Assessing Efficacy of Indirect Contact Water Spray in Arresting Thermal Runaway inside Vessels

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Executive Summary

Thermal runaway in a storage vessel can be particularly dangerous if the storage vessel contains self-reacting chemicals. In this project, the efficacy of indirect contact water spray in arresting thermal runaway inside vessels is investigated.

This project uses COMSOL Multiphysics to simulate water spray effect on vessel cooling for a first order, exothermic, irreversible reaction. Three vessels of different sizes have been simulated to evaluate the effect of water spray cooling.

The indirect water spray successfully controlled the boundary and near-boundary temperature to around the water's temperature of 298.15K. The water spray has a better result in controlling boundary are temperature in smaller vessels. However, it fails to stop the center of fluid in the vessel from rising to over 400K, which indicates a safety concern. Results show that despite the water spray having a cooling effect at the boundary of and for a very short distance from the boundary inside a vessel, it nevertheless has a poor effect in preventing overall thermal runaway and stopping the reaction from generating excessive heat. This suggests that water spray has very limited ability to stop an ongoing runaway reaction and thus should not be considered for extremely reactive and explosive cases. An alternative fluid cooling method needs to be studied and designed for more effective process safety.

Acknowledgement

First and foremost, I would like to thank the Executive Sponsor of the Dow Chemical Company for this great opportunity to design the project. I am extremely grateful to my Project Mentors: Dr. Jessica Nichols, Dr. Katie Mulligan and Dr. Steven Horsch from the Dow Chemical Company for their dedicated instruction and training.

I would also like to thank Purdue University Davidson School of Chemical Engineering for the tremendous support and resources provided for students. My biggest thank goes to the Project Manager Dr. William R. Clark. and to my Academic Mentor Dr. Ray Mentzer for their valuable advice and support. I would also like to thank Dr. Catherine Field for her coaching on technical writing. Lastly, I would like to thank my fellow ChE student Michael T. Bai for his great help and assistance with this project.

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1. Introduction

Thermal runaway is a very common yet extremely dangerous phenomenon that happens in reactors and storage vessels in chemical plants or labs. In an industry setting, it can be particularly dangerous if it occurs in a storage vessel containing a large amount of potentially reactive chemicals (for example, organic peroxides or monomers). The rapid change in temperature can lead to changes in properties of chemicals inside, potentially causing hazardous reactions, which can in turn lead to a further temperature increase, repeating the harmful cycle. If the temperature rise leads to an unwanted reaction happening that proceeds to run away thermally, it has the potential to eventually cause an explosion or worse, severely injuring people and damaging both facilities and the environment.

Emergency scenarios typically employ unsophisticated water spray techniques, such as a fire hose directed at the side of the vessel, and therefore the efficacy of water spray may not be well-understood. Through studying relevant topics on thermal runaway, this project with the Dow Chemical Company aims to provide an assessment to see how well water spray prevents thermal runaway in a storage vessel that could potentially bring up life-threatening situations.

COMSOL Multiphysics provides a great way to study this problem with the finite element analysis method, which provides the best analysis and visual display of the outcomes of a water spray's effect on temperature.

What sets this project apart from current research work is that this project and model explores more general features about water spray on stopping thermal runaway in a vessel rather than making reports on the thermal performance of any specific chemical, like DTBP (Di-tert-butyl peroxide) or others. Nevertheless, with the general model successfully designed, the parameters, assumption, and scope can be changed later for further study on a targeted chemical, reaction, or particular shape of vessel. In short, this simulation model is an inclusive and elementary piece of design that can be adapted to various systems with specification.

2. Objective

The purpose of this project is to understand water spray for chemical storage tank cool-down as well as understand the effectiveness of key parameters.

The objectives of this project are to design and run a model to represent the effectiveness of external water spray in cooling chemical storage vessels and to use this model to include and understand key parameters that affect or prevent thermal runaway for process safety.

3. Literature Review

Thermal runaway is by no means something new and unfamiliar to the chemical industry. It has happened throughout the history of development in the chemical industry. Some common chemicals and substances that initiate thermal runaway are highly exothermic and self-reacting [1]. Aside from conducting calculations solely based on thermal and transport equations, methods involving calorimetry such as differential scanning calorimetry are commonly used for assessing thermal properties and reactive potential of a specific chemical.[1] Many research papers have investigated the behavior of thermal runaway in various materials. For example, benzoyl peroxide has been studied thoroughly, and has been found to have a two-hundred-hour time to maximum rate.[2] The length of time to maximum rate being in terms of hundreds of hours indicates that this form of thermal runaway is relatively safe for workers to operate around without worrying about rapid change in the chemical's condition. In contrast, in this project with Dow, the focus is on a much more violent situation where temperature and properties may change in roughly several hours or less.

In emergency scenarios, as an individual operation, water spray cooling has not been fully researched on and put into practice. A water spray usually has various different parameters included despite only utilizing water as material. [3] Empirical parameters of a water spray like average droplet diameter or droplet velocity working together are very specific and different from the parameters involved with a constant flow of water.[3] Other types of water spray like evaporative cooling have been proven as a more efficient method by combining the use of water and ambient air, which results in more surface area exposed to cooling in a simulation.[4] However, such a system requires adaption to real scenarios to see the how well the computational results of cooling effect can be interpreted. [4]

In a batch reactor—which is more similar to a sealed storage vessel contacting self-reacting chemicals—important factors like threshold temperature and temperature change with time are largely responsible for the runaway.[5] This, along with other aforementioned papers, inspired this project to investigate indirect water spray arresting thermal runaway in a storage vessel.

4. Technical Description

COMSOL Multiphysics 4.3b is the software used in this project.

The model setup is as follows:

Reaction**:** The kinetics of the simulation have been provided by Dow in the project statement. A first-order, exothermic and irreversible reaction is suggested. Therefore, the reaction in the simulation model is designed as a simple chemical A to B transformation.

$$A \rightarrow B$$

The mass of A is 58.095 g/mol, B is 76.095 g/mol. The density of A is 830 kg/m^3. The density of B is 1040 kg/m^3. A and B here are chosen to represent low molecular weight organic species, and could be changed in future iterations of the model.

The initial storage or reaction temperature is 298.15 K. The initial concentration of A is 100wt%. The heat of reaction of is -500 J/g. The rate constant is described in the Arrhenius expression:

$$k^f = A^f T^{nf} \exp\left(-E^f / R_g T\right) \textit{ (Equation 1)}$$

with A^f=2e11[1/h], nf=0, E^f=15 kJ/mol as recommended in the project statement.

The water temperature is 298.15 K (25 °C). The parameter that differentiates no water spray vs. water spray cooling is the overall heat transfer coefficient. When running the no water spray cooling, U_k=2 W/m^2/K, which represents poor heat transfer by ambient air convection around an insulated tank. When running the water spray cooling as an external heat source, U_k =200 W/m^2/K, representing a consistent external free convective heat transfer.

The Heat Transfer in Liquids equation is as follows:

$$\rho C_p \frac{\partial T}{\partial t} + \rho C_p u \cdot \nabla T = \nabla \cdot \left(k \nabla T\right) + Q + Q_{vh} + W_p \textit{ (Equation 2)}$$

The velocity field of **u** in the cartesian coordinates is 0 [m/s] due to no inlet or outlet flow.

The Transport of Concentrated Species equation is as follows:

$$\rho \frac{\partial \omega_i}{\partial t} + \nabla \cdot j_i + \rho \left(u \cdot \nabla \right) \omega_i = R_i \textit{(Equation 3)}$$

Vessel geometry: The vessel designed for this model is a cylinder with a radius of Ra and the length of L, which the exact value is specified in the next section of results. The material of construction is Steel AISI 4340 with physical properties predefined by COMSOL.

