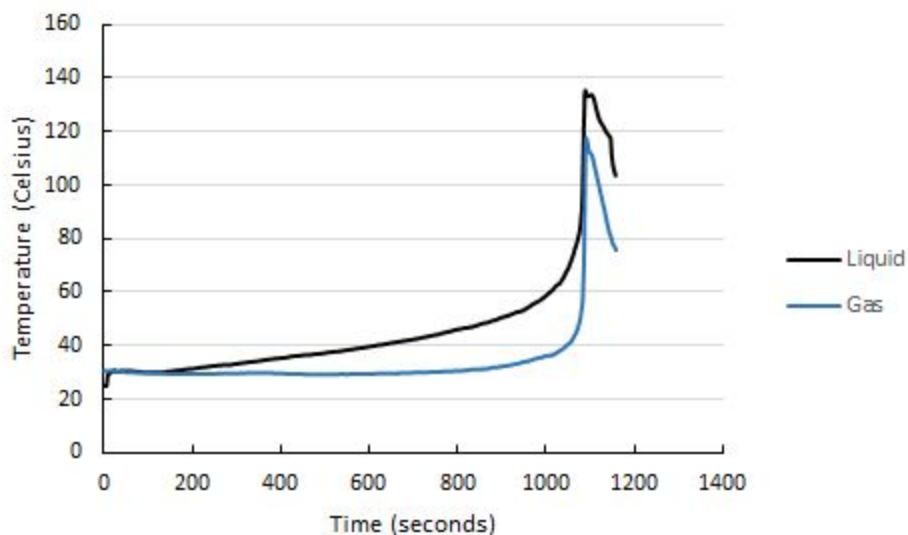


Figure 23. Large Vessel Trial 3 - (100 mL FA, 1 mL HCl)

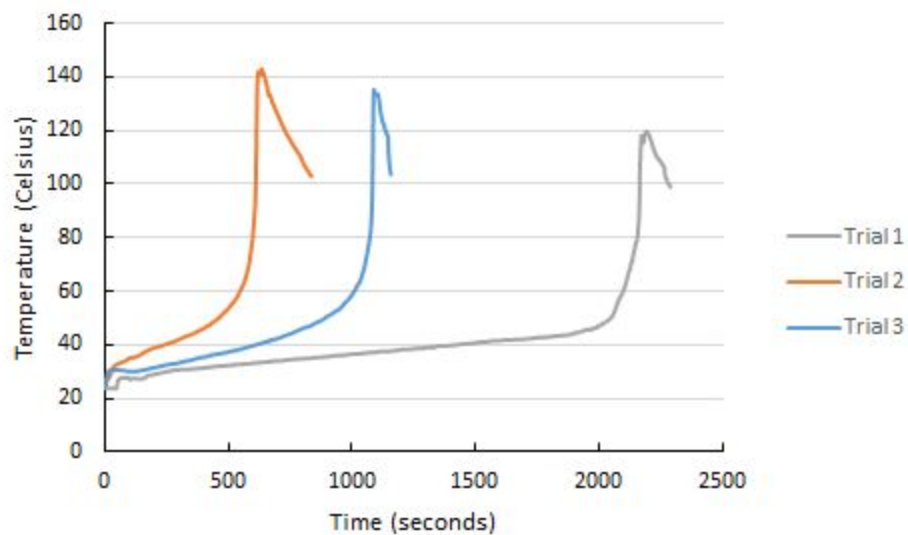


Figure 24. Large Vessel Comparison of Liquid Graphs - (100 mL FA, 1.0 mL HCl)

Once again, the team observed similar trends between the data collected from these trials was similar to the trials conducted in the smaller vessel. The one noticeable takeaway from these experiments is that the maximum temperatures do not differ greatly between these trials and the small scale trials. The team had hypothesized that the 100 mL trials would generate consistently higher temperatures than the small trials, but was proven wrong. This is most likely the result of the larger surface area of the large vessel, which allows for greater heat transfer.

The team then scaled up this reaction by adding 2 mL of HCl to 200 mL of furfuryl alcohol in the large reaction vessel. In each of these three trials the pressure release valve (PRV) was activated. The pressure relief valve was manufactured to activate once the pressure had exceeded 75 psi. In the trials, the team observed the pressure gauge reach a maximum of +100 psi (pegged out), at 84 psi, and at 70 psi respectively. Although the PRV had a maximum pressure rating of 75 psi, the point at which it was activated could have varied due to potential leakage that is difficult to detect by the naked eye and differences in gas velocities. The temperature peaks for all three trials occurred between 167 °C and 170.5 °C. These peaks occurred between 6.5 min and 11.5 min after the addition of HCl.

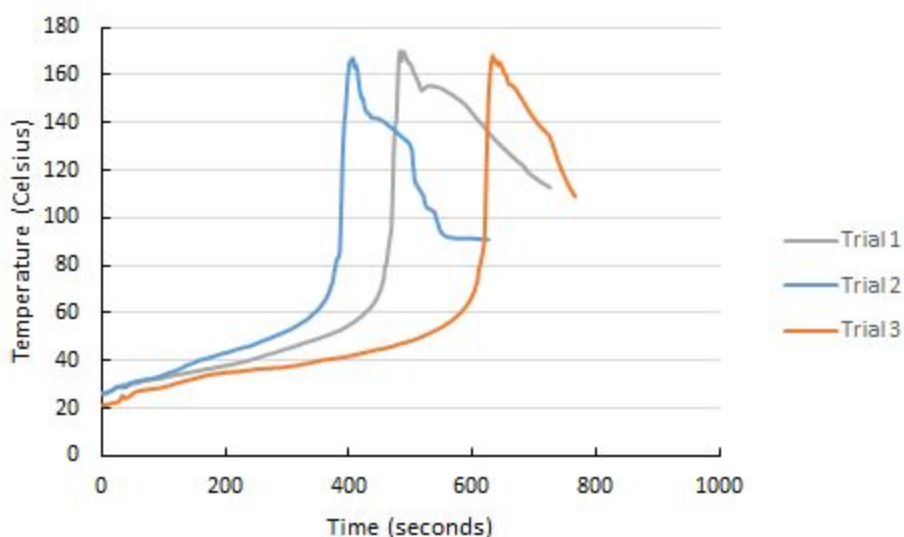


Figure 25. Large Vessel Comparison of Liquid Graphs - (200 mL FA, 2 mL HCl)

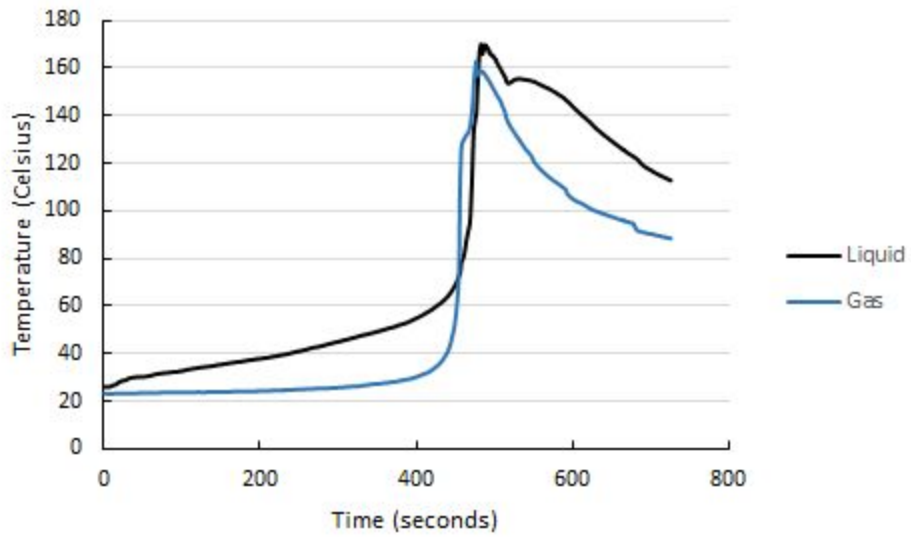


Figure 26. Large Vessel Trial 1 - (200 mL FA, 2 mL HCl)

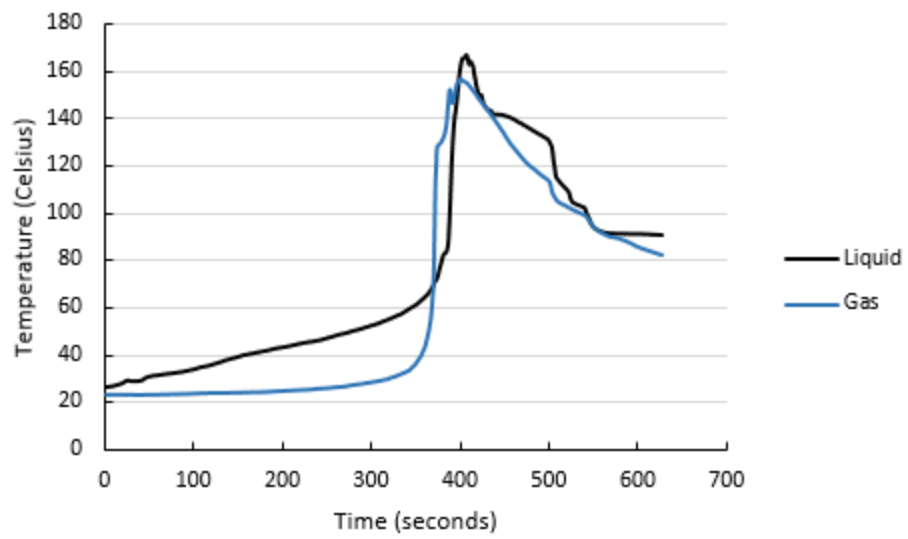


Figure 27. Large Vessel Trial 2 - (200 mL FA, 2 mL HCl)

