Modeling and Simulation of Chemical Reactors Cooled by Thermosyphons

by

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Abstract

In a theoretical study the use of thermosyphons to improve the safety and efficiency of chemical reactors have been evaluated. Thermosyphons is a simple form of a “heat pipe”, a hollow and closed tube that’s partially filled with a fluid. When the pipe is heated up to the boiling temperature of the fluid within a phase change is initiated. The phase-change is used to improve the thermal conductivity of the pipe. Three simulation models have been used in the study and two of the models is taken from previous studies regarding the thermal safety of chemical reactors. The results have been analyzed and presents an interesting indication of positive possibilities. The outstanding heat transfer of the thermosyphons gives according to the simulation good chance of a firmer control of the reactor temperature and thereby also the reaction process. Besides the improved temperature control the thermosyphons proved capable of preventing thermal runaways during scenarios when the cooling jacket was out of order.

Sammanfattning

I en teoretisk studie har användbarheten av thermosyphoner för att förbättra säkerheten och effektiviseringen av kemiska reaktorer. Thermosyphoner är en simpel form av en ”heat pipe”, ett ihåligt och slutet rör som är delvis fyllt av en fluid. Om röret värms upp till fluidens kokpunkt inleds en inre fasomvandling vilket används för att förbättra rörets värmeledningsförmåga. Tre simuleringsmodeller har använts i studien, varav två kommer från tidigare studier rörande reaktorsäkerhet. Resultaten har analyserats och ger en intressant inblick på potentiella möjligheter. Thermosyphonernas utomordentliga värmeledningsförmåga ger enligt studien väldigt goda möjligheter att kontrollera reaktorstemperaturen och därmed även reaktionsprocessen. Utöver den förbättrade temperaturkontrollen lyckades även thermosyphoner förhindra skenande reaktioner i scenarion där mantelvärmeväxlaren slutat fungera.

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1 Background

1.1 Thermal runaways

"The Chemical industry, more than any other industry, is perceived as a threat to humans, society and the environment." (Stoessel, Chapter 1 – Introduction to Risk Analysis of Fine Chemical Processes, 2008)

The reason for the statement above is not only due to the risks that comes with handling hazardous components such as acids and toxins. Chemical reactions can release large quantities of energy as well as gaseous by-products if not under sufficient control. One of the major threats that involves the chemical industry is chemical reactions on a runaway. In an investigation that was performed by the U.S Chemical Safety and Hazard Investigation Board (CSB) a total amount of 167 serious incidents that occurred in the United States from 1980 to 2001. Of all the 167 incidents thirty-five percent were the result of a runaway reaction and the most common location was the reactor. (Hazard Investigation - Improving Reactive Hazard Management, 2002)

Most reactions that occurs in main branches of the chemical industry such as the fine chemicals and the polymer industries involves exothermic reactions where thermal energy is released as the reaction proceeds. Since almost all chemical reactions have a positive activation energy the reaction rate increases with higher temperature, this can lead to what's best described as a bad cycle and that's called a runaway reaction or a thermal runaway. The reaction releases energy that leads to an increase of temperature, which in turn results in an exponential growth of both temperature and reaction rate (see Figure 1). All chemical reactors are "usually" installed with a heating/cooling system that is either to keep the up temperature if the main reaction is endothermic or keep it down if it's exothermic. For batch reactors, semi-batch reactors and CSTRs the cooling is usually performed using a cooling jacket, a heat exchanger that surrounds the shell of the reactor. For reasons such as faults in the process design, scale ups, fouling, human errors and malfunctions the cooling processes might however be unable to keep the reaction temperature under control. This leads to the bad cycle that was mentioned previously and what is called a thermal runway. (Stoessel, Chapter 2 – Fundamentals of Thermal Process Safety, 2008), (Karlsson, 2012)

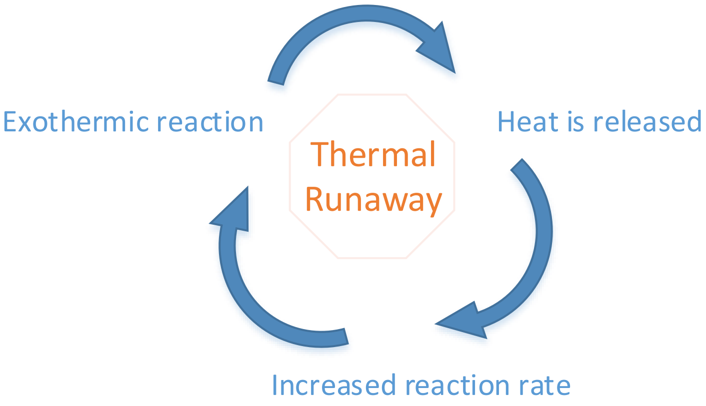

Figure 1. A visual display of the process behind a thermal runaway.

During a thermal runaway, the reaction rate of the exothermic reaction grows too high due to the temperature increases and the cooling system isn't capable of transferring of enough energy which results in a continuous temperature increase. The high temperature can thereby initiate undesired side reactions that can release even more energy and result in vaporization and growing pressure. The consequence of the pressure that builds up can be everything from nothing to severe, it depends on the number of reactants and how much energy that the reaction releases. In the more severe cases an explosion or possibly a leak of dangerous components from within the reactor can occur. In August 1998, an explosion and a fire took place in New Jersey, USA, causing nine people being injured, material damage and the release of hazardous material. The reason for this was a thermal runaway the occurred within a batch reactor, the temperature released initiated a decomposition reaction which in turn caused the explosion. (Guinand, 2016), (MAHBulletin, 2016)

There are two things that's required for a thermal runaway to occur:

- At least one exothermic reaction
- An improved reaction rate of the exothermic reaction due to the increased temperature within the reactor

As can be seen in Table 1 several reactions that plays an important part of the chemical industry involves exothermic reactions. The second part that is required for a thermal runaway is an improved reaction rate during a temperature increase. All reactions that possess a positive activation energy falls under this category and that's almost as good as all chemical reactions. Thereby a thermal runaway is very often a potential risk that needs consideration through risk analyzations and consequence evaluations. (Karlsson, 2012)

Table 1. A couple of classical reactions and their approximate (experimental) reaction enthalpies. (Grewer, 1999)

Reaction	**Reaction Enthalpies ($\Delta H_{reaction}$ [kJ/mol])**
Neutralization	-55
Polymerization (double bond)	-80
Sulfonation	-60
Nitration	-150
Amination	-220
Hydrogenation	-560