The volume of the vessel is:

$$V = \pi \cdot R_a^2 \cdot L \textit{ (Equation 4)}$$

Finite element analysis: A mesh is built in this model with COMSOL to solve the finite element analysis.[6] The physical size and structure of mesh largely affect the final result of analysis so the “extra fine” mesh is used run the simulation for the best outcome.

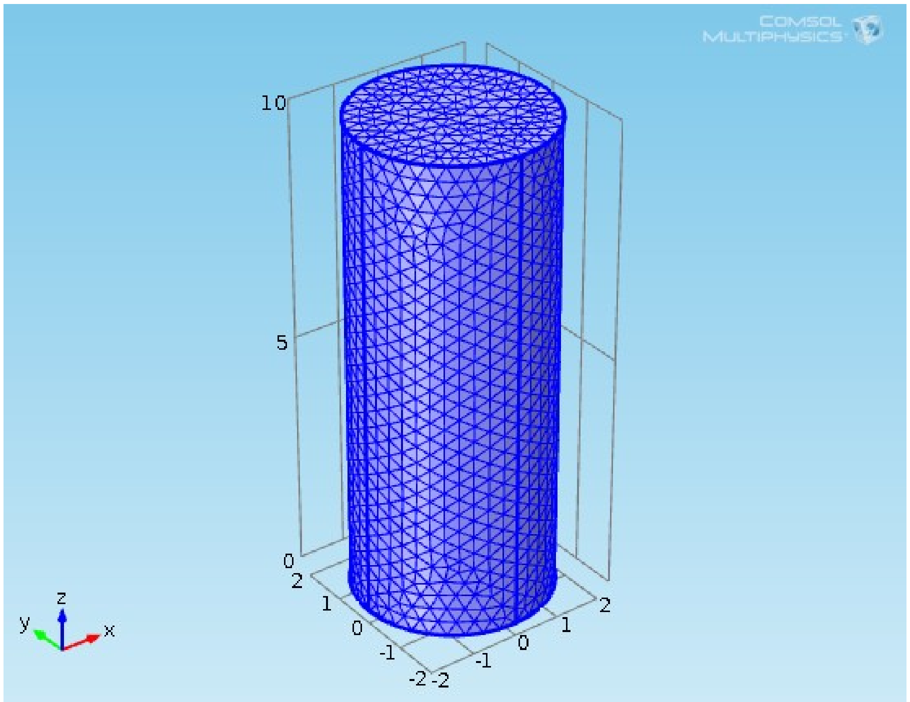


Figure4.1 Vessel#1 Mesh in COMSOL

Thermal resistance: A Biot number (Bi) is calculated for each scenario to assess the thermal resistance of the vessel.

$$Bi = \frac{h}{k} \cdot L \text{ (Equation 5)}$$

5. Results and Data

Due to the missing labels in the graphics produced by the COMSOL Multiphysics interface, the units of the measurement will be explained for the following figures shown in this section. The measurement of time was done in seconds, the measurement of distance in the (x, y, z) axes was done in meters, and the temperature was measured in Kelvin (K).

The key parameter being studied in this model for the project is the effect of vessel geometry on water spray cooling. Three individual tests have been run to study the effect of vessel size for water spray cooling.

In the first test (test #1), the cylinder (vessel #1) has a radius of 2 m, a length of 10 m; in the second test (test #2), the cylinder (vessel #2) has a radius of 1 m, a length of 5 m; in the third test (test #3), the cylinder(vessel#3) has a radius of 0.5 m, a length of 2.5 m.

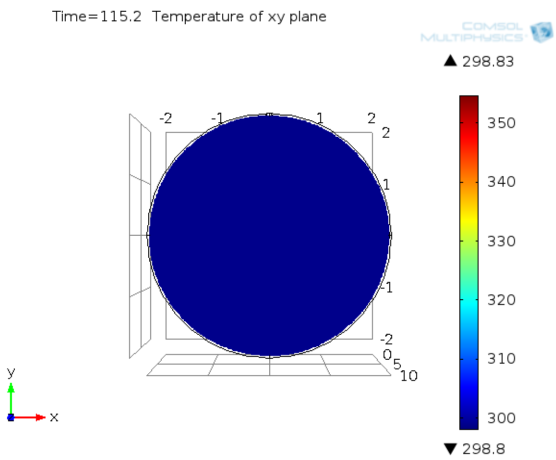
In each test, both cases of no water spray on vessel vs. water spray on vessel have been simulated to generate temperature results. For each cylinder, one center point and one edge point in the x-y plane have been picked out to study the water spray effect of temperature change.

Results in the y-z plane and x-z plane are shown in the Appendix.

In test #1, the center and edge coordinates picked out to be studied are (-0.03553, 0.0067. 5.1151) and (1.9699,0.3457,10.0000); in test #2, (-0.01776,0.0036,2.5575) and (0.9850,0.1728,5.0000); in test #3, (0.2092, -0.0021,1.2521) and (0.4925,0.0864,2.5000).

All of these coordinates are measured in meters from the origin (0,0,0).

Test#1: V= 125.66 m^3



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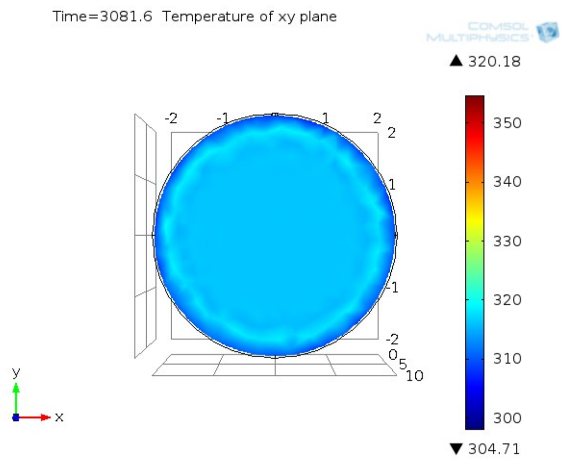

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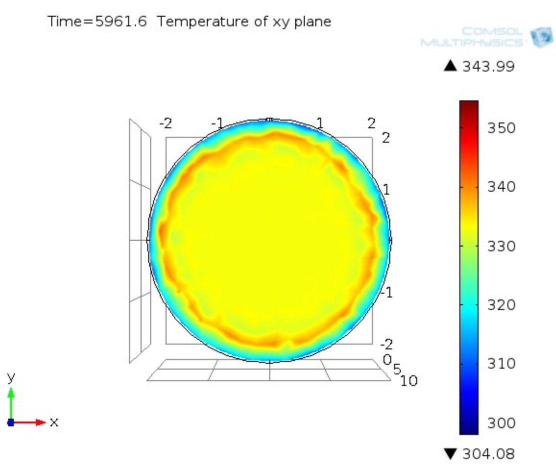