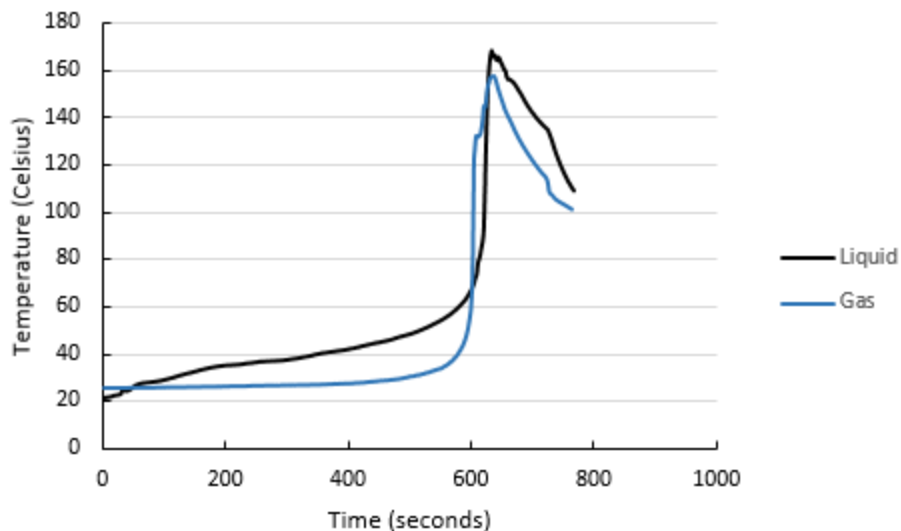


Figure 28. Large Vessel Trial 3 - (200 mL FA, 2 mL HCl)

To compare the 200 mL to the 100 mL trials, the 200 mL trials reached significantly higher temperatures than the 100 mL trials. The 200 mL trials generated maximum temperature approximately 30 °C greater than the 100 mL trials. These results were consistent with the team’s predictions as the greater amount of furfuryl alcohol allowed more heat to be released in the reaction. The team also observed the same two peaked phenomena as before in the large vessel trials. The resin that formed in all of the large scale experiments were similar to those formed in the small scale experiments, dense and odorous. An image of the resins formed can be found in Appendix H.

In general the team observed higher temperatures and pressures in the large-scale reaction vessel compared to the smaller vessel. These temperature trends are typical of exothermic reaction scale-up experiments. As the ratio of volume to surface area ratio increases the cooling system (walls of the reactor) becomes less effective and the vessel reaches greater temperatures. Thermal runaway is also more likely to occur. Thermal runaway begins when heat produced by the reaction exceeds rate at which heat is removed from the system. The rate of heat removal increases linearly while the rate of heat production increases exponentially. This can be dangerous in terms of material holding the exothermic reaction. The stainless steel is effective with housing the amount of heat produced by this reaction, but a weaker material, such as the HDPE in the drums that typically encase the furfuryl alcohol in industry, is not as effective and can pose a danger. For common commercial grade medium to high-density polyethylene the melting point is typically 120-180 °C (MatWeb, 2006). All of the liquid temperatures resulting from reactions in the large scale vessel were within this range of temperatures, and the liquid amount of furfuryl alcohol present was less than 1% of the storage capacity of a 55-gallon HDPE drum.

For all reaction vessel trials the gas temperatures followed similar trends as the liquid temperatures. In some trials the gas temperatures started to increase slightly before the liquid temperatures.

4.2.5 Discovering the Chemical Composition of the Resin Formed

In order to classify the functional groups in the resin formed, the team wanted to use NMR spectroscopy. In order to do this, two common solvents were tested to dissolve the resin so that it could be tested. The first solvent that was used was acetone. A small 27 mg piece of hardened resin was placed in 1 mL of acetone, and left to dissolve overnight in a fume hood. The following day it was observed that the resin had no physical changes, and there appeared to be nothing dissolved in the container.

Next, the team was instructed to place a 23 mg sample of the resin in 1 mL of dimethyl-sulfoxide (DMSO) at 50 °C for 24 hours. The sample was placed in a crucible to which the DMSO was then added and placed in an oven 50 °C for 24 hours. The following day the crucible was retrieved, and the team discovered that some of the sample had dissolved into the liquid as seen in the figure below.



Figure 29. Resin dissolved in DMSO at 50 °C for 24 hours

The dissolved sample was shared with a WPI Laboratory Technician who said that it “looks like you tried to dissolve a rock”. The dissolution of the solid sample was minimal and it was suggested that acquiring solution-state NMR spectra would be fruitless. There was no further investigation into gathering NMR spectra for this sample.

5.0 CONCLUSIONS AND RECOMMENDATIONS

5.1 COMSOL Modeling

The COMSOL model differed from the experimental observations, but many of the key takeaways from the model itself held true. First, the methanesulfonic acid sunk to the bottom immediately upon addition, which validated the geometry for the model. Additionally, the maximum temperature achieved in the model of approximately 525 K was similar to the maximum temperatures observed in the reactions at 444 K. Although the model predicted a higher maximum temperature achieved in the reaction, the model did not account for heat transfer to the surroundings. Also, the model used the volumes and concentrations present in the 55 gallon drum explosion, but the experiments conducted were done on a much smaller scale and only used a maximum of 200 mL of furfuryl alcohol.

The team acknowledges that there were some limitations of the model. One of the major limitations in the model was the inability for COMSOL to effectively model the transformation from the liquid to the solid state that occurred in the polymerization reaction. Additionally, while the convective heat transfer within the contents of the drum was considered in the model, the heat transfer to the walls of the container was not incorporated in the model which could be a significant source of heat transfer. Other phenomena like mixing and the release of gases, could not be accurately modeled and were omitted from the model developed. Another parameter that could not be accurately modeled was the pressure build-up within a closed container. In general, COMSOL is used to model steady state systems. Incorporating pressure increases into the model and the change of state is likely beyond the scope of this project and the capabilities of COMSOL. A potential solution to more accurately simulate the reaction is adding a surface reaction that simulates the amount of oxygen, water, and other vapors released by the reaction. This could potentially be achieved by adding a probe that calculates the gases released by the reaction, COMSOL may be able to predict the time at which a pressure limit of a given container is reached.

5.2 Process Safety Considerations

The primary purpose of this project was to develop process safety considerations and a timeline of events that one should expect to see in the event of an accidental contamination of furfuryl alcohol with acid. Throughout the course of our experiments the team determined that there are distinct variables of this reaction that can be manipulated to prevent a potential explosion from occurring. In the event of a contamination, the team has determined that there is approximately a 5-30 minute window where action can be taken before this reaction becomes a hazard.

Throughout all of the experiments in this project the reaction needed at least 5 minutes before it would rapidly go towards completion. This number is subject to change depending on the amount of acid that is added to the furfuryl alcohol, but if only a small amount of acid (a few milliliters) is added to the furfuryl alcohol, one can expect the reaction to take at least 5 minutes before going towards completion.

In the time following a potential contamination there are a few steps that can be taken to prevent a potential explosion. The first option is to cool the container of furfuryl alcohol. Throughout the course of the project the team observed several instances where the reaction did not fully propagate due to too much heat being transferred to the surroundings, and high temperatures and pressures were not achieved. The team hypothesizes that if one was able to cool the furfuryl alcohol quickly after it is contaminated, the reaction can be stopped all together. However, the team was able to conclude that if the temperature of the furfuryl alcohol goes above 60 °C, cooling the furfuryl alcohol will be a fruitless effort as that is the point at which the rate of the reaction increases drastically in a runaway reaction. Additionally, if furfuryl alcohol was stored in a temperature controlled facility, the containers would be at less of a risk of overheating, and there would be more time to take action after a potential contamination.

Another possible way to prevent an explosion from occurring is to have a pressure relief system in place for the container of furfuryl alcohol. In the preliminary stages of this project, the team was unable to propagate the reaction in an open container. The team observed that this particular reaction generates a large amount of fumes and vapors, and therefore a large amount of pressure when in a closed system. The team also concluded that the containment of these vapors is a critical factor in the propagation of this reaction. In the event that a contamination occurs, the team would recommend opening the container of furfuryl alcohol and exposing it to the surroundings, which would allow vapors to escape the container and mitigate the risk of explosion. Without the pressure build up in a given container, there would be no chance for the containment to fail due to pressure, and if the reaction was to propagate towards completion, the high temperatures generated by this reaction would become the main concern.

In addition, to minimize the risk posed to personnel in the event that a contamination is not detected, there are several safety precautions that could be implemented. First, there could be a written protocol/checklist on the steps for the handling and transferring of furfuryl alcohol, that would need to be signed off on everytime. Though this adds additional steps and time to the process, it would prevent personel from just going through the motions and growing complacent. Complacency can be a potential risk in any industry, and the team experienced it themselves during the initial experimentation, which led to a preventable explosion that caused a mess in the fume hood. Another possibility is to equip the storage drums of furfuryl alcohol with some type of pressure relief system. This could be in the form of either a pressure relief valve or a

strategically placed weak spot in the plastic. When using a pressure relief valve, the team recommends installing one that will release at 25 psi (1.8 bar) to ensure that there is no chance for explosion. This value is suggested based on both research and experimental observations. From research it was determined that a typical 55 gallon HDPE drum can withstand approximately 50 psi, before failing (exploding). Thus any psi release below 50 would be safe. However, from the experiments, the team observed that the pressure relief valve did not consistently release at the same pressure. Sometimes it lower than the intended pressure and sometimes it released higher. Due to this a pressure relief valve rated significantly lower than the failure pressure of the drum would be ideal. As for using a weak spot in the plastic, the team suggests placing this on the topside of the drum. This would allow for a safer release of pressure, but also prevent the drum from turning into a projectile object.

Additionally, furfuryl alcohol and any acids should be stored in separate places to prevent the two chemicals from coming in contact with one another. If that is not possible, having these chemical stored in separate areas and workers educated on the potential risks could help prevent potential contaminations.

5.3 Future Experimentation

Overall, the team attempted to explore many different aspects of this reaction, but was unable to achieve everything we wanted to. Here is a list of recommendations for future experimentation the team came up with:

Rate of Reaction: The team noticed variations in the rate of the reaction throughout their experimentation. The team observed that several variables played a role in how quickly the reaction proceeded such as the amount of acid added, the initial temperature of the furfuryl alcohol and surroundings, and the concentration of the acid.

Throughout the course of this project the team attempted to find the minimal amount of acid required to propagate the reaction towards completion. A potential future experiment could involve varying the amount of acid added to the furfuryl alcohol in the reaction vessel to determine the effect it has on the rate of the reaction. An example of this would involve adding 1.0 mL of any given acid to 100 mL of furfuryl alcohol, followed by an experiment with 1.5, 2.0, 2.5 mL of acid in 100 mL of furfuryl alcohol.