One of the many problems when it comes to the process of designing a batch reactor is the scale-up step. During a scale-up the volume of the reactor is increased to improve the production yet the surface area of the reactor doesn't grow at the same pace. Therefore, the area where the heat transfer occurs per unit of volume is lowered when the reactor volume grows. The reactor is now larger and will thereby release more energy due to the exothermic reaction yet at the same time the cooling area hasn't increased as much itself resulting in a higher temperature rise. This can of course be overcome with the aid of a lower temperature of the cooling medium or improvements of the overall heat transfer coefficient yet both can come at a good price. (Moulijn, 2008)

A process with absolute safety (no risks) isn't possible due to possibility that all the protective measurements that has been taken will fail simultaneously and secondly that there is always the potential of a human error. However, the more control that can be gained over the temperature of a chemical reaction the lower will the risk be for a thermal runaway.

1.2 Heat Pipes

A heat pipe is a very efficient tool to achieve thermal control since they have very good heat transfer capabilities. The idea of what's today called a heat pipe originated from Gauger in 1944 yet it wasn't until 1963 that G. M. Grover created the first patent of a heat pipe. During the last decades, quite many studies have been performed regarding this device and today they are used in engineering fields such as electronics, aerospace, food and energy for purposes such as cooling and heat recovery. In later years, the studies regarding their uses for environmental issues as well as safety problems have also been growing. There are patents displaying chemical reactors where the temperature is being controlled through heat pipes yet the tool hasn't been used as much in the reaction industry as in several others so far.

All types of heat pipe consist of a hollow, sealed metal pipe which contains a liquid. The pipe can then be used as an effective way of transferring energy from one end of the other, Figure 2. The reason they are of such interest is that they can transfer impressive amounts of heats with almost no heat loss. The heat transfer rate that they are capable of achieving is thousands of times greater than that which a solid heat conductor of equal size could perform and this is the reason they are sometimes referred to as the superconductors. (Dincer, Chapter 7 - Heat Pipes)

The heat transfer is achieved through a phase-changes within the pipe. One part (most often the lower) of the pipe is heated at a temperature above the boiling limit of the working fluid within the pipe which leads to an evaporation. The vapor that's created causes a forced convection on the inside of the heat pipe which increases the heat transfer coefficient. The vapor then rises to the opposite end of the pipe where the heat pipe is cooled and a condensation is performed as the vapor meets the inner wall of the pipe. The condensate then slides down along the pipes surface to the end where the evaporation takes place creating a passive loop. The great effect of the heat pipe is mainly because of the high heat transfer coefficient that the tube can reach and the high latent heat of the fluids that's being used.

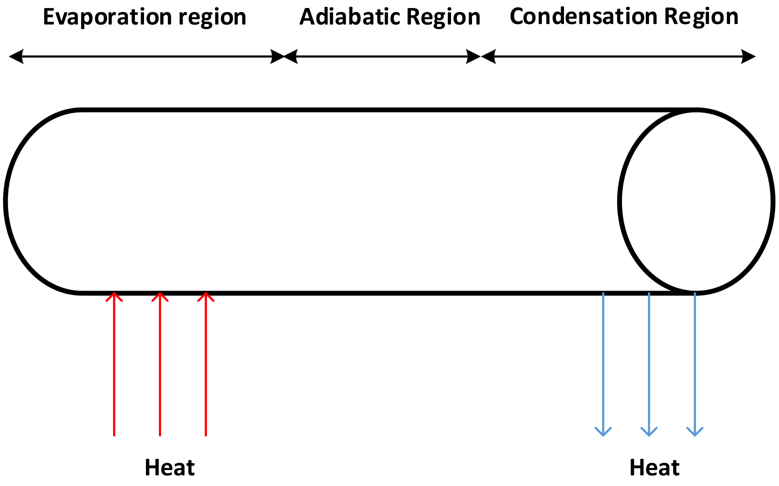

Figure 2. A simple display of a heat pipe and the three separate regions that its length is divided into.

There are many kinds of working fluids that can be used such as water, acetone, ethanol, sodium and potassium depending on which temperature the boiling point is desired. Alkali metals such as sodium and lithium are for example formidable for the purpose due to their massive latent heat yet they can't be used at low temperatures due to their high boiling temperatures. In temperature ranges of between twenty to two-hundred degrees Celsius water is very common since it has high latent heat and a low cost.

The simple construction, impressive heat transfer capabilities and the reliability of the heat pipe makes it a promising tool to be used. They themselves don't require regulations since the main motions within is based almost purely on phase changes. For this study two main kinds of heat pipes will be analyzed and be used for theoretical studies regarding their capabilities to improve the temperature control as well as the efficiency of a chemical reactor.

1.2.1 Thermosyphons

The thermosyphon (or thermosiphon, heat pipes assisted by gravity, Two-phase closed thermosyphon) is the simplest kind of a heat pipe, it's a simple hollow metal pipe that's partly filled with a working fluid and sealed under a suitable pressure to ensure the desired boiling point. They can perform good heat transfer and are very cheap due to their simple construction. They are being used for many purposes for example transferring solar energy and cooling electronics. Thermosyphons is often used and in reboilers as well since they generally provide higher heat fluxes and an improved heat transfer coefficient. As one of the device many names states however it has one weakness compared to other heat pipes, it requires the assistance of gravity. The evaporator end of the thermosyphon must be beneath the condenser end or the device won't function properly. Considering however that chemical reactors tends to be stationary this isn't much of a problem in this case. (Abdollahi, 2015)

1.2.2 Wicked Heat Pipes

A wicked heat pipe has a wick at the inside of the hollow tube, the wick is a structure that allows the vapor to pass through it yet can't be penetrated by the liquid. This causes the wicked heat pipe to have two cross sectional regions, the liquid region that's in contact with the inner surface of the pipe and the vapor region that’s within the wick structure. By adding a wick to a heat pipe the device now functions even if it’s not gravity assisted yet its angle and position still matters when the full capacity of the heat pipe is to be determined as will be discussed later.