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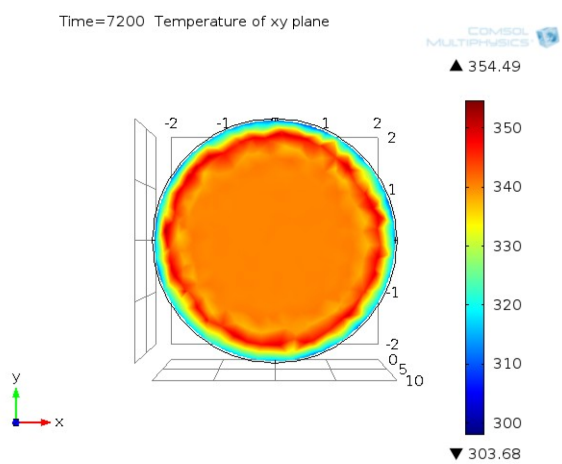
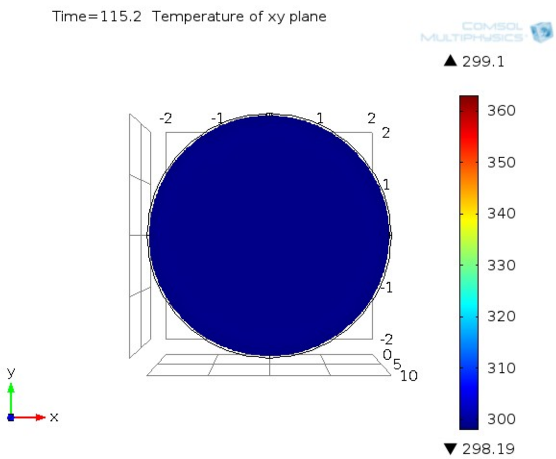


5.1.1(d)

Figure 5.1.1(a)-(d) Vessel#1: T distribution with no water spray with t up to 7200 seconds



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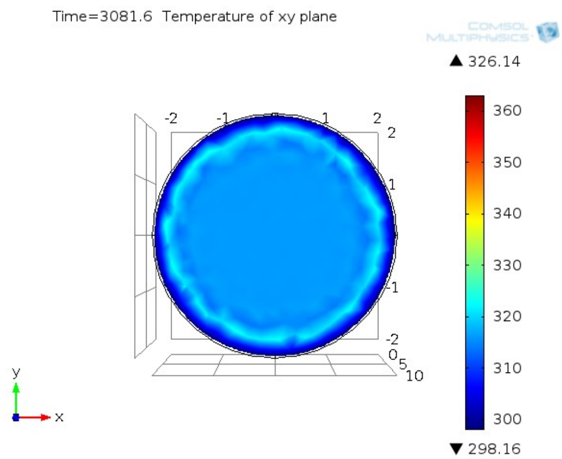

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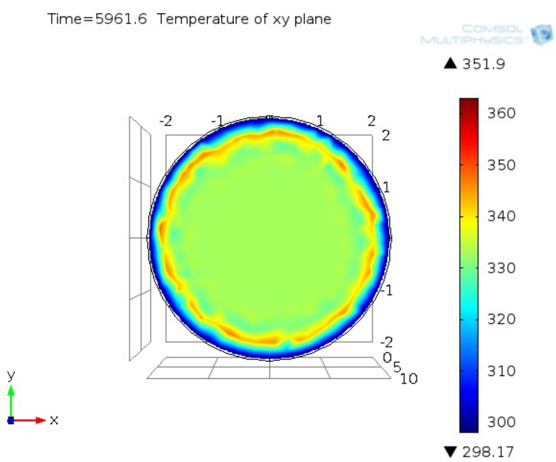

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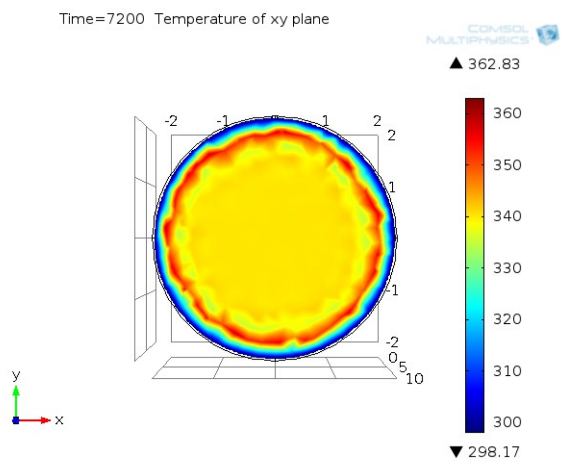


5.1.2(d)

Figure 5.1.2(a)-(d) Vessel#1: T distribution with water spray with t up to 7200 seconds

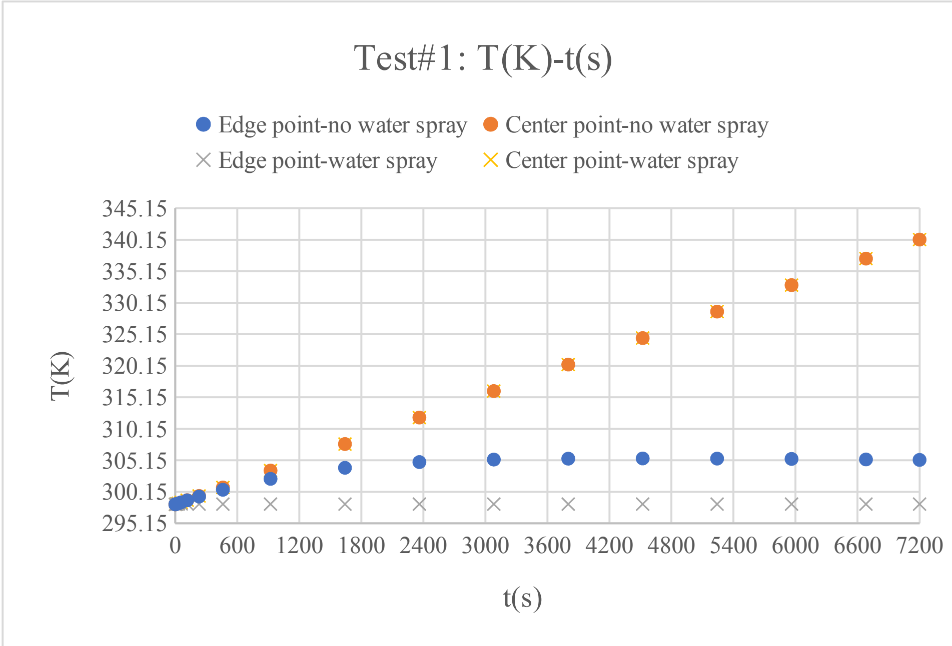
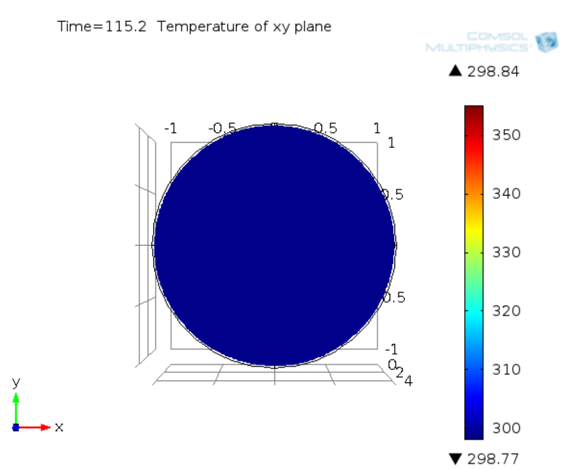


Figure5.1.3 Vessel#1: Temperature vs. time

At 7200 s, vessel#1 without water spray cooling has a temperature distribution from 303.68 K to 354.49 K and a Bi number of 0.4494; the vessel with water spray cooling has a temperature distribution from 298.17 K to 362.83 K and a Bi number of 44.94.