The initial temperature of the furfuryl alcohol and the ambient temperature of the surroundings had an effect on the rate of reaction and could potentially prevent the reaction. Further experimentation should be done to determine the initial temperature of the furfuryl alcohol required for this type of reaction to proceed.

The team would also recommend conducting experiments with different concentrations of acids. For the majority of the experiments in this project, 98% methanesulfonic acid and 37% hydrochloric acid were used. It would be interesting to see how the rate of reaction varies in response to the concentration of the acid added.

Dissolving the Resin: Throughout the course of this project, the team was unable to dissolve the resin formed in this polycondensation reaction. The team found that the solid resin was slightly soluble in acetone, and could be completely dissolved in acetone when the resin was still in the liquid state. Moving forward, the team suggests determining the structure and composition of the resin formed, and working with a chemist to determine what solvents might work best. This could be potentially be achieved through NMR or mass spectroscopy. Ultimately, it would be beneficial to determine the differences in the composition of the resins formed, and how they could be solvated. This information could also help with cleaning up the resin formed during experiments or in industry.

Stopping the Reaction: The team also recommends investigating if there are ways to stop the reaction from proceeding once it has been initialized. From the experiments the team conducted, it was observed the reaction is heavily dependent on temperatures achieved at the beginning of the reaction (i.e if the reaction reached 60°C it would most likely propagate). Thus, further experimentation on the potential of cooling the reaction once it passes certain temperature could be beneficial. Based on the results of this experiment, potential explosions could be prevented if the system is cooled to the point where the reaction will no longer proceed. Future experimentation could also be conducted to determine if a total release of pressure (ie. rupture plate) before the reaction reaches 60 °C stops the reaction from further propagating.

Manipulating End Product: The team observed that the resin was able to withstand extremely high temperatures after placing the resin in a furnace over 750°C for a sustained period of time with no apparent effect. As such, there could be potential industrial applications for this resin if it were malleable enough to mold into a specific shape. The resin also acts like a thermoset plastic, which we observed to set at temperatures above 80 °C. Future testing could be performed to see if a reaction with low amounts of acid could be placed in a mold and then set in a furnace. Applications for this material would be similar to most resins, but this resin would be able to withstand extreme temperature conditions.

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APPENDICES

APPENDIX A: Safety Data Sheets

APPENDIX B: Compatibility Charts

APPENDIX C: Summary of Setting and Inputs for COMSOL

APPENDIX D: Small Scale Vessel Design and Internal Dimensions

APPENDIX E: Large Scale Vessel Design and Internal Dimensions

APPENDIX F: Hydrochloric Acid and Furfuryl Alcohol Completed Reaction

APPENDIX G: Resin Solids Formed by Small Scale Vessel

APPENDIX H: Resin Solid Formed by Large Scale Vessel

APPENDIX A: Safety Data Sheets

SIGMA-ALDRICH

sigma-aldrich.com

SAFETY DATA SHEET

Version 4.12
Revision Date 08/21/2018
Print Date 11/09/2018

1. PRODUCT AND COMPANY IDENTIFICATION

1.1 Product identifiers

Product name : Furfuryl alcohol

Product Number : 185930
Brand : Aldrich
Index-No. : 603-018-00-2

CAS-No. : 98-00-0

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Synthesis of substances

1.3 Details of the supplier of the safety data sheet

Company : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USA

Telephone : +1 800-325-5832
Fax : +1 800-325-5052

1.4 Emergency telephone number

Emergency Phone # : +1-703-527-3887 (CHEMTREC)

2. HAZARDS IDENTIFICATION

2.1 Classification of the substance or mixture

GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)

Flammable liquids (Category 4), H227

Acute toxicity, Oral (Category 3), H301

Acute toxicity, Inhalation (Category 2), H330

Acute toxicity, Dermal (Category 3), H311

Eye irritation (Category 2A), H319

Carcinogenicity (Category 2), H351

Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335

Specific target organ toxicity - repeated exposure, Inhalation (Category 2), Nose, H373

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 GHS Label elements, including precautionary statements

Pictogram



Signal word

Danger

Hazard statement(s)

H227

Combustible liquid.

H301 + H311

Toxic if swallowed or in contact with skin.

H319

Causes serious eye irritation.

H330

Fatal if inhaled.

H335

May cause respiratory irritation.

H351

Suspected of causing cancer.

H373

May cause damage to organs (Nose) through prolonged or repeated

exposure if inhaled.

Precautionary statement(s)	
P201	Obtain special instructions before use.
P202	Do not handle until all safety precautions have been read and understood.
P210	Keep away from heat/sparks/open flames/hot surfaces. No smoking.
P260	Do not breathe dust/ fume/ gas/ mist/ vapours/ spray.
P264	Wash skin thoroughly after handling.
P270	Do not eat, drink or smoke when using this product.
P271	Use only outdoors or in a well-ventilated area.
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P284	Wear respiratory protection.
P301 + P310 + P330	IF SWALLOWED: Immediately call a POISON CENTER/doctor. Rinse mouth.
P302 + P352 + P312	IF ON SKIN: Wash with plenty of water.Call a POISON CENTER/doctor if you feel unwell.
P304 + P340 + P310	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/doctor.
P305 + P351 + P338	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing.
P308 + P313	IF exposed or concerned: Get medical advice/ attention.
P337 + P313	If eye irritation persists: Get medical advice/ attention.
P362	Take off contaminated clothing and wash before reuse.
P370 + P378	In case of fire: Use dry sand, dry chemical or alcohol-resistant foam to extinguish.
P403 + P233	Store in a well-ventilated place. Keep container tightly closed.
P403 + P235	Store in a well-ventilated place. Keep cool.
P405	Store locked up.
P501	Dispose of contents/ container to an approved waste disposal plant.

2.3 Hazards not otherwise classified (HNOC) or not covered by GHS - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Synonyms	: 2-(Hydroxymethyl)furan
Formula	: C ₅ H ₆ O ₂
Molecular weight	: 98.10 g/mol
CAS-No.	: 98-00-0
EC-No.	: 202-626-1
Index-No.	: 603-018-00-2

Hazardous components

Component	Classification	Concentration
Furfuryl alcohol	Fam. Liq. 4; Acute Tox. 3; Acute Tox. 2; Acute Tox. 3; Eye Irrit. 2A; Carc. 2; STOT SE 3; STOT RE 2; H227, H301 + H311, H319, H330, H335, H351, H373	90 - 100 %

For the full text of the H-Statements mentioned in this Section, see Section 16.

4. FIRST AID MEASURES

4.1 Description of first aid measures

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance. Move out of dangerous area.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Wash off with soap and plenty of water. Take victim immediately to hospital. Consult a physician.

In case of eye contact

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician.

If swallowed

Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

5. FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

Unsuitable extinguishing media

Do NOT use water jet.

5.2 Special hazards arising from the substance or mixture

No data available

5.3 Advice for firefighters

Wear self-contained breathing apparatus for firefighting if necessary.

5.4 Further information

Use water spray to cool unopened containers.

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures

Wear respiratory protection. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Remove all sources of ignition. Evacuate personnel to safe areas. Beware of vapours accumulating to form explosive concentrations. Vapours can accumulate in low areas.

For personal protection see section 8.

6.2 Environmental precautions

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

6.3 Methods and materials for containment and cleaning up

Contain spillage, and then collect with non-combustible absorbent material, (e.g. sand, earth, diatomaceous earth, vermiculite) and place in container for disposal according to local / national regulations (see section 13). Keep in suitable, closed containers for disposal.

6.4 Reference to other sections

For disposal see section 13.

7. HANDLING AND STORAGE

7.1 Precautions for safe handling

Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.

Keep away from sources of ignition - No smoking. Take measures to prevent the build up of electrostatic charge.
For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities

Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.

Air sensitive.

Storage class (TRGS 510): 6.1B: Non-combustible, acute toxic Cat. 1 and 2 / very toxic hazardous materials

7.3 Specific end use(s)

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

Component	CAS-No.	Value	Control parameters	Basis
Furfuryl alcohol	98-00-0	TWA	0.2 ppm	USA. ACGIH Threshold Limit Values (TLV)
	Remarks	Upper Respiratory Tract irritation Eye irritation 2017 Adoption Confirmed animal carcinogen with unknown relevance to humans Danger of cutaneous absorption		
		TWA	10 ppm 40 mg/m ³	USA. NIOSH Recommended Exposure Limits
		Potential for dermal absorption		
		ST	15 ppm 60 mg/m ³	USA. NIOSH Recommended Exposure Limits
		Potential for dermal absorption		
		TWA	50 ppm 200 mg/m ³	USA. Occupational Exposure Limits (OSHA) - Table Z-1 Limits for Air Contaminants
		The value in mg/m ³ is approximate.		
		PEL	10 ppm 40 mg/m ³	California permissible exposure limits for chemical contaminants (Title 8, Article 107)
		Skin		
		STEL	15 ppm 60 mg/m ³	California permissible exposure limits for chemical contaminants (Title 8, Article 107)
		Skin		

8.2 Exposure controls

Appropriate engineering controls

Avoid contact with skin, eyes and clothing. Wash hands before breaks and immediately after handling the product.

Personal protective equipment

Eye/face protection

Face shield and safety glasses Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Full contact

Material: butyl-rubber

Minimum layer thickness: 0.3 mm

Break through time: 480 min

Material tested: Butoject® (KCL 897 / Aldrich Z677647, Size M)

Splash contact

Material: Nitrile rubber

Minimum layer thickness: 0.4 mm

Break through time: 30 min

Material tested: Camatril® (KCL 730 / Aldrich Z677442, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374

If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection

Complete suit protecting against chemicals, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection

Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure

Prevent further leakage or spillage if safe to do so. Do not let product enter drains.