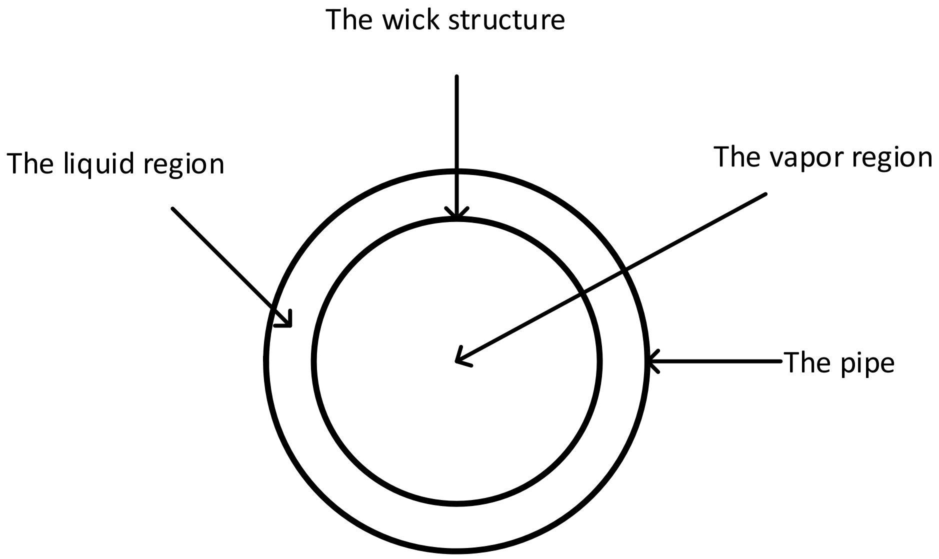

Figure 3. A cross-sectional picture that displays the wick structure within the wicked heat pipe and the regions for liquid and gas.

2 Aim

If heat pipes were installed in a reactor a large amount of heat could be transferred from away from the reaction to keep the reaction rate from reaching dangerous levels. This could either be as a safety precaution or as a standard cooling mechanism. For instance, in a batch reactor that's cooled by a cooling jacket heat pipes could be installed with a boiling point that is above the desired temperature within the reactor. If the temperature would grow above the desired level the boiling point will be reached and the heat pipes could begin to transfer heat away from the reactor.

The heat pipes possess excellent thermal conductivity and therefor a big heat transfer can be reached without high temperatures rises within the reactor. This as well as the flexibility of the number of pipes that can be installed could be of useful aid for controlling the temperature within the chemical reactor.

The aim of this work is to perform an initial theoretical study and perform simulations to analyze the value of the cooling devices known as wicked heat pipes and thermosyphons. The simulations will be regarding the additional cooling can grant beneficial results without escalating into something of unreasonable scale. The emphasis of the discussions regarding the results will then be placed on process safety and reactor efficiency.

3 Method:

The test is performed using several different simulations of reaction processes that occurs within a batch rector and a semi batch reactor. The reason for this choice is to the initial non-steady state in both reactors and that semi-batch reactors is most often used to reduce the risk of a thermal runaways. A comparison of the results is then performed in the following combinations:

- A reactor cooled only by a cooling jacket
- A reactor that's cooled by both a cooling jacket and heat pipes
- A reactor where the efficiency of the cooling jacket is completely removed yet where the heat pipes is still functional

Every process that's simulated will be gone over separately and the mathematical model that's being used will be explained. However, for each simulation, the following assumptions are made:

- Ideal heat pipes that's both adiabatic and isothermal. It's assumed that there is no superheating of the working fluid and total condensation occurs of the vapor in the condensation region.
    - For thermosyphons the temperature difference is dependent on the length of the pipe. Tests have been performed that examined the wall temperature of a wickless heat pipe (at an inclination angle of 90 degrees and diameter of 20 mm) which contained water. These proved that the temperature difference decreased with length up to the longest pipe that was examined (950 mm). (Khalid, 2000)
- Adiabatic reactors and isothermal.
- The volume of the heat pipes is neglected and not added to re-calculate the size of the reactor to uphold the decided volume.

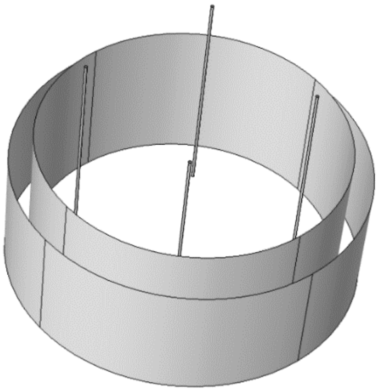

Figure 4. A figure displaying a cooling jacket surrounding a batch reactor along with four installed heat pipes.

3.1 Heat Pipes – Theoretical Design

3.1.1 Geometry of the pipes:

Since heat pipes of various sizes will be used for the simulations certain simplifications will be made. First off is an assumption of the correlation between the inner radius of the pipe and the outer radius of the pipe. The inner radius covers the distance from the inner surface of the pipe to the center while the outer radius includes the thickness of the surrounding metal. The assumption is that the outer radius is always 10% of the inner radius.

$The\ Pipes\ inner\ radius: r_{inner}$

$The\ Pipes\ Outer\ radius: r_{outer} = 1.1r_{inner}$

The length of a heat pipe can be divided up into three sections dependent on the what kind of heat transfer that occurs in the region, see Figure 2.

- The evaporation region
- The adiabatic region
- The condensation region

In the evaporator region the heat transfer into the heat pipe takes place while the heat transferred out of the pipe takes place in the condensation region. Within the adiabatic region no heat transfer occurs whether into or out of the pipe and the fluid simply flows though it without any changes.

To determine the length of the different heat pipe regions the geometry of the reactor is required. For each reactor, an assumption is made that the height and radius of the reactor is the same. Thereby the radius and height of the reactor can be calculated according to:

$$Reactor\ height\ \&\ radius: h_{reactor} = r_{reactor} = \left(\frac{V_{Total}}{\pi}\right)^{1/3}\ [m]$$

The height of the fluid within the reactor can be considered as the evaporator region while the reminding height of the reactor is the adiabatic region. This results in a difference between the calculations for a semi-batch reactor and a batch reactor. In a semi-batch reactor, the filled volume within the reactor increases during the dosing period while in a batch reactor the height is constant.