Test#2: V=15.71 m^3



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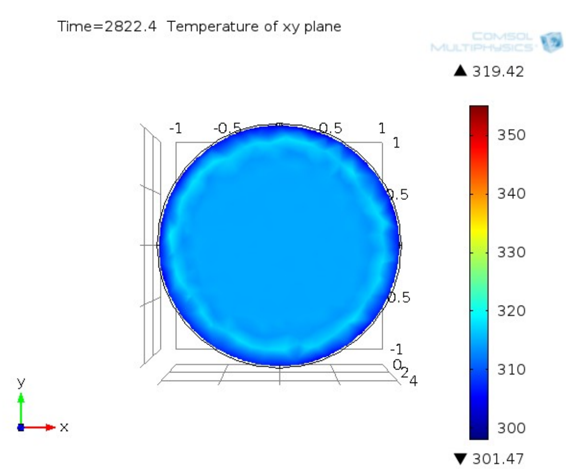

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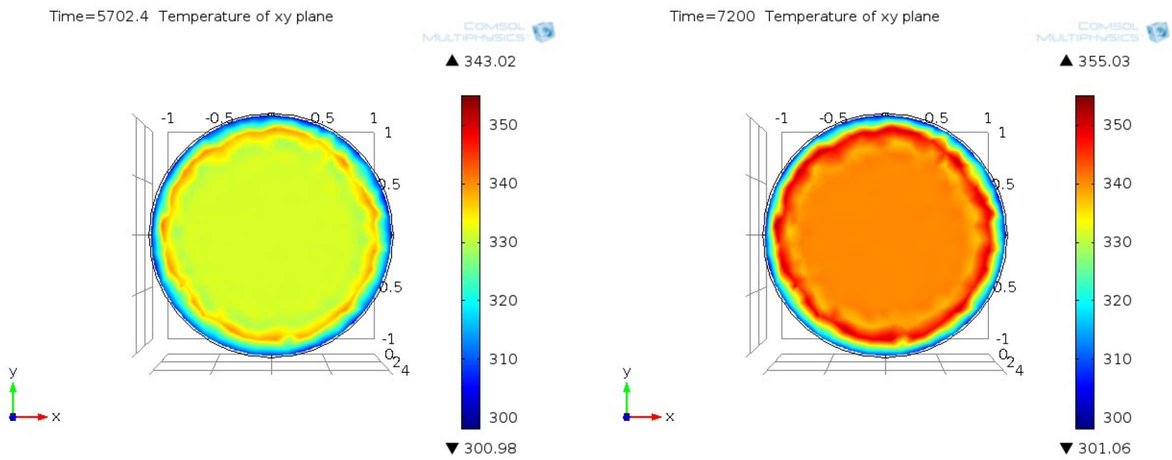

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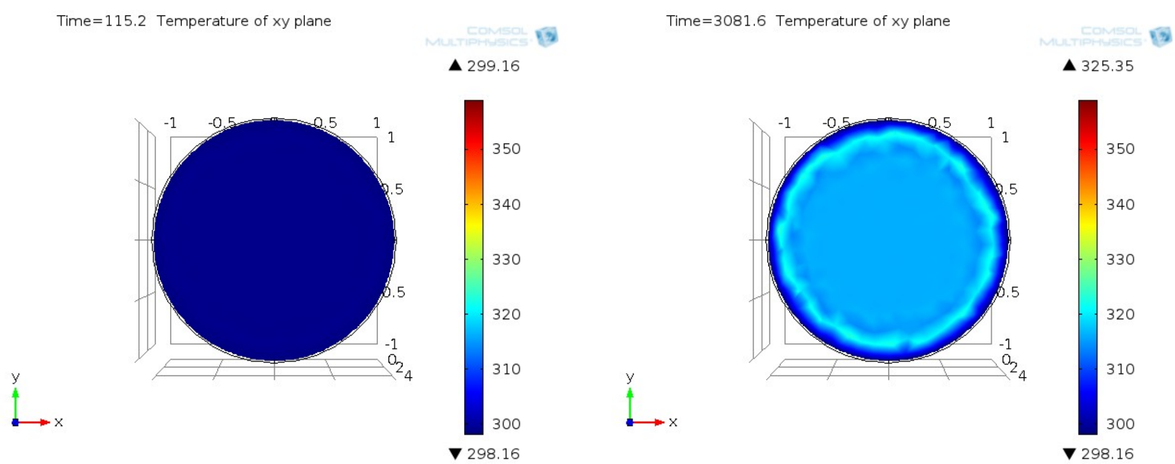
Figure 5.2.1(a)-(d) Vessel #2: T distribution with no water spray with t up to 7200 seconds



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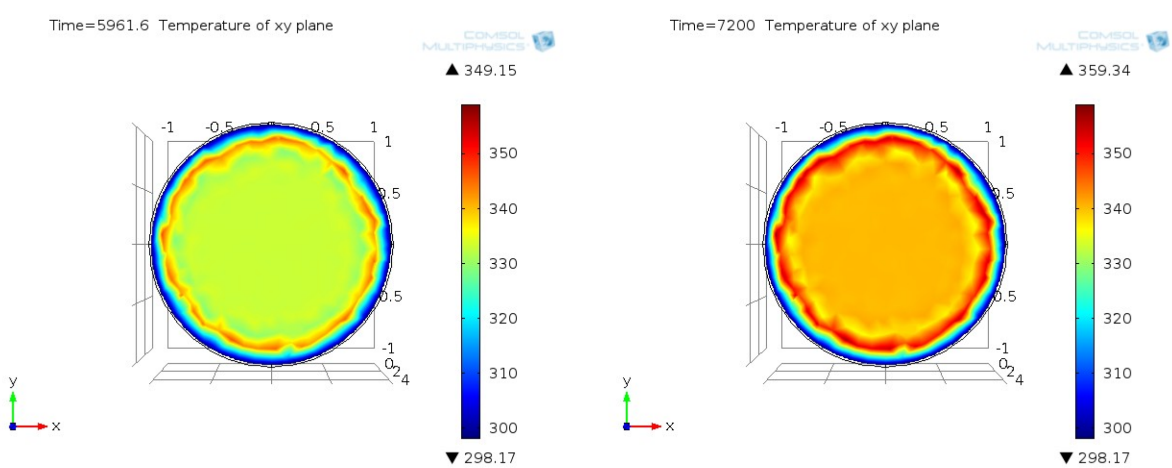


5.2.2(c) 5.2.2(d)

Figure 5.2.2(a)-(d) Vessel #2: T distribution with water spray with t up to 7200 seconds

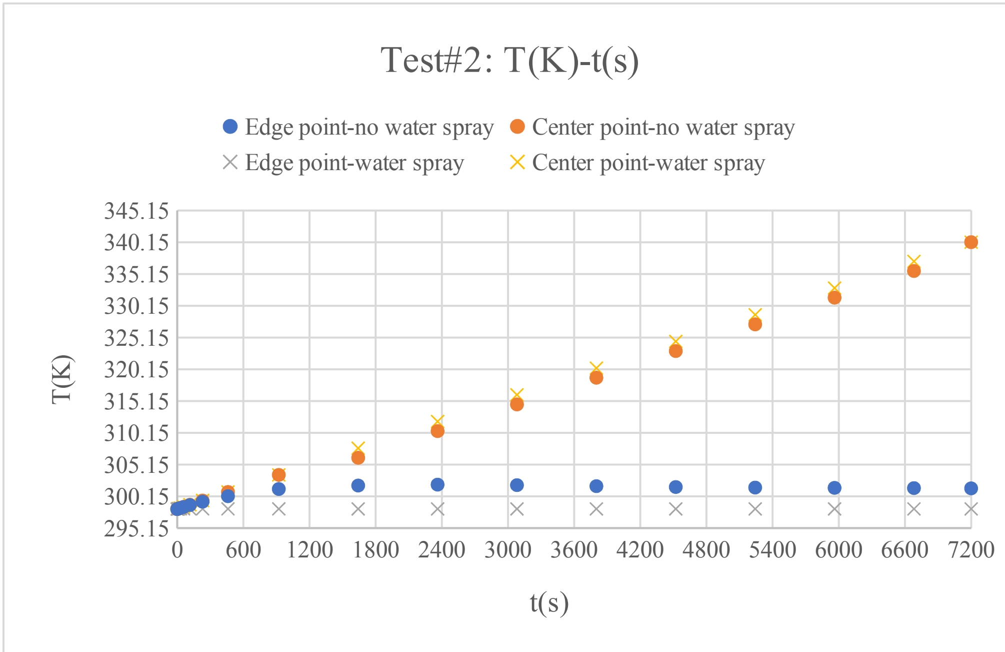
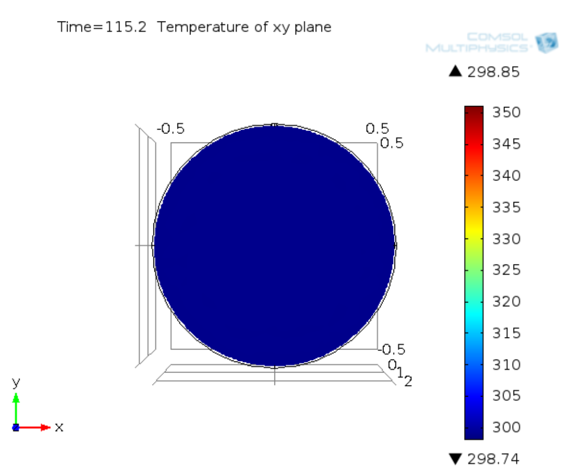