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

a) Appearance	Form: clear, liquid Colour: colourless
b) Odour	No data available
c) Odour Threshold	No data available
d) pH	No data available
e) Melting point/freezing point	Melting point/range: -29 °C (-20 °F) - lit.
f) Initial boiling point and boiling range	170 °C (338 °F) - lit.
g) Flash point	65 °C (149 °F) - closed cup
h) Evaporation rate	No data available
i) Flammability (solid, gas)	No data available
j) Upper/lower flammability or explosive limits	Upper explosion limit: 16.3 %(V) Lower explosion limit: 1.8 %(V)
k) Vapour pressure	7.3 hPa (5.5 mmHg) at 55 °C (131 °F) 0.7 hPa (0.5 mmHg) at 20 °C (68 °F)
l) Vapour density	3.39 - (Air = 1.0)
m) Relative density	1.135 g/cm ³ at 25 °C (77 °F)
n) Water solubility	No data available
o) Partition coefficient: n-octanol/water	log Pow: 0.3 at 25 °C (77 °F)
p) Auto-ignition temperature	No data available
q) Decomposition temperature	No data available

- r) Viscosity No data available
- s) Explosive properties No data available
- t) Oxidizing properties No data available

9.2 Other safety information

Relative vapour density 3.39 - (Air = 1.0)

10. STABILITY AND REACTIVITY

10.1 Reactivity

No data available

10.2 Chemical stability

Stable under recommended storage conditions.

10.3 Possibility of hazardous reactions

No data available

10.4 Conditions to avoid

Heat, flames and sparks.

10.5 Incompatible materials

Do not store near acids., Oxygen, Strong oxidizing agents

10.6 Hazardous decomposition products

Hazardous decomposition products formed under fire conditions. - Carbon oxides

Other decomposition products - No data available

In the event of fire: see section 5

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity

LD50 Oral - Rat - 177 mg/kg

Remarks: Behavioral:Excitement. Behavioral:Ataxia. Cyanosis

LC50 Inhalation - Rat - male and female - 4 h - > 0.82 - < 2.07 mg/l
(OECD Test Guideline 403)

LD50 Dermal - Rabbit - 400 mg/kg

Remarks: Behavioral:Convulsions or effect on seizure threshold.

No data available

Skin corrosion/irritation

No data available

Serious eye damage/eye irritation

Eyes - Rabbit

Result: Moderate eye irritation - 24 h

Respiratory or skin sensitisation

No data available

Germ cell mutagenicity

Ames test

Salmonella typhimurium

Result: negative

Mouse - male

Result: negative

Carcinogenicity

Carcinogenicity - Rat - Inhalation

Tumorigenic: Carcinogenic by RTECS criteria. Sense Organs and Special Senses (Nose, Eye, Ear, and Taste): Olfaction: Tumors.

Carcinogenicity - Mouse - Inhalation
Tumorigenic: Carcinogenic by RTECS criteria. Kidney, Ureter, Bladder: Kidney tumors.
Limited evidence of carcinogenicity in animal studies

IARC: 2B - Group 2B: Possibly carcinogenic to humans (Furfuryl alcohol)
NTP: No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.
OSHA: No component of this product present at levels greater than or equal to 0.1% is on OSHA's list of regulated carcinogens.

Reproductive toxicity
No data available

No data available

Specific target organ toxicity - single exposure
Inhalation - May cause respiratory irritation. - Nose

Specific target organ toxicity - repeated exposure
Inhalation - May cause damage to organs through prolonged or repeated exposure. - Nose

Aspiration hazard
No data available

Additional Information

Repeated dose toxicity Rat - male - Oral - NOAEL : 53 mg/kg - OECD Test Guideline 408
RTECS: LU9100000

Central nervous system depression, Nausea, Dizziness, Headache, Exposure to and/or consumption of alcohol may increase toxic effects.
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

Stomach - Irregularities - Based on Human Evidence
Stomach - Irregularities - Based on Human Evidence

12. ECOLOGICAL INFORMATION

12.1 Toxicity

12.2 Persistence and degradability

Biodegradability aerobic - Exposure time 14 d
Result: 77.7 % - Readily biodegradable.
(OECD Test Guideline 301C)

12.3 Bioaccumulative potential

No data available

12.4 Mobility in soil

No data available

12.5 Results of PBT and vPvB assessment

PBT/vPvB assessment not available as chemical safety assessment not required/not conducted

12.6 Other adverse effects

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product

Offer surplus and non-recyclable solutions to a licensed disposal company. This combustible material may be burned in a chemical incinerator equipped with an afterburner and scrubber. Contact a licensed professional waste disposal service to dispose of this material.

Contaminated packaging
Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)

UN number: 2874 Class: 6.1 Packing group: III
Proper shipping name: Furfuryl alcohol
Reportable Quantity (RQ):
Poison Inhalation Hazard: No

IMDG

UN number: 2874 Class: 6.1 Packing group: III EMS-No: F-A, S-A
Proper shipping name: FURFURYL ALCOHOL

IATA

UN number: 2874 Class: 6.1 Packing group: III
Proper shipping name: Furfuryl alcohol

15. REGULATORY INFORMATION

SARA 302 Components

This material does not contain any components with a section 302 EHS TPQ.

SARA 313 Components

This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards

Fire Hazard, Acute Health Hazard, Chronic Health Hazard

Massachusetts Right To Know Components

	CAS-No.	Revision Date
Furfuryl alcohol	98-00-0	2007-03-01

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Furfuryl alcohol	98-00-0	2007-03-01

California Prop. 65 Components

	CAS-No.	Revision Date
, which is/are known to the State of California to cause cancer. For more information go to www.P65Warnings.ca.gov .	98-00-0	2016-09-30
Furfuryl alcohol		

16. OTHER INFORMATION

Full text of H-Statements referred to under sections 2 and 3.

Acute Tox.	Acute toxicity
Carc.	Carcinogenicity
Eye Irrit.	Eye irritation
Flam. Liq.	Flammable liquids
H227	Combustible liquid.
H301	Toxic if swallowed.
H301 + H311	Toxic if swallowed or in contact with skin.
H311	Toxic in contact with skin.
H319	Causes serious eye irritation.
H330	Fatal if inhaled.
H335	May cause respiratory irritation.
H351	Suspected of causing cancer.

Further information

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The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

Preparation Information

Sigma-Aldrich Corporation
Product Safety – Americas Region
1-800-521-8956

Version: 4.12

Revision Date: 08/21/2018

Print Date: 11/09/2018

1. PRODUCT AND COMPANY IDENTIFICATION**1.1 Product identifiers**

Product name : Methanesulfonic acid

Product Number : 471356
Brand : Sigma-Aldrich
Index-No. : 607-145-00-4

CAS-No. : 75-75-2

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Synthesis of substances

1.3 Details of the supplier of the safety data sheetCompany : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USATelephone : +1 800-325-5832
Fax : +1 800-325-5052**1.4 Emergency telephone number**

Emergency Phone # : +1-703-527-3887 (CHEMTREC)

2. HAZARDS IDENTIFICATION**2.1 Classification of the substance or mixture****GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)**Corrosive to metals (Category 1), H290
Acute toxicity, Oral (Category 4), H302
Acute toxicity, Dermal (Category 4), H312
Skin corrosion (Category 1B), H314
Serious eye damage (Category 1), H318
Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335
Acute aquatic toxicity (Category 2), H401

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 GHS Label elements, including precautionary statements

Pictogram



Signal word

Danger

Hazard statement(s)

H290 : May be corrosive to metals.
H302 + H312 : Harmful if swallowed or in contact with skin.
H314 : Causes severe skin burns and eye damage.
H335 : May cause respiratory irritation.
H401 : Toxic to aquatic life.

Precautionary statement(s)

P234 : Keep only in original container.

P261	Avoid breathing dust/ fume/ gas/ mist/ vapours/ spray.
P264	Wash skin thoroughly after handling.
P270	Do not eat, drink or smoke when using this product.
P271	Use only outdoors or in a well-ventilated area.
P273	Avoid release to the environment.
P280	Wear protective gloves/ protective clothing/ eye protection/ face protection.
P301 + P312 + P330	IF SWALLOWED: Call a POISON CENTER/doctor if you feel unwell. Rinse mouth.
P301 + P330 + P331	IF SWALLOWED: Rinse mouth. Do NOT induce vomiting.
P303 + P361 + P353	IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower.
P304 + P340 + P310	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/doctor.
P305 + P351 + P338 + P310	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a POISON CENTER/doctor.
P363	Wash contaminated clothing before reuse.
P390	Absorb spillage to prevent material damage.
P403 + P233	Store in a well-ventilated place. Keep container tightly closed.
P405	Store locked up.
P406	Store in corrosive resistant container with a resistant inner liner.
P501	Dispose of contents/ container to an approved waste disposal plant.

2.3 Hazards not otherwise classified (HNOC) or not covered by GHS - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.1 Substances

Formula	: CH ₄ O ₃ S
Molecular weight	: 96.11 g/mol
CAS-No.	: 75-75-2
EC-No.	: 200-898-6
Index-No.	: 607-145-00-4
Registration number	: 01-2119491166-34-XXXX

Hazardous components

Component	Classification	Concentration
Methanesulphonic acid	Met. Corr. 1; Acute Tox. 4; Skin Corr. 1B; Eye Dam. 1; STOT SE 3; Aquatic Acute 2; H290, H302 + H312, H314, H335, H401	90 - 100 %

For the full text of the H-Statements mentioned in this Section, see Section 16.

4. FIRST AID MEASURES

4.1 Description of first aid measures

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance. Move out of dangerous area.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Consult a physician.

In case of eye contact

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician. Continue rinsing eyes during transport to hospital.

If swallowed

Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

5. FIREFIGHTING MEASURES

5.1 Extinguishing media

Suitable extinguishing media

Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.

5.2 Special hazards arising from the substance or mixture

No data available

5.3 Advice for firefighters

Wear self-contained breathing apparatus for firefighting if necessary.

5.4 Further information

No data available

6. ACCIDENTAL RELEASE MEASURES

6.1 Personal precautions, protective equipment and emergency procedures

Wear respiratory protection. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Evacuate personnel to safe areas.

For personal protection see section 8.

6.2 Environmental precautions

Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

6.3 Methods and materials for containment and cleaning up

Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal.

6.4 Reference to other sections

For disposal see section 13.

7. HANDLING AND STORAGE

7.1 Precautions for safe handling

Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.

For precautions see section 2.2.

7.2 Conditions for safe storage, including any incompatibilities

Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.

Heat sensitive.

Storage class (TRGS 510): 8A: Combustible, corrosive hazardous materials

7.3 Specific end use(s)

Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

Contains no substances with occupational exposure limit values.