It’s assumed that the heat pipe reaches all the way down to the bottom of the reactor which allows the length to be calculated as the height of the reactants within the reactor:

$$l_{evaporator} = \frac{V(t)}{(\pi * r_{reactor}{}^2)}\ [m]$$

Where the volume functions calculate the fluid volume within the reactor, which means that for a batch reactor V is constant yet for a semi-batch reactor the volume is:

$$V_{Final} = V\left(t_{dosing}\right)$$

$$V_0 = V(0)$$

The length of the condenser is assumed to be twice the length of the evaporator region, this is due to the lower heat transfer coefficient in the condensation region:

$$l_{condenser} = 2 * l_{evap,max} \ [m]$$

The total length of the heat pipe is therefor to be the same as the sum of the assumed condenser region along with the maximal height of the reactor:

$$Total\ length\ of\ the\ HP: \ l_{HP} = Height_{Reactor} + l_{condenser} \ [m]$$

$$l_{adiabatic} = l_{HP} - l_{evaporator} - l_{condenser} \ [m]$$

Effective length:

To determine the maximal heat transfer capacity of the heat pipe the so-called effective length is required to be determined. It is needed for the equations that involves the vapor and liquid pressure drops along within the pipe. The calculation bases on simple one-dimensional equations and the “effective length” makes up for the different velocities in the evaporator and condenser regions of the heat pipe. The velocity is at its highest in the adiabatic section and then linearly lowered within the evaporator and condenser sections as can be seen in Figure 5.

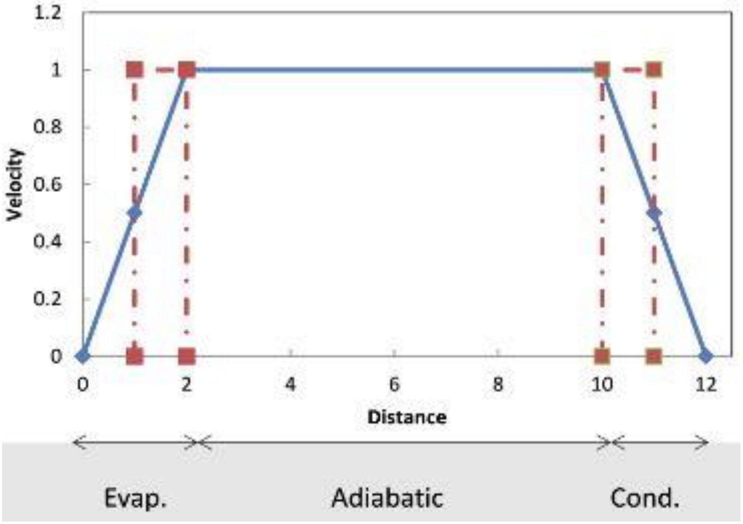

Figure 5. A graph displaying the velocity differences of the vapor inside the heat pipe.

Thereby only half of the length of the evaporator and condenser region is considered for determining the effective length:

$$l_{eff} = l_{adiabatic} + \frac{l_{evaporator} + l_{condensor}}{2} \quad [m]$$

3.1.2 Suitable working fluids:

To reach an optimal heat transfer the working fluid within the heat pipe is of great importance.

A suitable working fluid comes with:

- Good thermal stability
- High latent heat
- High thermal conductivity
- Low liquid and vapor viscosities
- High surface tension
- Compatibility with the wick and the container

Two fluids that is often used for lower or medium temperatures is ammonia and water due to properties such as their high latent heat and reasonably high densities.

To simplify the simulation the properties of working fluid have been assumed to be constant.

Table 2. A table displaying the physical parameters of the working fluids that's used in this work. (Reay, Appendix 1, Working fluid properties, 2013)

Working Fluid Parameter:	**Ammonia (273 K)**	**Water (313 K)**
Vapor pressure (P_{vapor})	4.24 bar	0.07 bar
Vapor density (ρ_{vapor})	3.48 kg/m^3	0.05 kg/m^3
Liquid density (ρ_{liquid})	638.6 kg/m^3	992.3 kg/m^3
Surface tension (σ_{liquid})	2.48*10^{-2} N/m	6.96*10^{-2} N/m
Liquid viscosity (μ_{liquid})	0.25*10^{-3} Pa*s	0.65*10^{-3} Pa*s
Vapor viscosity (μ_{vapor})	0.92*10^{-5} Pa*s	1.04*10^{-5} Pa*s
Latent heat (L)	1263 kJ/kg	2402 kJ/kg

3.2 The Overall Heat Transfer Coefficient

> "For a well-designed heat pipe, effective thermal conductivity can range from 10-10 000 times the effective conductivity of copper depending on the length of the pipe." (Dincer, Chapter 7 - Heat Pipes)

Considering the high thermal conductivity of copper as well as the heat coefficient that the boiling within the pipe will create the dominant process that will determine the speed of the heat transfer is the heat coefficient of the liquids inside the reactor. To determine this the correlation between the dimensionless numbers along with the Chilton-Colburn Analogy will be used. Beside this a rough surface is sometimes used to intensify the turbulence at the pipe's surface (and therefor also the heat coefficient).

Since it's a matter of a flow across tubes (pipes) the characteristic length that's used to determine the Reynold's number is the diameter of the tube.

$$Re = \frac{\rho v d}{\mu} \qquad\qquad Pr = \frac{\mu C_p}{\lambda}$$

Fanning Friction (f):

$$f = \left(-1.737\ln\left(0.269\frac{\varepsilon}{d} - \frac{2.185}{Re}\ln\left(0.269\frac{\varepsilon}{d} + \frac{14.5}{Re}\right)\right)\right)^{-2}$$

Where d is the charismatic length of the pipe (the outer diameter), and the ε is the roughness of the outer surface of the pipe. The Chilton-Colburn Analogy then uses the fanning friction as a factor to determine the heat transfer coefficient of the fluid within the reactor.

$$Chilton - Colburn\ Analogy\!:\ \ j_h = \frac{f}{2} = \frac{h}{\rho C_p v}Pr^{2/3} \rightarrow h = \frac{j_h \rho C_p v}{Pr^{2/3}}$$

Considering that the heat conductivity of copper and the nucleate boiling that takes place within the heat pipe it can be assumed that the heat transfer coefficient can be roughly estimated as:

$$k_{Pipe} \approx h$$

This heat coefficient along with the surface area of the evaporator region and the boiling temperature of the working liquid is then used to determine the heat transfer that the heat pipe is capable of accomplishing. The equation presented is dependent on the assumption that the temperature within the heat pipe remains constant after the working fluid reaches its saturation temperature.

$$Q_{Pipe} = k_{Pipe}Area_{Pipe}(T - T_{Boil})$$

$$Area_{Pipe} = \pi 2 r_{outer} l_{evap}$$

It’s assumed that the stirring within the reactor gives a constant velocity to the fluid of three meters per second. The physical parameters are then assumed to be the same as water and the heat coefficient is calculated according to different temperatures, roughness of the metal and sizes of the pipes.