Figure5.2.3 Vessel#2: Temperature vs. time

At 7200 s, vessel #2 without water spray cooling has a temperature distribution from 301.06 K to 355.03 K and a Bi number of 0.2247 while the vessel with water spray cooling has a temperature distribution from 298.17 K to 359.34 K, and a Bi number of 22.47.

Test#3: V=1.96 m^3



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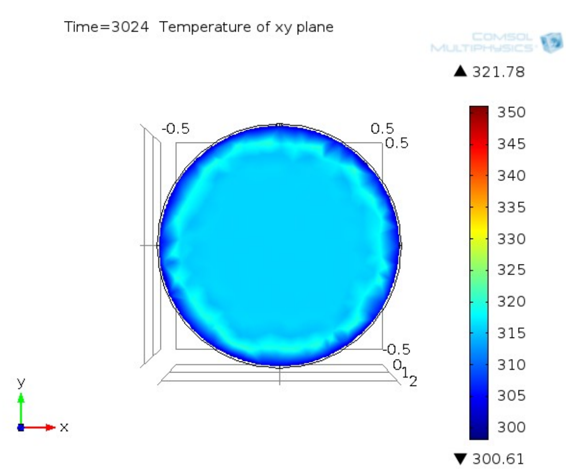

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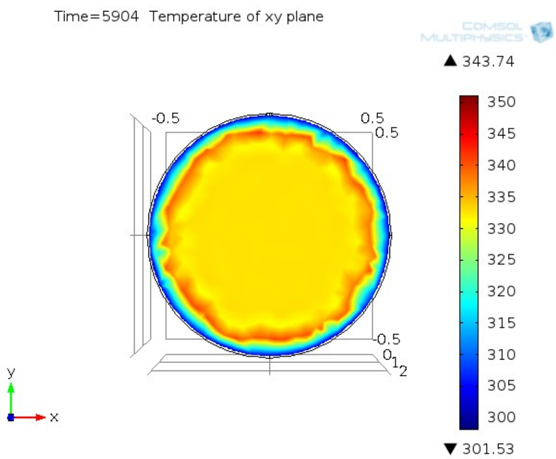
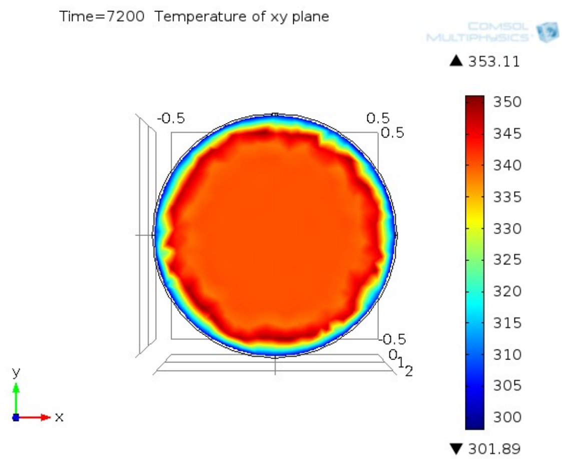
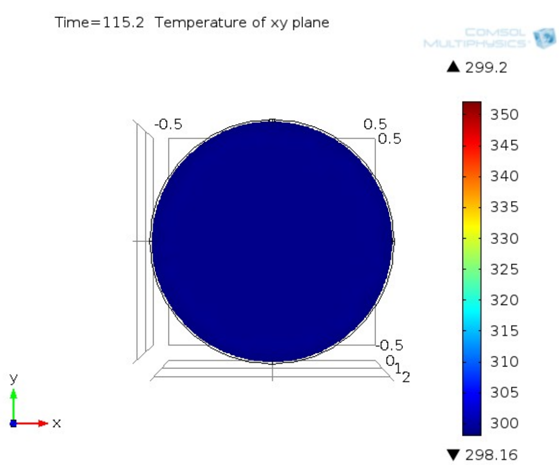
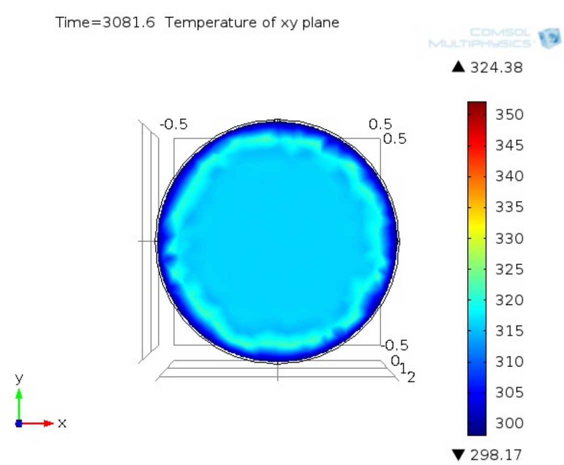




5.3.1(c) 5.3.1(d)

Figure 5.3.1(a)-(d) Vessel #3: T distribution with no water spray with t up to 7200 seconds





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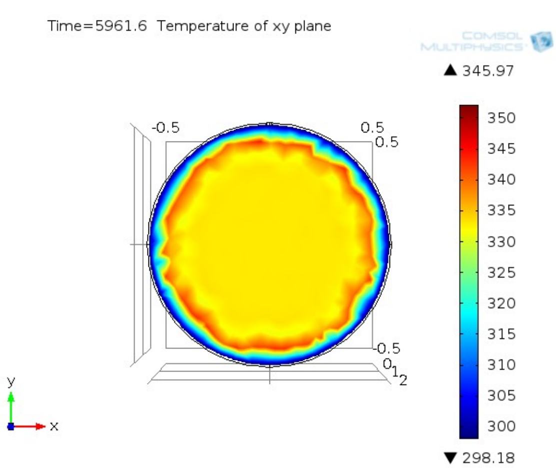

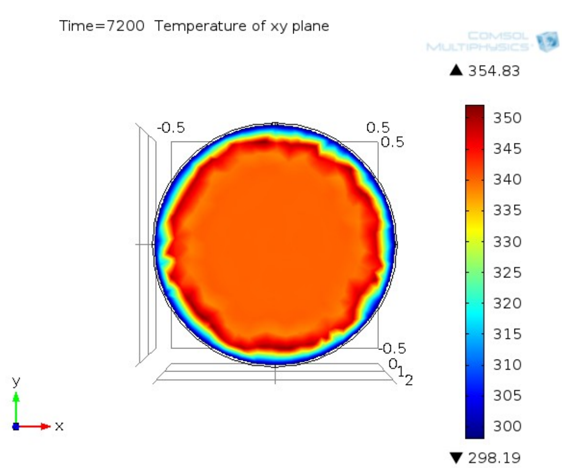

5.3.2(c) 5.3.2(d)