Hazardous components without workplace control parameters

8.2 Exposure controls

Appropriate engineering controls

Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Personal protective equipment

Eye/face protection

Tightly fitting safety goggles. Faceshield (8-inch minimum). Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Full contact

Material: Nature latex/chloroprene

Minimum layer thickness: 0.6 mm

Break through time: 480 min

Material tested: Lapren® (KCL 706 / Aldrich Z677558, Size M)

Splash contact

Material: Nitrile rubber

Minimum layer thickness: 0.2 mm

Break through time: 52 min

Material tested: Dermatril® P (KCL 743 / Aldrich Z677388, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374

If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection

Complete suit protecting against chemicals, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection

Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure

Prevent further leakage or spillage if safe to do so. Do not let product enter drains. Discharge into the environment must be avoided.

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

- | | |
|--------------------|--------------------------------------|
| a) Appearance | Form: liquid
Colour: light yellow |
| b) Odour | characteristic |
| c) Odour Threshold | No data available |

d) pH	< 1 at 20 °C (68 °F)
e) Melting point/freezing point	Melting point/range: 17 - 19 °C (63 - 66 °F) - lit.
f) Initial boiling point and boiling range	167 °C (333 °F) at 13 hPa (10 mmHg) - lit.
g) Flash point	189 °C (372 °F) - closed cup - DIN 51755 Part 1
h) Evaporation rate	No data available
i) Flammability (solid, gas)	No data available
j) Upper/lower flammability or explosive limits	Upper explosion limit: 24.3 %(V) Lower explosion limit: 11.4 %(V)
k) Vapour pressure	0.112 hPa (0.084 mmHg) at 80 °C (176 °F) - OECD Test Guideline 104 0.224 hPa (0.168 mmHg) at 90 °C (194 °F) - OECD Test Guideline 104
l) Vapour density	3.32 - (Air = 1.0)
m) Relative density	1.481 g/cm ³ at 25 °C (77 °F) - lit.
n) Water solubility	ca.1,000 g/l at 20 °C (68 °F) - completely miscible
o) Partition coefficient: n-octanol/water	log Pow: -2.38 at 20 °C (68 °F) -
p) Auto-ignition temperature	535 °C (995 °F) at 1,010 hPa (758 mmHg)
q) Decomposition temperature	No data available
r) Viscosity	7.86 mm ² /s at 25 °C (77 °F) -
s) Explosive properties	No data available
t) Oxidizing properties	No data available

9.2 Other safety information

Dissociation constant	-1.54 at 25 °C (77 °F)
Relative vapour density	3.32 - (Air = 1.0)

10. STABILITY AND REACTIVITY

10.1 Reactivity

No data available

10.2 Chemical stability

Stable under recommended storage conditions.

10.3 Possibility of hazardous reactions

No data available

10.4 Conditions to avoid

Heat

10.5 Incompatible materials

Amines, Strong reducing agents, Strong oxidizing agentsBases

10.6 Hazardous decomposition products

Hazardous decomposition products formed under fire conditions. - Carbon oxides, Sulphur oxides

Other decomposition products - No data available

In the event of fire: see section 5

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity

LD50 Oral - Rat - male and female - 648.7 mg/kg
(OECD Test Guideline 401)

LC0 Inhalation - Rat - 6 h - 1.1 - 1.4 mg/l

LD50 Dermal - Rabbit - > 1,000 - < 2,000 mg/kg
(OECD Test Guideline 402)

No data available

Skin corrosion/irritation

Skin - Rabbit

Result: Corrosive

Serious eye damage/eye irritation

Eyes - Rabbit

Result: Risk of serious damage to eyes.

Respiratory or skin sensitisation

Buehler Test - Guinea pig

Result: Does not cause skin sensitisation.
(OECD Test Guideline 406)

Germ cell mutagenicity

Hamster

ovary

Result: negative

OECD Test Guideline 474

Mouse - male and female

Result: negative

Carcinogenicity

IARC: No component of this product present at levels greater than or equal to 0.1% is identified as probable, possible or confirmed human carcinogen by IARC.

NTP: No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.

OSHA: No component of this product present at levels greater than or equal to 0.1% is on OSHA's list of regulated carcinogens.

Reproductive toxicity

No data available

Reproductive toxicity - Rat - male and female - Oral

No adverse effect has been observed in chronic toxicity tests.

Specific target organ toxicity - single exposure

No data available

Specific target organ toxicity - repeated exposure

No data available

Aspiration hazard

No data available

Additional Information

Repeated dose toxicity Rat - male - Oral - NOAEL : \geq 1,805 mg/kg

RTECS: PB1140000

burning sensation, Cough, wheezing, laryngitis, Shortness of breath, spasm, inflammation and edema of the larynx, spasm, inflammation and edema of the bronchi, pneumonitis, pulmonary edema, Material is extremely destructive to tissue of the mucous membranes and upper respiratory tract, eyes, and skin.
To the best of our knowledge, the chemical, physical, and toxicological properties have not been thoroughly investigated.

12. ECOLOGICAL INFORMATION

12.1 Toxicity

Toxicity to fish	static test LC50 - Oncorhynchus mykiss (rainbow trout) - 73 mg/l - 96 h (OECD Test Guideline 203)
Toxicity to daphnia and other aquatic invertebrates	static test EC50 - Daphnia (water flea) - 70 mg/l - 48 h (OECD Test Guideline 202)
Toxicity to algae	static test EC50 - Selenastrum capricornutum (green algae) - 7.2 - 20 mg/l - 96 h (OECD Test Guideline 201)
Toxicity to bacteria	Respiration inhibition EC50 - Sludge Treatment - > 1,000 mg/l - 30 min (OECD Test Guideline 209)

12.2 Persistence and degradability

Biodegradability	aerobic Chemical oxygen demand - Exposure time 28 d Result: 90 - 100 % - Readily biodegradable. (OECD Test Guideline 301A)
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12.3 Bioaccumulative potential

No data available

12.4 Mobility in soil

No data available

12.5 Results of PBT and vPvB assessment

PBT/vPvB assessment not available as chemical safety assessment not required/not conducted

12.6 Other adverse effects

An environmental hazard cannot be excluded in the event of unprofessional handling or disposal.
Toxic to aquatic life.

No data available

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product

Offer surplus and non-recyclable solutions to a licensed disposal company. Contact a licensed professional waste disposal service to dispose of this material. Dissolve or mix the material with a combustible solvent and burn in a chemical incinerator equipped with an afterburner and scrubber.

Contaminated packaging

Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)

UN number: 3265 Class: 8 Packing group: II
Proper shipping name: Corrosive liquid, acidic, organic, n.o.s. (Methanesulphonic acid)
Reportable Quantity (RQ):
Poison Inhalation Hazard: No

IMDG

IATA

UN number: 3265 Class: 8 Packing group: II

Proper shipping name: Corrosive liquid, acidic, organic, n.o.s. (Methanesulphonic acid)

15. REGULATORY INFORMATION

SARA 302 Components

No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components

This material does not contain any chemical components with known CAS numbers that exceed the threshold (De Minimis) reporting levels established by SARA Title III, Section 313.

SARA 311/312 Hazards

Acute Health Hazard

Massachusetts Right To Know Components

No components are subject to the Massachusetts Right to Know Act.

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Methanesulphonic acid	75-75-2	1994-07-31

	CAS-No.	Revision Date
Methanesulphonic acid	75-75-2	1994-07-31

New Jersey Right To Know Components

	CAS-No.	Revision Date
Methanesulphonic acid	75-75-2	1994-07-31

California Prop. 65 Components

This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

Full text of H-Statements referred to under sections 2 and 3.

Acute Tox.	Acute toxicity
Aquatic Acute	Acute aquatic toxicity
Eye Dam.	Serious eye damage
H290	May be corrosive to metals.
H302	Harmful if swallowed.
H302 + H312	Harmful if swallowed or in contact with skin.
H312	Harmful in contact with skin.
H314	Causes severe skin burns and eye damage.
H318	Causes serious eye damage.

Further information

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Preparation Information

Sigma-Aldrich Corporation
Product Safety – Americas Region
1-800-521-8956

Version: 4.15

Revision Date: 07/12/2018

Print Date: 11/10/2018

1. PRODUCT AND COMPANY IDENTIFICATION**1.1 Product identifiers**

Product name : Hydrochloric acid

Product Number : 320331
Brand : Sigma-Aldrich
Index-No. : 017-002-01-X

CAS-No. : 7647-01-0

1.2 Relevant identified uses of the substance or mixture and uses advised against

Identified uses : Laboratory chemicals, Synthesis of substances

1.3 Details of the supplier of the safety data sheetCompany : Sigma-Aldrich
3050 Spruce Street
SAINT LOUIS MO 63103
USATelephone : +1 800-325-5832
Fax : +1 800-325-5052**1.4 Emergency telephone number**

Emergency Phone # : +1-703-527-3887 (CHEMTREC)

2. HAZARDS IDENTIFICATION**2.1 Classification of the substance or mixture**

GHS Classification in accordance with 29 CFR 1910 (OSHA HCS)

Corrosive to metals (Category 1), H290

Skin corrosion (Category 1B), H314

Serious eye damage (Category 1), H318

Specific target organ toxicity - single exposure (Category 3), Respiratory system, H335

For the full text of the H-Statements mentioned in this Section, see Section 16.

2.2 GHS Label elements, including precautionary statements

Pictogram



Signal word

Danger

Hazard statement(s)

H290

May be corrosive to metals.

H314

Causes severe skin burns and eye damage.

H335

May cause respiratory irritation.

Precautionary statement(s)

P234

Keep only in original container.

P261

Avoid breathing dust/ fume/ gas/ mist/ vapours/ spray.

P264

Wash skin thoroughly after handling.

P271

Use only outdoors or in a well-ventilated area.

P280

Wear protective gloves/ protective clothing/ eye protection/ face protection.

P301 + P330 + P331 P303 + P361 + P353	IF SWALLOWED: Rinse mouth. Do NOT induce vomiting. IF ON SKIN (or hair): Take off immediately all contaminated clothing. Rinse skin with water/shower.
P304 + P340 + P310	IF INHALED: Remove person to fresh air and keep comfortable for breathing. Immediately call a POISON CENTER/doctor.
P305 + P351 + P338 + P310	IF IN EYES: Rinse cautiously with water for several minutes. Remove contact lenses, if present and easy to do. Continue rinsing. Immediately call a POISON CENTER/doctor.
P363 P390 P403 + P233 P405 P406	Wash contaminated clothing before reuse. Absorb spillage to prevent material damage. Store in a well-ventilated place. Keep container tightly closed. Store locked up. Store in corrosive resistant stainless steel container with a resistant inliner.
P501	Dispose of contents/ container to an approved waste disposal plant.