If the roughness is set as zero then the results indicates clearly that a smaller diameter of the pipe will have a large influence of the heat coefficient.

$$\varepsilon = 0$$

The fanning friction decreases with temperature as well as increased diameter of the pipes which must be the reason for the clear difference the pipe diameter provides.

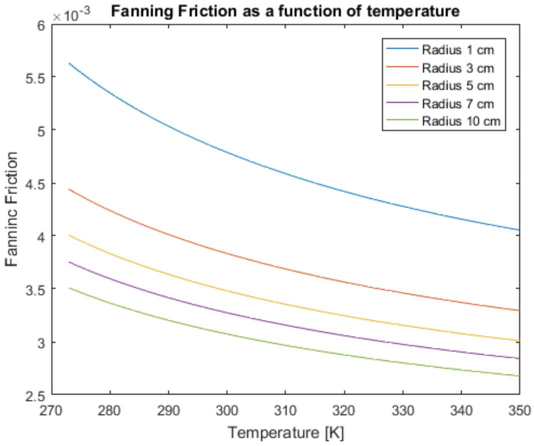

Figure 6. A graph displaying the changes of the fanning friction due to temperature of a pipe with a smooth surface

A roughness that's independent of the pipe's diameter is also tested to observe the results. For the pipes with an inner radius of beneath 5 cm a roughness of 5 mm was used and for the larger pipes it was set as 1 mm.

The results on the heat transfer coefficient can be seen in Figure 7 and 8.

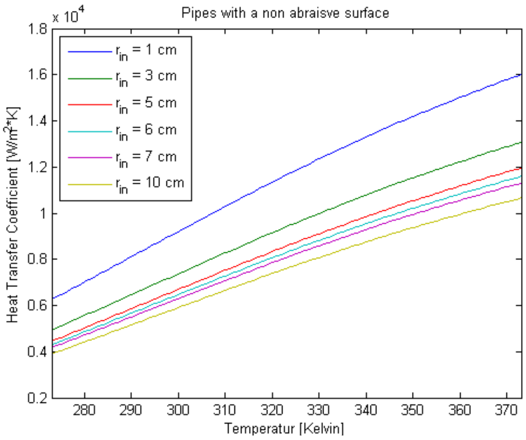

Figure 7. A graph displaying the heat transfer coefficient of pipes (with a smooth surface) of various radiuses at different temperature.

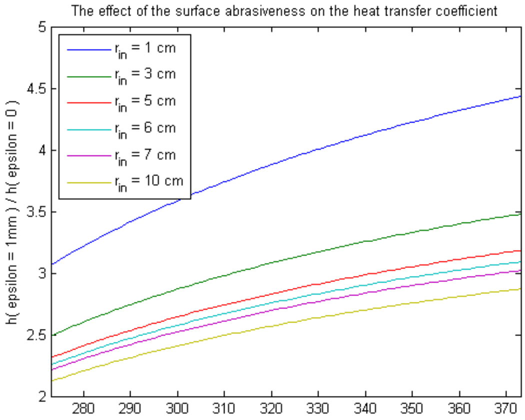

Figure 9. A graph displaying the difference that the roughness of 1 mm brings to the heat coefficient compared with a pipe without a rough surface.

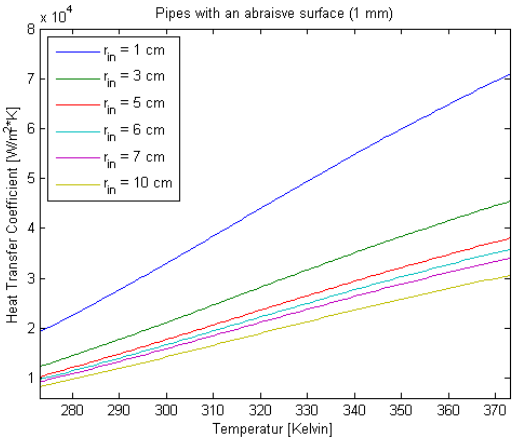

Figure 8. A graph displaying the heat transfer coefficient at different temperatures, roughness and pipe radiuses.

The two graphs show that the rough surface of the pipe increases a large increase to the heat transfer coefficient that determines the heat transfer from the reactor fluid to the pipe. In Figure 8 a comparison of the two coefficients can be viewed. It's clear that the smaller the radius the bigger is the effect and that the heat transfer coefficient of the pipe with an inner radius of 1 cm is at least three times bigger when a rough surface of 1 mm is added to the pipe. Yet it's still also very clear that the roughness has a big influence even at the pipes with of larger size and that their heat coefficients are increased of something between two to three times depending on the fluid temperature.

3.3 The Pipes Operating Limit:

The capability of the heat pipe depends greatly on the operational limitation. The operating limit gives a perspective of the heat transfer capacity that the heat pipe is capable of accomplishing. These limitations depend greatly on the working fluid, the size of the heat pipe as well as the wick structure that is been used for a wicked heat pipe.

If the heat transfer would overcome the operating limit, the heat transfer will either decrease or cease to function for various reasons.

The five major operating limits for a *wicked heat pipe* is the:

- Sonic limit
- Entrainment limit
- Capillary limit
- Vapor pressure limit
- Boiling limit

Three of these are linked to the liquid flow (Entrainment, Capillary and Boiling) while the remaining two (Sonic and Vapor pressure) are connected to the vapor flow.

A *thermosyphon* has only four major operating limits due to the removal of the wick structure:

- Sonic limit
- Vapor pressure limit
- Boiling limit
- Flooding limit

For both types:

3.3.1 The Sonic limit:

The vapor between the evaporator and the condenser must not exceed the local speed of sound, if the vapor velocity is too high the flow will choke. This limits the mass transfer ability and thereby also the heat transfer capabilities of the heat pipe. The working medium and the cross-area of the vapor section is very important when determining the sonic limitation.