Figure 5.3.2(a)-(d) Vessel #3: T distribution with water spray with t up to 7200 seconds

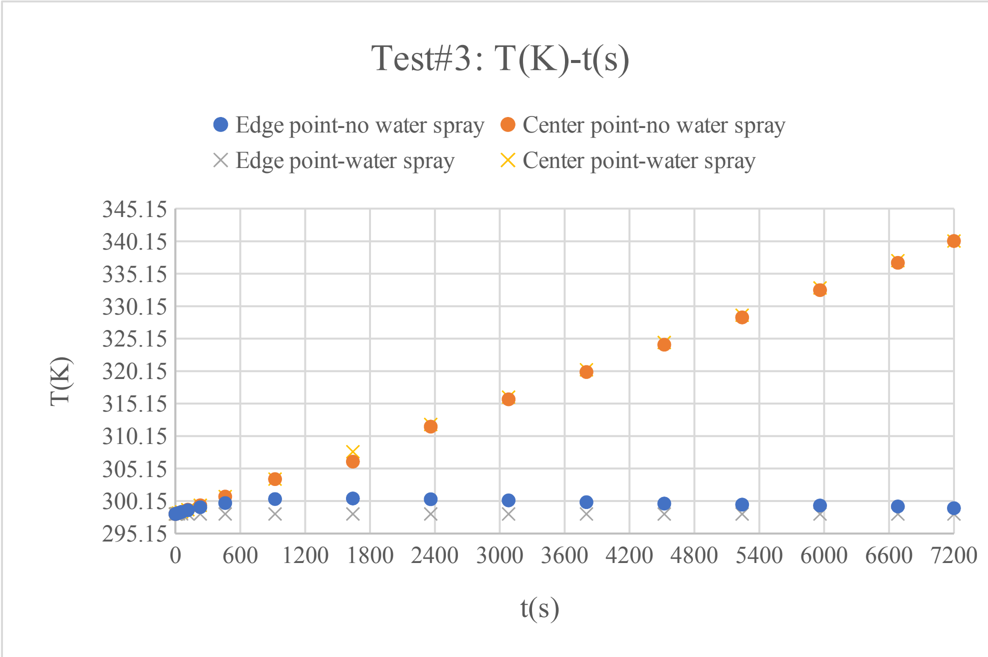

Figure5.3.3 Vessel#3: Temperature vs. time

At 7200s, vessel #3 without water spray cooling has a temperature distribution from 301.89 K to 353.11 K and a Bi number of 0.1124; the vessel with water spray cooling has a temperature distribution from 298.19K to 354.83 K and a Bi number of 11.24.

The following figures are generated to compare the effectiveness of the same water spray on different vessel sizes.

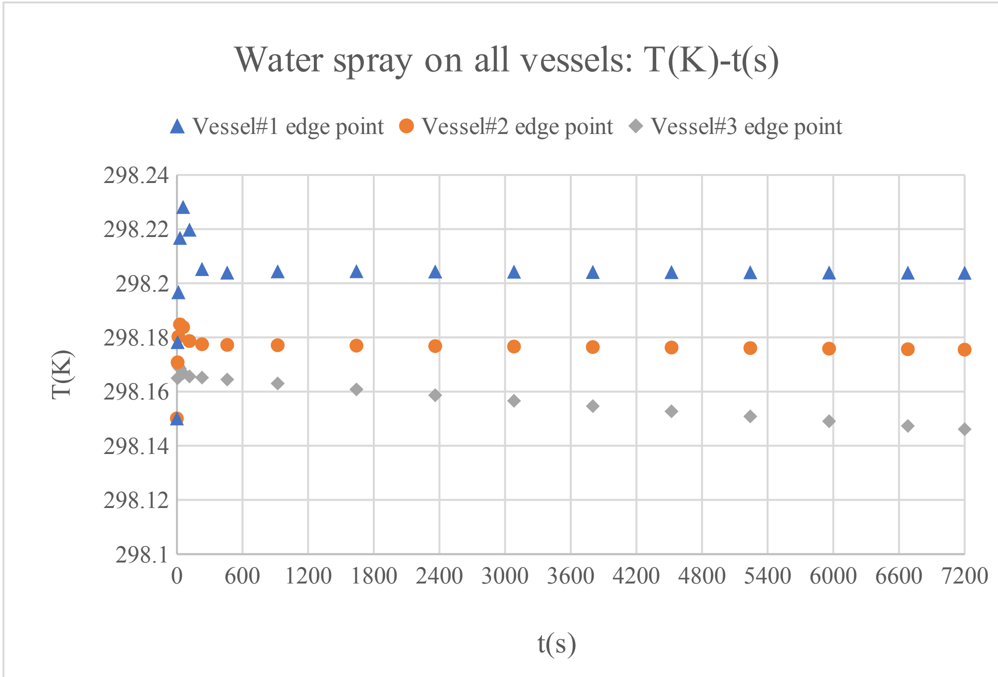

Figure5.4 Edge point temperature vs. time with water spray

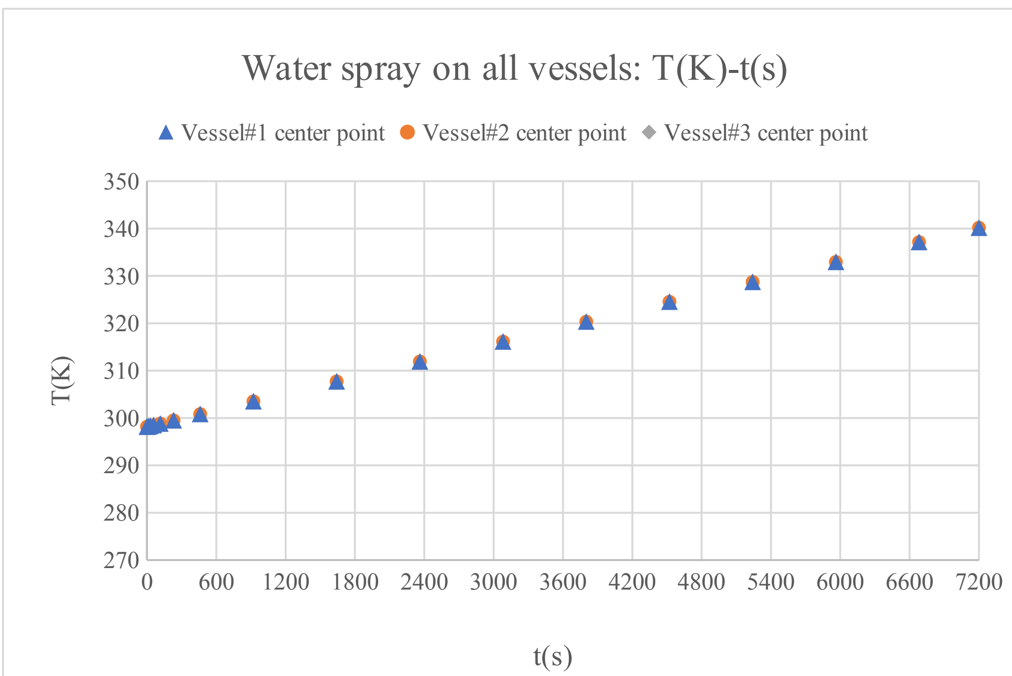

Figure5.5 Center point temperature vs. time with water spray

6. Discussion and Conclusion

In **Figures 5.1.3, 5.2.3 and 5.3.3**, the center point temperatures show a roughly linear growth from 298.15 K to 340 K within 7200 s, which indicates that the reactions have not slowed during this timeframe and suggests that the reactions would continue with more heat generated, regardless of the presence of a water spray cooling system.