2.3 Hazards not otherwise classified (HNOC) or not covered by GHS - none

3. COMPOSITION/INFORMATION ON INGREDIENTS

3.2 Mixtures

Formula	:	HCl
Molecular weight	:	36.46 g/mol

Hazardous components

Component	Classification	Concentration
Hydrochloric acid		
CAS-No.	7647-01-0	30 - 50 %
EC-No.	231-595-7	
Index-No.	017-002-01-X	
Registration number	01-2119484862-27-XXXX	

For the full text of the H-Statements mentioned in this Section, see Section 16.

4. FIRST AID MEASURES

4.1 Description of first aid measures

General advice

Consult a physician. Show this safety data sheet to the doctor in attendance.

If inhaled

If breathed in, move person into fresh air. If not breathing, give artificial respiration. Consult a physician.

In case of skin contact

Take off contaminated clothing and shoes immediately. Wash off with soap and plenty of water. Consult a physician.

In case of eye contact

Rinse thoroughly with plenty of water for at least 15 minutes and consult a physician. Continue rinsing eyes during transport to hospital.

If swallowed

Do NOT induce vomiting. Never give anything by mouth to an unconscious person. Rinse mouth with water. Consult a physician.

4.2 Most important symptoms and effects, both acute and delayed

The most important known symptoms and effects are described in the labelling (see section 2.2) and/or in section 11

4.3 Indication of any immediate medical attention and special treatment needed

No data available

5. FIREFIGHTING MEASURES

- 5.1 **Extinguishing media**
Suitable extinguishing media
Use water spray, alcohol-resistant foam, dry chemical or carbon dioxide.
- 5.2 **Special hazards arising from the substance or mixture**
No data available
- 5.3 **Advice for firefighters**
Wear self-contained breathing apparatus for firefighting if necessary.
- 5.4 **Further information**
No data available

6. ACCIDENTAL RELEASE MEASURES

- 6.1 **Personal precautions, protective equipment and emergency procedures**
Wear respiratory protection. Avoid breathing vapours, mist or gas. Ensure adequate ventilation. Evacuate personnel to safe areas.
For personal protection see section 8.
- 6.2 **Environmental precautions**
Do not let product enter drains.
- 6.3 **Methods and materials for containment and cleaning up**
Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal. Soak up with inert absorbent material and dispose of as hazardous waste. Keep in suitable, closed containers for disposal.
- 6.4 **Reference to other sections**
For disposal see section 13.

7. HANDLING AND STORAGE

- 7.1 **Precautions for safe handling**
Avoid contact with skin and eyes. Avoid inhalation of vapour or mist.
For precautions see section 2.2.
- 7.2 **Conditions for safe storage, including any incompatibilities**
Keep container tightly closed in a dry and well-ventilated place. Containers which are opened must be carefully resealed and kept upright to prevent leakage.
Storage class (TRGS 510): 8B: Non-combustible, corrosive hazardous materials
- 7.3 **Specific end use(s)**
Apart from the uses mentioned in section 1.2 no other specific uses are stipulated

8. EXPOSURE CONTROLS/PERSONAL PROTECTION

8.1 Control parameters

Components with workplace control parameters

Component	CAS-No.	Value	Control parameters	Basis
Hydrochloric acid	7647-01-0	C	2 ppm	USA. ACGIH Threshold Limit Values (TLV)
	Remarks	Upper Respiratory Tract irritation Not classifiable as a human carcinogen		
		C	5 ppm 7 mg/m ³	USA. NIOSH Recommended Exposure Limits
		Often used in an aqueous solution.		
		C	5 ppm 7 mg/m ³	USA. Occupational Exposure Limits (OSHA) - Table Z-1 Limits for Air Contaminants
		The value in mg/m ³ is approximate. Ceiling limit is to be determined from breathing-zone air samples.		

		PEL	0.3 ppm 0.45 mg/m ³	California permissible exposure limits for chemical contaminants (Title 8, Article 107)
		C	2 ppm	California permissible exposure limits for chemical contaminants (Title 8, Article 107)

8.2 Exposure controls

Appropriate engineering controls

Handle in accordance with good industrial hygiene and safety practice. Wash hands before breaks and at the end of workday.

Personal protective equipment

Eye/face protection

Tightly fitting safety goggles. Faceshield (8-inch minimum). Use equipment for eye protection tested and approved under appropriate government standards such as NIOSH (US) or EN 166(EU).

Skin protection

Handle with gloves. Gloves must be inspected prior to use. Use proper glove removal technique (without touching glove's outer surface) to avoid skin contact with this product. Dispose of contaminated gloves after use in accordance with applicable laws and good laboratory practices. Wash and dry hands.

Full contact

Material: Nitrile rubber

Minimum layer thickness: 0.4 mm

Break through time: 480 min

Material tested: Camatril® (KCL 730 / Aldrich Z677442, Size M)

Splash contact

Material: Nitrile rubber

Minimum layer thickness: 0.11 mm

Break through time: 69 min

Material tested: Dermatril® (KCL 740 / Aldrich Z677272, Size M)

data source: KCL GmbH, D-36124 Eichenzell, phone +49 (0)6659 87300, e-mail sales@kcl.de, test method: EN374

If used in solution, or mixed with other substances, and under conditions which differ from EN 374, contact the supplier of the CE approved gloves. This recommendation is advisory only and must be evaluated by an industrial hygienist and safety officer familiar with the specific situation of anticipated use by our customers. It should not be construed as offering an approval for any specific use scenario.

Body Protection

Complete suit protecting against chemicals, The type of protective equipment must be selected according to the concentration and amount of the dangerous substance at the specific workplace.

Respiratory protection

Where risk assessment shows air-purifying respirators are appropriate use a full-face respirator with multi-purpose combination (US) or type ABEK (EN 14387) respirator cartridges as a backup to engineering controls. If the respirator is the sole means of protection, use a full-face supplied air respirator. Use respirators and components tested and approved under appropriate government standards such as NIOSH (US) or CEN (EU).

Control of environmental exposure

Do not let product enter drains.

9. PHYSICAL AND CHEMICAL PROPERTIES

9.1 Information on basic physical and chemical properties

- | | |
|---------------------------|--------------------------------------|
| a) Appearance | Form: liquid
Colour: light yellow |
| b) Odour | pungent |
| c) Odour Threshold | No data available |
| d) pH | No data available |
| e) Melting point/freezing | -30 °C (-22 °F) |

	point	
f)	Initial boiling point and boiling range	> 100 °C (> 212 °F)
g)	Flash point	Not applicable
h)	Evaporation rate	No data available
i)	Flammability (solid, gas)	No data available
j)	Upper/lower flammability or explosive limits	No data available
k)	Vapour pressure	226.636 hPa (169.991 mmHg) at 21.1 °C (70.0 °F) 546.596 hPa (409.981 mmHg) at 37.7 °C (99.9 °F)
l)	Vapour density	No data available
m)	Relative density	1.18 g/mL at 25 °C (77 °F)
n)	Water solubility	soluble
o)	Partition coefficient: n-octanol/water	No data available
p)	Auto-ignition temperature	No data available
q)	Decomposition temperature	No data available
r)	Viscosity	No data available
s)	Explosive properties	No data available
t)	Oxidizing properties	No data available

9.2 Other safety information
No data available

10. STABILITY AND REACTIVITY

- 10.1 Reactivity**
No data available
- 10.2 Chemical stability**
Stable under recommended storage conditions.
- 10.3 Possibility of hazardous reactions**
No data available
- 10.4 Conditions to avoid**
No data available
- 10.5 Incompatible materials**
Bases, Amines, Alkali metals, Metals, permanganates, e.g. potassium permanganate, Fluorine, metal acetylides, hexalithium disilicide
- 10.6 Hazardous decomposition products**
Hazardous decomposition products formed under fire conditions. - Hydrogen chloride gas
Other decomposition products - No data available
In the event of fire: see section 5

11. TOXICOLOGICAL INFORMATION

11.1 Information on toxicological effects

Acute toxicity

No data available (Hydrochloric acid)

Inhalation: Inhalation may provoke the following symptoms: Respiratory irritation Cough Difficulty in breathing Pneumonia (Hydrochloric acid)

Dermal: No data available (Hydrochloric acid)

No data available (Hydrochloric acid)

Skin corrosion/irritation

Skin - Rabbit (Hydrochloric acid)

Result: Causes burns.

Serious eye damage/eye irritation

Eyes - Rabbit (Hydrochloric acid)

Result: Corrosive to eyes

Respiratory or skin sensitisation

Did not cause sensitisation on laboratory animals. (Hydrochloric acid)

Germ cell mutagenicity

No data available (Hydrochloric acid)

Carcinogenicity

This product is or contains a component that is not classifiable as to its carcinogenicity based on its IARC, ACGIH, NTP, or EPA classification. (Hydrochloric acid)

(Hydrochloric acid)

(Hydrochloric acid)

IARC: 3 - Group 3: Not classifiable as to its carcinogenicity to humans (Hydrochloric acid)

NTP: No component of this product present at levels greater than or equal to 0.1% is identified as a known or anticipated carcinogen by NTP.

OSHA: No component of this product present at levels greater than or equal to 0.1% is on OSHA's list of regulated carcinogens.

Reproductive toxicity

No data available (Hydrochloric acid)

No data available (Hydrochloric acid)

Specific target organ toxicity - single exposure

The substance or mixture is classified as specific target organ toxicant, single exposure, category 3 with respiratory tract irritation. (Hydrochloric acid)

Specific target organ toxicity - repeated exposure

The substance or mixture is not classified as specific target organ toxicant, repeated exposure.