It’s assumed that the vapor flow inside the vapor section is one dimensional.

$$q_{sonic} = \rho_{vapor} L \sqrt{\frac{\gamma * R_0 * T_{minimum}}{2(\gamma+1)}}$$ (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

$$Q_{sonic} = q_{sonic} * Area_{vapor}$$

For ammonia and water the heat capacity ratio (gamma, γ) can be taken as:

$$\gamma_{ammonia} = \frac{C_p}{C_V} = 1.4$$

$$\gamma_{water} = 1.3$$

3.3.2 The Vapor Pressure limit (Viscous limit):

The vapor pressure limitation is encountered at low temperatures, when the heat pipe operates at a temperature below its design. At these low temperatures, the viscous forces are dominant in the vapor flow and the vapor pressure is very small. (Heat Transfer Limitations of Heat Pipes, 2017)

$q_{vapor} = \frac{r_{inre} L * rho_{liquid} P_{vapor}}{16 \mu_{vapor} l_{eff}}$ (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

$P_{vapor} = 4.24 * 10^5 \; [Pa]$

$Q_{vapor} = q_{vapor} * Area_{vapor}$

Specific limitations for Wicked Heat Pipes:

3.3.3 The Entrainment limit:

The vapor and liquid moves in opposite directions which creates a shear force at the liquid-vapor interface. In case of very high velocities the liquid particles can be pulled from the structure of the wick and entrain it into the vapor that streams towards the condenser. If too much liquid is entrained into the vapor flow the evaporator will eventually dry out and the heat pipe will no longer be functional.

$q_{entrainment} = \sqrt{\frac{2\pi \rho_{vapor} L^2 \sigma_l}{z}}$ (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

For water (0.01 – 647°C) the following equations and values can be used to calculate the surface tension as a function dependent on the temperature:

$\sigma_l = B(1 - T_r)^u * (1 - b(1 - T_r))$ (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

$T_r = \frac{T_{max}}{T_{critical}}$

$T_{critical} = 647.096 \; [K]$

$B = 235.8 * 10^{-3} \; [N/m]$

$b = 0.625$

$u = 1.256$

To determine the entrainment limit of the wicked heat pipe the characteristic dimension of the liquid-water interface must be known. It's dependent of the mesh that's used to separate the two phases from each other inside the pipe. If it's assumed that a fine mesh is being used the value of z can be taken as:

$z = 0.036 * 10^{-3} \; [m]$ (Reay, Chapter 4 Design Guide, 2014)

$Q_{entrainment} = q_{entrainment} * Area_{vapor}$

3.3.4 The Boiling Limit:

When a high radial heat flux causes the boiling to occur in the wick structure which results in that the mass circulation is seriously reduced and the boiling limit is reached. The boiling limit depends quite a bit on the wick structure that's being used and for a screen wick the limit is usually reached at a heat flux of about 5-10 watts per square centimeter. If the wick is made of powder metal a higher heat flux can be achieved and the boiling limit is only reached at about 20-30 watts per square centimeter. (Dincer, Chapter 7 - Heat Pipes)

Water and non-metallic liquids: 130 kW/m^2 (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

$$Q_{Boiling,wicked} = Area_{Evap,surface} * 5 * 10^4 \; [W]$$

3.3.5 The Capillary limit (Wick & Fluid limit):

Sometimes called the hydrodynamic limitation, it occurs when the pumping rate within the heat pipe is insufficient and too little liquid is brought to the evaporation section. It's the most common limitation for low-temperature heat pipes. It occurs when the capillary pressure doesn't meet up to the pressure drops and depends on the working fluid as well as the wick structure and material. In case the capillary limit is exceeded a dry out will occur in the evaporator. (Heat Transfer Limitations of Heat Pipes, 2017)

To express the maximum heat flow due to the wick and fluid limitations there is three assumptions that is required. (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

- The liquid properties are constant within the length of the pipe
- The wick is uniform along the pipe
- The pressure drop that's caused by the vapor flow is neglected

The maximum capillary pressure drop needs to sum up to the liquid and gravitational pressure drops:

$$\Delta p_c = \Delta p_l + \Delta p_g$$

The different pressure drops can be calculated and if put together the capillary limit of the wicked heat pipe can be determined. (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

$$Capillary\ pressure\ drop: \Delta p_c = \frac{2*\sigma_l*\cos\theta}{r_{capillary}}$$

$$Liquid\ pressure\ drop: \Delta p_l = \frac{\mu_l Q_{wick} l_{eff}}{\rho_l L A_w K}$$

$$Gravitational\ pressure\ drop: \Delta p_g = \rho_l g h$$

$$Q_{capillary} = \left(\frac{\rho_l \sigma_l L}{\mu_l}\right)\left(\frac{K A_{wick}}{l}\right)\left(\frac{2}{r_e} - \frac{\rho_l g l}{\sigma_l}\sin\phi\right)$$

Since the evaporator is below the condenser and working at an inclination of 90 degrees to the horizontal the equation becomes:

$$Q_{capillary} = \left(\frac{\rho_l \sigma_l L}{\mu_l}\right)\left(\frac{K A_{wick}}{l}\right)\left(\frac{2}{r_e} + \frac{\rho_l g l}{\sigma_l}\right)$$

The wick diameter, capillary radius and volume fraction (of the solid phase, ε) are assumed to be: (Reay, Chapter 4 Design Guide, 2014)

$$d_{wick} = 0.025 * 10^{-3}\ [m]$$

$$r_{capillary} = 0.029 * 10^{-3}\ \ [m]$$

$$\varepsilon = 0.314$$

This wick permeability can then be calculated as:

$$K = d_{wick}^2 \frac{(1-\varepsilon)^3}{66.6*\varepsilon^2}$$

Perfect wetting is assumed which means that the contact angle is to be. (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

$$\theta = 0°$$

The capillary limit can then be calculated as:

$m_{max} = \frac{\rho_{liquid}\sigma_l}{\mu_{liquid}} * \frac{K*A_{wick}}{\mu_{liquid} l_{eff}} * \left(\frac{2\sigma_l}{r_{pore}} - \rho_{liquid} g l_{eff}\right)$ (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014)

$$Q_{wicking} = m_{max} * L$$

Specific limitations for Thermosyphons:

3.3.6 The Boiling limit:

Just like in a wicked heat pipe the boiling limit can be reached in a thermosyphon even without the wick. This limitation often occurs in thermosyphons with a high radial heat flux along with a large liquid fill ratio. It's based on that the amount of vapor bubbles that's being created at the inner surface of the pipe can create a vapor surface that prevents the liquid from coming in contact with the surface of the evaporator region. (Dr. Ahmad, 2013)

$$d = 2r_{outer}$$

$$Area_{radial} = \pi d l_{evap}$$

$$Ku_{BL} = 0.16\left(1 - e^{\left(\frac{-d}{l_{evap}}\right)\left(\frac{\rho_{liquid}}{\rho_{vapor}}\right)^{0.13}}\right)$$

$$Q_{Boil} = Area_{radial} L \sqrt{\rho_{vapor}} g \sigma_l \left(\rho_{liquid} - \rho_{vapor}\right)^{0.25} Ku_{BL}$$

3.3.7 The Flooding limit:

The flooding limit (also called the counter current flow) is a very important limitation that's often the dominant one for thermosyphons that operates with a high fillers ratio along with a high axial heat flux and a small radial heat flux. When it's overstepped then the condensate from can't return to the evaporator region due to the vapor shear within the pipe. (Dr. Ahmad, 2013)

$$Area_{Axial} = \pi r_{outer}^2$$

$$Bo = d\sqrt{\frac{g(\rho_{liquid}-\rho_{vapor})}{\sigma_l}}$$

$$Ku_{ccl} = \left(\frac{\rho_{liquid}}{\rho_{vapor}}\right)^{0.14} * \tanh(Bo^{0.25})^2$$

$$Q_{Flood} = Ku_{ccl} L Area_{Axial} g \sigma_l (\rho_{liquid} - \rho_{vapor})^{0.25} (\rho_{vapor}^{-0.25} - \rho_{liquid}^{-0.25})^{-2}$$

3.3.8 The maximal heat transfer capacity of the heat pipe and the selection:

The lowest limitation is the dominating one and determines the maximum heat transfer that the pipe can accomplish. The dominating limitation is the lowest limitation of the ones that effect either the heat pipe or the thermosyphon: (Reay, Chapter 2 Heat transfer and fluid flow theory, 2014), (Dr. Ahmad, 2013)

The wicked heat pipe:

$$Q_{limit} = min(Q_{Sonic}, Q_{Entrainment}, Q_{Capillary}, Q_{Vapor}, Q_{Boiling})$$

The thermosyphon:

$$Q_{limit} = min(Q_{Sonic}, Q_{Boiling}, Q_{Flooding}, Q_{Vapor})$$

In the simulation, this is considered in the following fashion:

$$if\ Q_{Pipe} > Q_{limit} \rightarrow Q_{Pipe} = Q_{limit}$$

This prevents the pipes from providing heat transfer that over exceeds their capability. However, the processes will be designed to make sure that the heat transfer does not reach the operating limit. The easiest way to accomplish this is to increase the number of heat pipes since this will lower the temperature rise as well as the heat transfer coefficient.

In general, the thermosyphons is capable to transferring more energy than the wicked heat pipe due to the capillary limit and therefore thermosyphons have been determined to be used for the simulations. A study that performed a comparison on the overall heat transfer coefficient of a wicked heat pipe and a thermosiphon evaluated however that the wicked heat pipe possessed the better coefficient. A smooth surfaced wicked heat pipe and a thermosiphon of equal dimensions and during the same heat transfer (700 W) obtained an overall heat transfer coefficient of 9950 respectively 4950 W/m^2*K. The difference between the two values is significant considering that the heat transfer coefficient of the wicked heat pipe is more than twice that of the thermosiphon. Since this study doesn't evaluate different heat transfer coefficients for the two kinds of heat pipes this is however neglected though it's noted as something that needs to be examined later. Another thing that's worth to take into consideration is that the wicked heat pipe required a much larger amount of working fluid to gain its optimal heat transfer coefficient than the thermosiphon. This could have an important effect on the time that it takes for the working fluid to reach its saturation temperature which is something that will be discussed further on. (Dr. Ahmad, 2013)

3.4 Simulations Models:

3.4.1 The Steinbach Case

It is now time to make an overview of the different processes that is simulated and examined. The first one is an exothermic reaction that has been used for studies regarding thermal runaways before.

The model consists of a reaction that occurs within the semi-batch reactor. The reaction is irreversible, of second order, homogeneous, carried out in liquid phase and does not involve any phase changes.

The reaction formula is:

$$C_A + C_B \rightarrow C_C$$

Table 3. A table that displays the initial conditions of the reactor model. (Mas, 2006)

Parameter	Initial Condition
$C_{A,0}$	3400 [mol/m^3]
$C_{B,0}$	0 [mol/m^3]
$C_{C,0}$	0 [mol/m^3]
V_0	10.43 m^3
T_0	263 K

A continuous and constant feed streams into the reactor during the dosing period and the reactor reaches a final volume after a long dosing period of 18 000 seconds.

$V_{final} = 17.73\ [m^3]$

$t_{dosing} = 18\ 000\ [s]$

The volumetric flow is calculated using the volume changes during the process cycle and the dosing time.

$v_{Feed} = \frac{V_{final} - V_0}{t_{dosing}}\ [m^3/s]$

Something that is interesting with this is that the final reactor volume (20 m^3) is not reached during the entire cycle. This means that there will always be an adiabatic region of the thermosyphons that’s used to cool the process.

The feed stream consists purely of component B and is dosed into the reactor with a constant concentration during the entire dosing period.

The reaction kinetics:

$$r = kC_A C_B$$

$$k = k_0 e^{\left(\frac{-E}{R*T}\right)}$$

Table 4. The reaction kinetics and volumetric heat capacity of the reactor fluid. (Mas, 2006)

Reaction Parameter	**Value**
Frequency Factor (k_0)	$4.43*10^9$ $m^3/mol*s$
Activation Energy (E)	86 881.3 J/mol
Reaction enthalpy ($\Delta H_{reaction}$)	85 000 J/mol
Volumetric heat capacity (ρc_p)	1700 kJ/m^3*K
The concentration of the feed ($C_{B,feed}$)	4860 mol/m^3