Figure 5.1.3 shows that the temperature of the edge point has been cooled from 305.21K to 298.20 K after the application of a water spray. **Figure 5.2.3** shows that the temperature of the edge point has been cooled from 301.48 K to 298.17 K, while **Figure 5.3.3** shows that the temperature of the edge point has been cooled from 299.05K to 298.15K. These changes suggest that the water spray successfully cools down the boundaries of the cylinder.

In **Figure 5.4**, comparing edge point temperatures of all three vessels, vessel #3 has the smallest temperature rise, and it has biggest temperature gap with the edge point temperature of vessel #1, which shows that water spray cools down the boundary of a smaller vessel more efficiently than that of a vessel with a larger volume. Noticeably, the temperature difference at the boundary from t=0 and t=7200s for all vessels is relatively small, within 0.2K. This indicates that the water cooling maintains a roughly constant temperature at the edge of the vessel, near the temperature of the water used.

However, **Figure 5.5 -** where center point temperature values overlap for all three vessels - shows that water spray has a poor and almost negligible cooling effect on the center area of the vessel where the reaction happens the most violently.

In conclusion, for this reaction setup with the proposed assumptions, the indirect contact water spray has a low efficacy in arresting thermal runaway inside vessels. The external convective cooling provided by water spray fails to stop reaction from going on within two hours. In a real-life emergency scenario, this temperature rise (>40K) will trigger safety alarms and would signal that an incident is occurring, that would likely lead to an immediate evacuation order or other appropriate emergency response.

7. Future Steps Forward

Several aspects of changes and further studies can be considered for future research.

1. This project only studies the effect of one form of vessel geometry in terms of sizing for water spray effect. It can be modified to see how other shapes of the vessels with different geometry, such as spheres, or vessels having multiple external layers or different thicknesses are affected by water spray cooling. Other parameters proposed in the project statement like viscosity and external temperature can also be further studied within this simulation model.
2. The scope of the project can be enlarged to involve stirred reactors or complex flowing systems instead of the current focus on a simple batch reaction. A more complicated chemical reaction and transport system may be more representative of certain real scenarios.
3. More heat transfer modules can be added to simulate additional sources of heat, such as solar radiation, to establish a more sophisticated heat transfer system to simulate outdoor storage conditions.
4. An alternative to water spray will need to be studied, found and adapted to vessel cooling. Other fluids with appropriate heat capacity can and should be investigated and studied to be incorporated into the model to develop a much more successful and effective form of cooling.

8. References

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Appendix

Every test run has analyzed the temperature change in a three-dimensional way with finite element analysis method.

Here, as representation, the complete visual effect of temperature distribution provided by COMSOL Multiphysics in all three dimensions have been shown for Vessel#1 (water spray) without contradicting the results or analysis above.

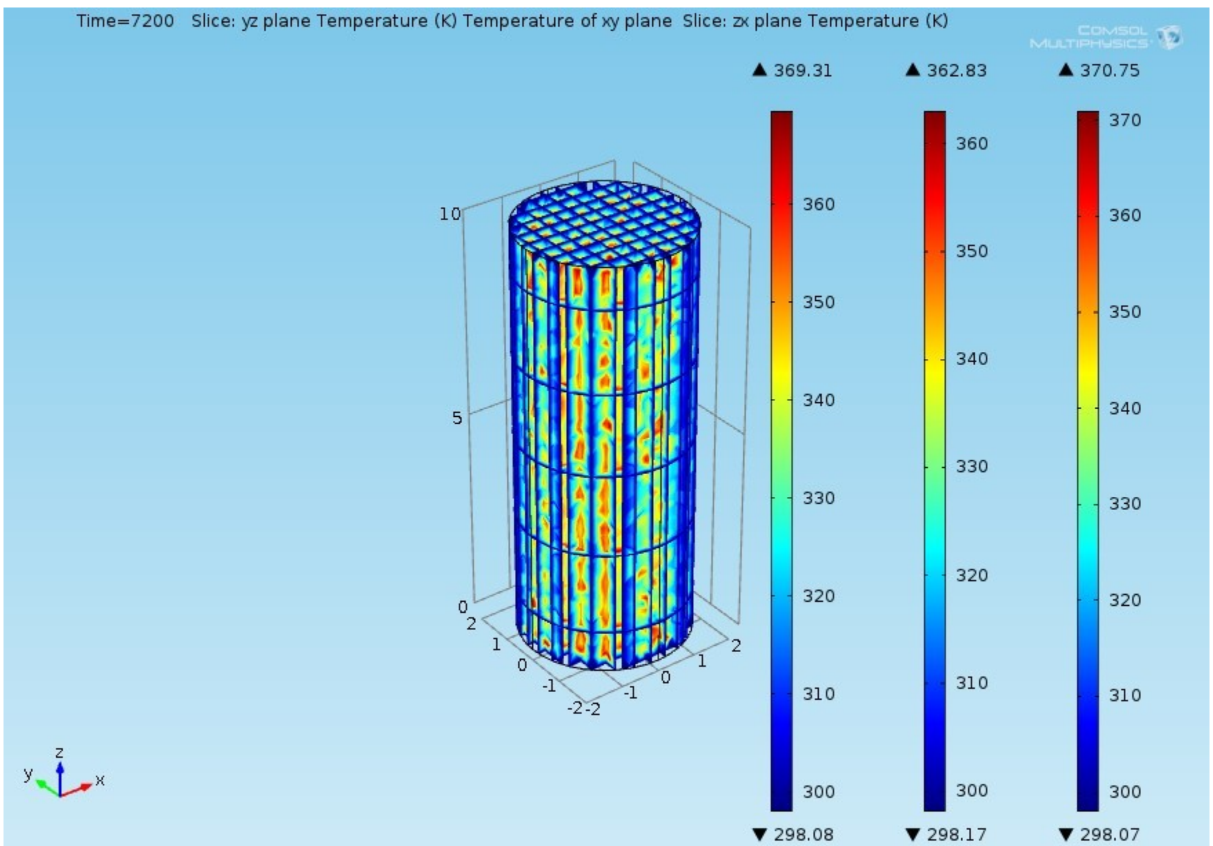

Figure A.1 Vessel#1: T distribution with water spray at 7200 seconds(x-y-z)