Aspiration hazard

No aspiration toxicity classification (Hydrochloric acid)

Additional Information

RTECS: MW4025000

Inhalation of vapors may cause:; burning sensation, Cough, wheezing, Shortness of breath, spasm, inflammation and edema of the larynx, spasm, inflammation and edema of the bronchi, pneumonitis, pulmonary edema (Hydrochloric acid)

12. ECOLOGICAL INFORMATION

12.1 Toxicity

Toxicity to fish LC50 - Lepomis macrochirus (Bluegill) - 24.6 mg/l - 96 h (Hydrochloric acid)

Toxicity to daphnia and other aquatic invertebrates EC50 - Daphnia magna (Water flea) - 4.91 mg/l - 48 h (Hydrochloric acid)

12.2 Persistence and degradability

No data available

12.3 Bioaccumulative potential

No data available

- 12.4 **Mobility in soil**
No data available (Hydrochloric acid)
- 12.5 **Results of PBT and vPvB assessment**
PBT/vPvB assessment not available as chemical safety assessment not required/not conducted
- 12.6 **Other adverse effects**
May be harmful to aquatic organisms due to the shift of the pH. Do not empty into drains.

13. DISPOSAL CONSIDERATIONS

13.1 Waste treatment methods

Product

Offer surplus and non-recyclable solutions to a licensed disposal company.

Contaminated packaging

Dispose of as unused product.

14. TRANSPORT INFORMATION

DOT (US)

UN number: 1789 Class: 8 Packing group: II
 Proper shipping name: Hydrochloric acid
 Reportable Quantity (RQ):
 Poison Inhalation Hazard: No

IMDG

UN number: 1789 Class: 8 Packing group: II EMS-No: F-A, S-B
 Proper shipping name: HYDROCHLORIC ACID

IATA

UN number: 1789 Class: 8 Packing group: II
 Proper shipping name: Hydrochloric acid

15. REGULATORY INFORMATION

SARA 302 Components

No chemicals in this material are subject to the reporting requirements of SARA Title III, Section 302.

SARA 313 Components

The following components are subject to reporting levels established by SARA Title III, Section 313:

	CAS-No.	Revision Date
Hydrochloric acid	7647-01-0	2013-02-08

SARA 311/312 Hazards

No SARA Hazards

Massachusetts Right To Know Components

	CAS-No.	Revision Date
Hydrochloric acid	7647-01-0	2013-02-08

Pennsylvania Right To Know Components

	CAS-No.	Revision Date
Water	7732-18-5	
Hydrochloric acid	7647-01-0	2013-02-08

New Jersey Right To Know Components

	CAS-No.	Revision Date
Water	7732-18-5	
Hydrochloric acid	7647-01-0	2013-02-08

California Prop. 65 Components

This product does not contain any chemicals known to State of California to cause cancer, birth defects, or any other reproductive harm.

16. OTHER INFORMATION

Full text of H-Statements referred to under sections 2 and 3.

Eye Dam.	Serious eye damage
H290	May be corrosive to metals.
H314	Causes severe skin burns and eye damage.
H318	Causes serious eye damage.
H335	May cause respiratory irritation.
Met. Corr.	Corrosive to metals
Skin Corr.	Skin corrosion
STOT SE	Specific target organ toxicity - single exposure

Further information

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The above information is believed to be correct but does not purport to be all inclusive and shall be used only as a guide. The information in this document is based on the present state of our knowledge and is applicable to the product with regard to appropriate safety precautions. It does not represent any guarantee of the properties of the product. Sigma-Aldrich Corporation and its Affiliates shall not be held liable for any damage resulting from handling or from contact with the above product. See www.sigma-aldrich.com and/or the reverse side of invoice or packing slip for additional terms and conditions of sale.

Preparation Information

Sigma-Aldrich Corporation
Product Safety – Americas Region
1-800-521-8956

Version: 6.14

Revision Date: 08/20/2018

Print Date: 11/10/2018

Chemical Compatibility Chart

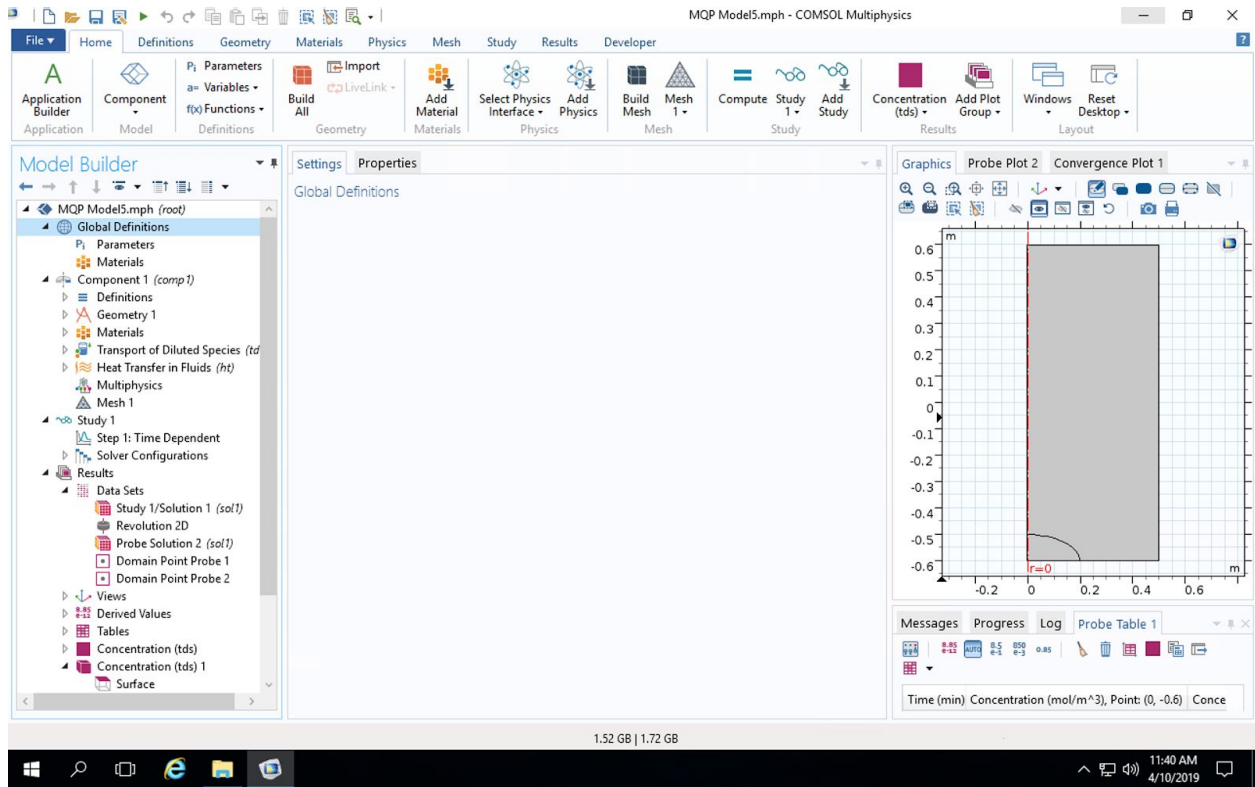
Below is a chart adapted from the CRC Laboratory Handbook, which groups various chemicals in to 23 groups with examples and incompatible chemical groups. This chart is by no means complete but it will aid in making decisions about storage. For more complete information please refer to the MSDS for the specific chemical. Examples of each group can be found on the next pages.

Group Number/Chemical Type	1 Inorganic Acids	2 Organic Acids	3 Caustics	4 Amines and Alkanolamines	5 Halogenated Compounds	6 Alcohols, Glycols, Glycol Ether	7 Aldehydes Acetaldehyde	8 Ketones	9 Saturated Hydrocarbons	10 Aromatic Hydrocarbons	11 Olefins	12 Petroleum Oils	13 Esters	14 Monomers Polymerizable Esters	15 Phenols	16 Alkyene Oxides	17 Cyanohydrins	18 Nitriles	19 Ammonia	20 Halogens	21 Ethers	22 Phosphorus	23 Acid Anhydrides
1 Inorganic Acids		x	x	x	x	x	x	x		x			x	x		x	x	x		x	x	x	x
2 Organic Acids	x		x	x			x							x		x	x	x				x	
3 Caustics	x	x				x	x	x					x	x	x	x	x			x			x
4 Amines and Alkanolamines	x	x			x		x	x					x	x	x	x	x						x
5 Halogenated Compounds	x		x	x							x			x			x						
6 Alcohols, Glycols, Glycol Ether	x						x							x						x			x
7 Aldehydes Acetaldehyde	x	x	x	x		x		x							x	x	x		x	x			x
8 Ketones	x		x	x			x												x	x			
9 Saturated Hydrocarbons																				x			
10 Aromatic Hydrocarbons	x																			x			
11 Olefins	x				x															x			
12 Petroleum Oils																				x			
13 Esters	x		x	x															x	x			
14 Monomers Polymerizable Esters	x	x	x	x	x	x									x	x			x	x	x		x
15 Phenols			x	x			x							x		x			x	x			
16 Alkyene Oxides	x	x	x	x		x	x							x	x		x	x	x				x
17 Cyanohydrins	x	x	x	x	x		x								x				x				x
18 Nitriles	x	x	x	x												x							x
19 Ammonia	x	x					x	x					x	x	x	x	x			x			x
20 Halogens			x			x	x	x	x	x	x	x	x	x	x				x		x	x	
21 Ethers	x													x							x		
22 Phosphorus	x	x	x																		x		
23 Acid Anhydrides	x		x	x		x	x							x		x	x	x					

X - Indicates chemicals that are incompatible and should not be stored together.

Figure 2. Chemical Compatibility Chart Provided by Worcester Polytechnic Institute

APPENDIX C: Summary of Settings and Inputs for COMSOL



Parameters:

Parameters

Parameters

Name	Expression	Value	Description
A	$4.89E9[\text{m}^3/\text{mol}/\text{s}]$	$4.89E9 \text{ m}^3/(\text{s} \dots)$	Frequency Factor
Cfa	$11529.8[\text{mol}/\text{m}^3]$	$11530 \text{ mol}/\text{m}^3$	Initial Concentration of Furfuryl Alcohol
Cms	$.74[\text{mol}/\text{m}^3]$	$0.74 \text{ mol}/\text{m}^3$	Initial Concentration of Methane Sulfonic Acid
DHr	$-84366[\text{J}/\text{mol}]$	$-84366 \text{ J}/\text{mol}$	Heat of Reaction
E	$64200[\text{J}/\text{mol}]$	$64200 \text{ J}/\text{mol}$	Activation Energy
R_g	$8.314[\text{J}/\text{mol}/\text{K}]$	$8.314 \text{ J}/(\text{mol} \cdot \text{K})$	Gas Constant
Ti	$293.15[\text{K}]$	293.15 K	Initial Temperature
U	$280[\text{W}/\text{m}^2/\text{K}]$	$280 \text{ W}/(\text{m}^2 \cdot \text{K})$	Overall Heat Transfer Coefficient

Variables:

The screenshot shows the 'Model Builder' interface on the left and the 'Settings' panel for 'Variables 1' on the right. The 'Variables' section in the settings panel is active, showing a table of defined variables.