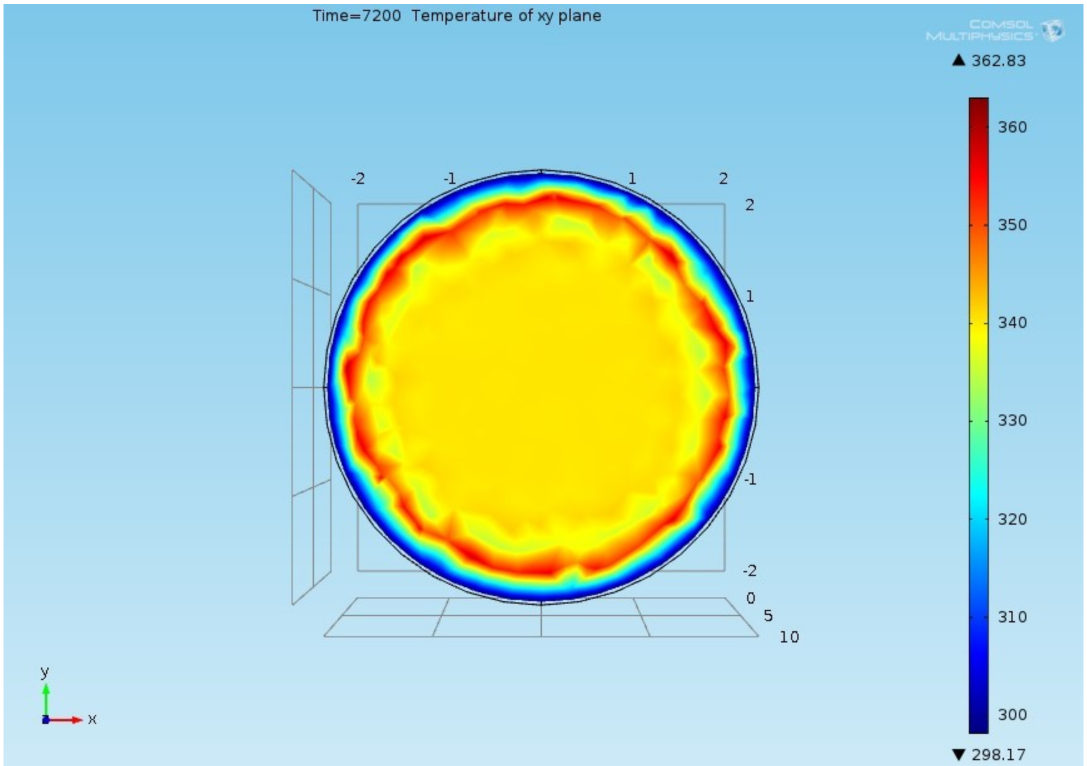

Figure A.2 Vessel#1: T distribution with water spray at 7200 seconds(x-y)

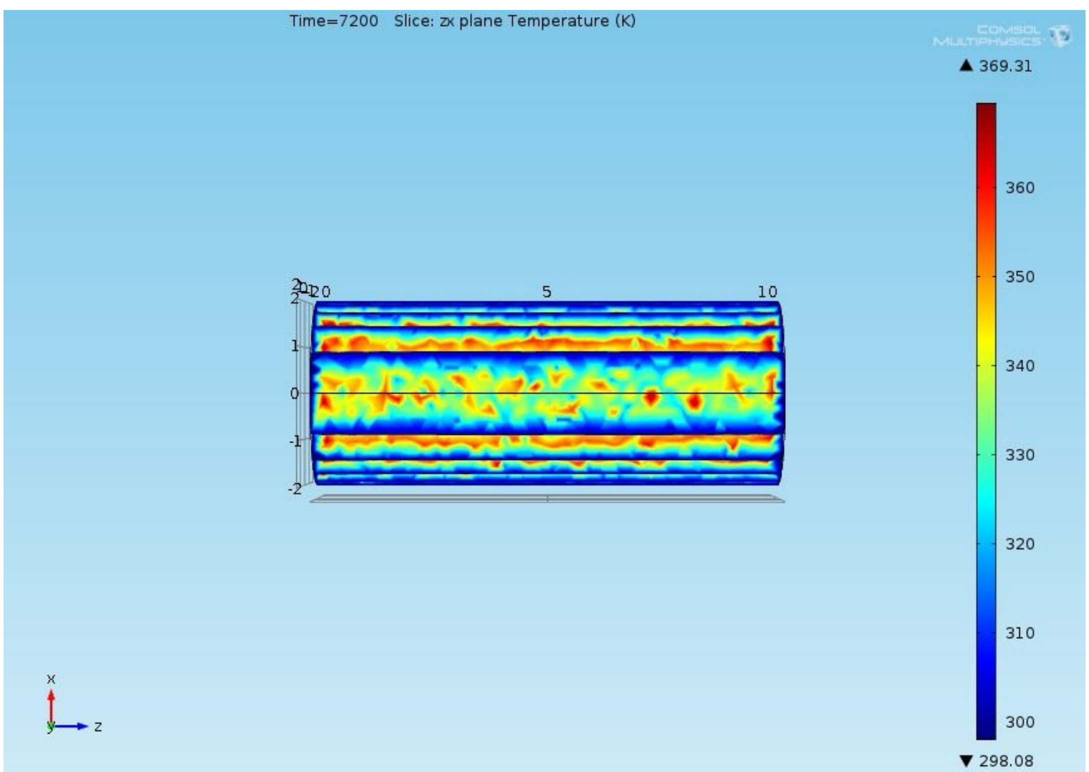

Figure A.3 Vessel#1: T distribution with water spray at 7200 seconds(x-z)

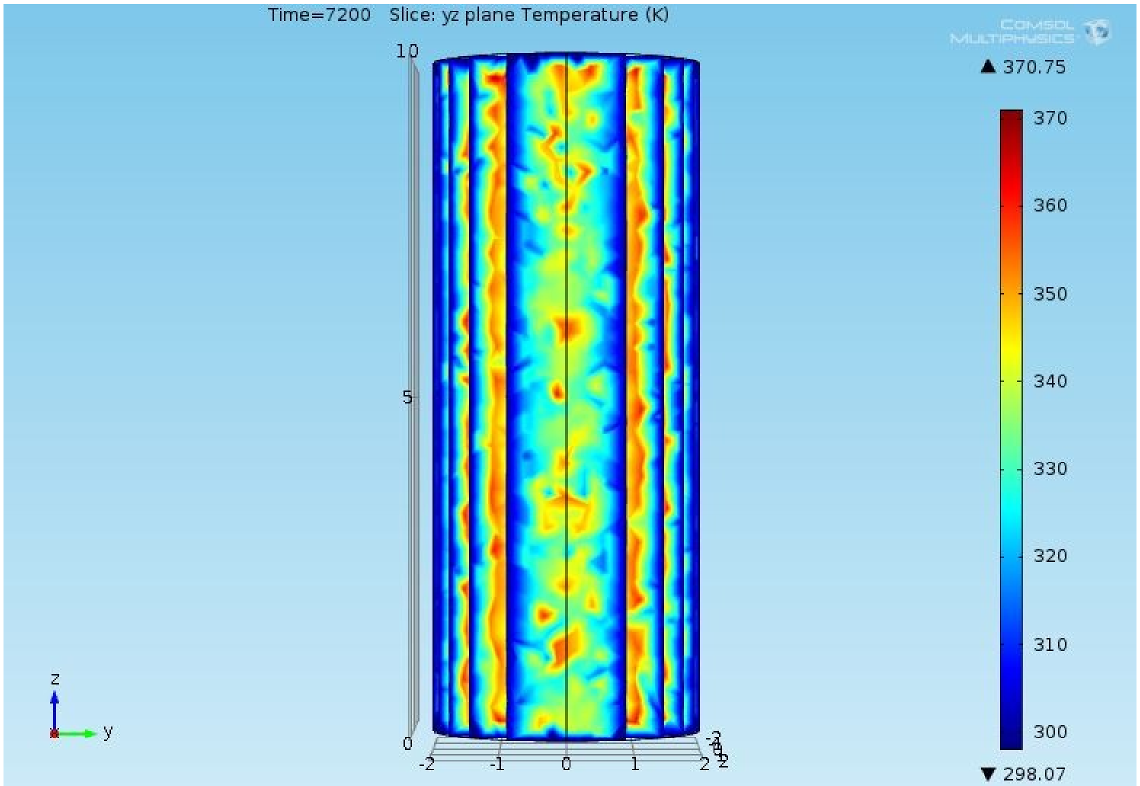

Figure A.4 Vessel#1: T distribution with water spray at 7200 seconds(y-z)