Name	Expression	Unit	Description
k	$A \cdot \exp(-E/(R_g \cdot T))$	$\text{m}^3/(\text{s} \cdot \text{m} \dots)$	
rate	$k \cdot c \cdot c^2$	$\text{mol}/(\text{m} \dots)$	

Geometry:

The screenshot shows the 'Geometry 1' panel on the left and a 2D plot of the geometry on the right. The geometry is a rectangular domain with a quarter-circle cutout at the bottom-left corner. The x-axis is labeled with values 2, 0, 0.2, 0.4, and 0.6. The y-axis is labeled with values 0, 0.2, 0.4, and 0.6. A red line indicates the boundary at $r=0$.

Transport Properties:

Transport Properties

Override and Contribution

Equation

$$\frac{\partial c_i}{\partial t} + \nabla \cdot (-D_i \nabla c_i) = R_i$$

$$\mathbf{N}_i = -D_i \nabla c_i$$

Model Input

Temperature:

T User defined

293.15[K] K

Coordinate System Selection

Diffusion

Material:

None

Diffusion coefficient:

D_c User defined

1.5e-9[m^2/s] m^2/s

Isotropic

D_{c2} User defined

1.5e-9[m^2/s] m^2/s

Isotropic

Initial Values

Label: Initial Values 2

Domain Selection

Selection: Manual

1

Active

Override and Contribution

Initial Values

Concentration

c Cms mol/m³

$c2$ 0 mol/m³

Reactions

Label: Reactions 1

Domain Selection

Selection: Manual

1

2

Active

Override and Contribution

Equation

Reaction Rates

R_c User defined

0 mol/(m²·s)

R_{c2} User defined

-rate mol/(m²·s)

Heat Transfer:

Heat Transfer in Fluids

Label: Heat Transfer in Fluids

Name: ht

- Domain Selection
- Equation
- Physical Model
- Ambient Settings

Ambient data:

User defined

Ambient temperature:

T_{amb} 293.15[K] K

Ambient absolute pressure:

p_{amb} 1[atm] Pa

Ambient relative humidity:

ϕ_{amb} 0 1

Wind velocity:

v_{amb} 0 m/s

Clear sky noon beam normal irradiance:

$I_{sn,amb}$ 1000[W/m²] W/m²

Clear sky noon diffuse horizontal irradiance:

$I_{sh,amb}$ 0[W/m²] W/m²

Fluid

Label: Fluid 1

- Domain Selection
- Override and Contribution
- Equation
- Model Input

Temperature:

T Temperature (ht)

Absolute pressure:

p_A User defined 1[atm] Pa

Velocity field:

u User defined

0	r
0	z


m/s

- Coordinate System Selection
- Heat Conduction, Fluid

Thermal conductivity:

k User defined 0.1799 W/(m·K)

Heat Source


Label: Heat Source 1 

▸ Domain Selection

▸ Override and Contribution

▼ Equation


Show equation assuming:

Study 1, Time Dependent 

$Q = Q_0$


▼ Material Type

Material type:

Nonsolid 

▼ Heat Source

General source

Q_0 User defined 

rate*-Dhr W/m³

Linear source

$Q_0 = q_s \cdot T$

Heat rate

$Q_0 = \frac{P_0}{V}$

Mesh:

Mesh

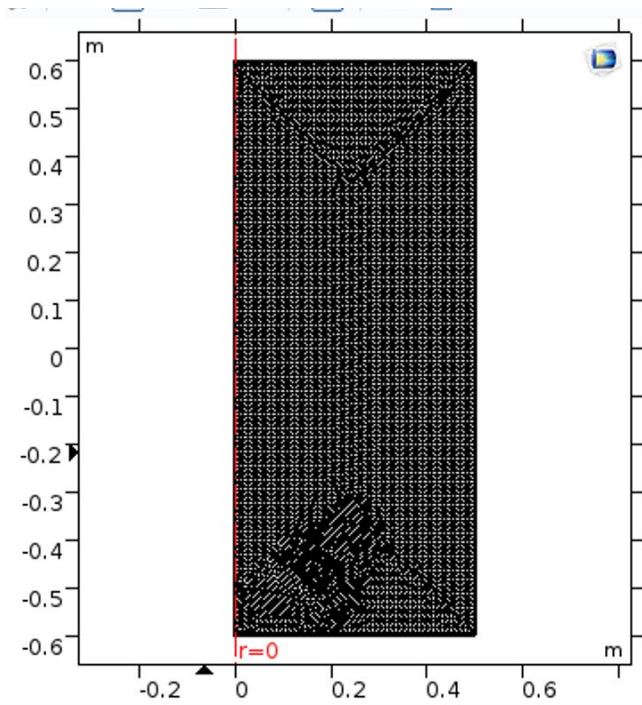
 Build All

Label: Mesh 1 


▼ Mesh Settings


Sequence type:
Physics-controlled mesh ▼

Element size:
Extremely fine ▼




Study:

Time Dependent
= Compute  Update Solution

Label: Time Dependent 

▼ Study Settings

Time unit: min

Times: range(0,.1,30) min 

Tolerance: Physics controlled

▷ Results While Solving

▼ Physics and Variables Selection

Modify model configuration for study step

Physics interface	Solve for	Discretization
Transport of Diluted Species	<input checked="" type="checkbox"/>	Physics settings
Heat Transfer in Fluids	<input checked="" type="checkbox"/>	Physics settings

▷ Values of Dependent Variables

▷ Mesh Selection

▷ Study Extensions

APPENDIX D: Small Scale Vessel Design and Internal Dimensions

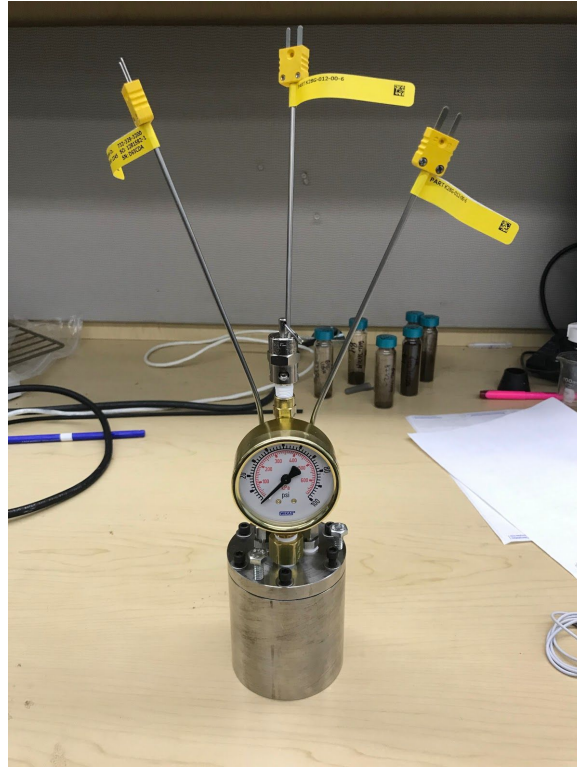


Figure 3. Small sized vessel

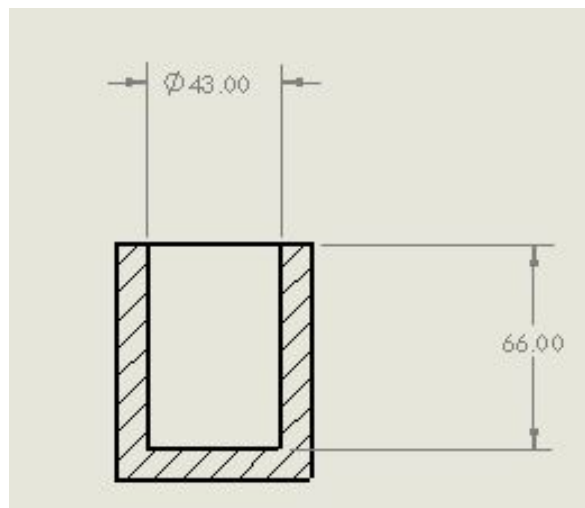


Figure 4. Cross sectional diagram of small vessel with internal dimensions (mm)

APPENDIX E: Large Scale Vessel Design and Internal Dimensions



Figure 5. Large sized vessel

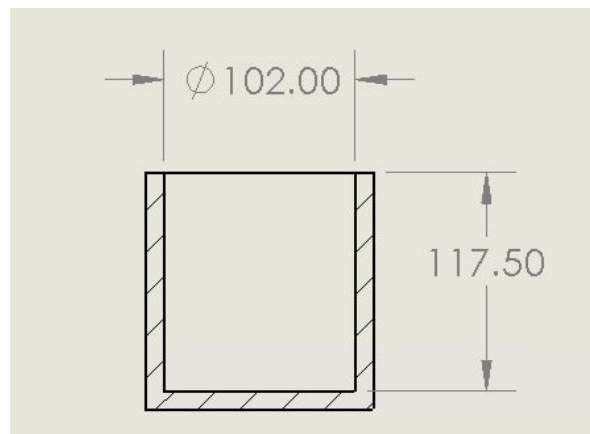


Figure 6. Cross sectional diagram of large vessel with internal dimensions (mm)

APPENDIX F: Hydrochloric Acid and Furfuryl Alcohol Completed Reaction



Figure 7. Overpressurized 250 mL HDPE bottle. Hole blown out at bottom.



Figure 8. Overpressurized 250 mL HDPE bottle. Cap blown out.



Figure 9. Overpressurized 250 mL HDPE bottle aftermath.



Figure 10. Overpressurized 250 mL HDPE bottle aftermath.



Figure 11. Overpressurized 250 mL HDPE bottle aftermath.

APPENDIX G: Resin Solids Formed by Small Scale Vessel



APPENDIX H: Resin Solid Formed by Large Scale Vessel