Differential equations for concentrations and volume:

$$\frac{dC_A}{dt} = -r - \frac{C_A v_{Feed}}{V}$$

$$\frac{dC_B}{dt} = -r - \frac{v_{Feed} C_B}{V} + \frac{C_{B,feed} v_{Feed}}{V}$$

$$\frac{dC_C}{dt} = r - \frac{v_{Feed} * C_C}{V}$$

$$0 < t < t_{dosing} \quad \rightarrow \frac{dV}{dt} = v$$

$$t > t_{dosing} \quad \rightarrow \frac{dV}{dt} = 0$$

3.4.1.1 The cooling systems:

3.4.1.1.1 Cooling jacket:

The reactor is assumed to be both adiabatic and isothermal. The cooling capacity is also assumed to have a constant heat transfer factor (that doesn’t change as the surface area increases) and that’s set as: (Mas, 2006)

$$UA_0 = 6000 \ W/K$$

$$T_{feed} = 298 \, °K$$

By summarizing the energy that the exothermic reaction releases along with the heat transfer of the cooling jacket and the energy that's required to warm up the cold feed the differential equation for the reactor temperature can be written as:

$$\frac{dT}{dt} = \frac{r * \Delta H_{reaction}}{c_p \rho} - \frac{v(T - T_{feed})}{V} - \frac{UA_0(T - T_{cooler})}{V c_p \rho}$$

3.4.1.1.2 A Cooling jacket along with thermosyphons

A simplified simulation where the thermosyphons is assumed to reach the boiling temperature at the same moment as the reactor enables the following model to be used for thermosyphons operating in combination with a cooling jacket.

$If: T_{reaction} \geq T_{boiling}$

$$\frac{dT}{dt} = \frac{r * dH_{reaktion}}{c_p \rho} - \frac{v(T - T_{feed})}{V} - \frac{UA_0(T - T_{cooler})}{V c_p \rho} - Number * \frac{Q_{Pipe}}{V \rho C_p}$$

$$Q_{Pipe} = k_{Pipe} Area_{Pipe} (T - T_{Boiling})$$

$$Area_{Pipe} = \pi 2 r_{outer} l_{evap}$$

$$l_{evap} = \frac{V}{\pi Radius_{Reactor}^2}$$

$$Radius_{Reactor} = \left(\frac{V_{Total}}{\pi}\right)^{1/3}$$

$If: T_{reaction} < T_{boiling}$

$$\frac{dT}{dt} = \frac{r * dH_{reaktion}}{c_p \rho} - \frac{v(T - T_{feed})}{V} - \frac{UA_0(T - T_{cooler})}{V c_p \rho}$$

3.4.2 Hydrolysis of Acetic Anhydride:

The second process that's to be simulated and examined is a hydrolysis of acetic anhydride which produces acetic acid. Acetic anhydride is a common component that's used in the production of products such as aspirin, organic synthesis, explosives and of course acetic acid. The reaction is exothermic with a reaction enthalpy more than twice as high as the one that was used in the previous model. Moreover, acetic anhydride is a dangerous component as it's a highly flammable liquid, can release toxic vapor when in gas phase. Besides this mixtures of acetic anhydride and air can become explosive at temperatures above 322 degrees Kelvin. (García, 2016)[1]

The process that will be simulated is a hydrolysis reaction of acetic anhydride in a semi-batch reactor. Just like in the previous model the reaction that occurs within the semi-batch reactor in the simulation is irreversible, homogeneous, liquid phase, doesn't involve any phase changes and of second order. The reactor size and the reaction kinetics is based on a previous study

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[1] García, M. Thermal stability and dynamic analysis of the acetic anhydride hydrolysis reaction, Elsevier, Chemical Engineering Science, Vol. 142, 2016.

regarding dimensioning and simulations of batch reactors. (Bjerle, I , Berggren, J-C och Karlson, H., 1977)

The reaction formula is:

$$(CH_3CO)_2O + H_2O \rightarrow 2CH_3COOH$$

The reactor that's simulated in the process has a full capacity of 235 liters and the dosing time is determined to be 20 minutes. During the dosing, a full amount of 235 mol of acetic anhydride is to be fed into the reactor.

Table 5. The density and molar weight of the two reactants along with the final volume of the semi-batch reactor. (Bjerle, I , Berggren, J-C och Karlson, H., 1977)

Parameter	**Value**
$\rho_{\text{Acetic Anhydride}}$	1082 kg/m^3
ρ_{Water}	1000 kg/m^3
$M_{\text{Acetic Anhydride}}$	102.09 kg/kmol
M_{Water}	18 kg/kmol
V_{Final}	235 dm^3
n_{AcAN}	235 mol

$$C_{AcAn,feed} = \frac{\rho_{Ac\,An}}{M_{Ac\,An}} = 10.599 \approx 10.6\ \frac{kmol}{m^3}$$

$$t_{dosing} = 20\ \ [min]$$

$$v_{Feed} = \frac{n_{AcAn}}{C_{AcAn,feed} * t_{Dosing}} = 1.109 * 10^{-3}\ \frac{m^3}{min}$$

Before the dosing cycle begins the reactor is filled with 213 liters of pure water. This enables the last of the initial condition to be determined as:

$$C_{Water,0} = \frac{\rho_{Wa}}{M_{Wa}} = 55.56\ \frac{kmol}{m^3}$$

Table 6. The initial conditions of the reaction process.

Parameter	**Initial Condition**
$C_{\text{Acetic Anhydride,0}}$	0 mol/m^3
$C_{\text{Water,0}}$	55.56 kmol/m^3

C$_{\text{Acetic Acid,0}}$	0 mol/m^3
V$_0$	213 dm^3
T$_0$	303 K

The volumetric flow:

$$0 < t < t_{dosing} \quad \rightarrow v_{Feed} = \frac{V_{Final} - V_0}{t_{dosing}}$$

$$t > t_{dosing} \quad \rightarrow v_{Feed} = 0$$

$$\frac{dV}{dt} = v_{Feed}$$

The reaction kinetics:

$$r = kC_A$$

$$k = k_0 e^{\left(\frac{-E_A}{R*T}\right)}$$

Table 7. The reaction kinetics that's used to simulate the reaction. (Bjerle, I , Berggren, J-C och Karlson, H., 1977)

Reaction Parameter	**Value**
Frequency Factor (k$_0$)	7.94*10^7 [m^3/mol*min]
(E$_A$/R)	5949 [K]
Reaction enthalpy (ΔH$_{\text{reaction}}$)	2.1*10^5 [J/mol]

In the semi batch reactor, the differential equations for component concentrations can be written as:

$$\frac{dC_{AcAn}}{dt} = \frac{\left(C_{AcAn,feed} - C_{AcAn}\right)}{V} v_{Feed} - r$$

$$\frac{dC_{Wa}}{dt} = -r - \frac{C_{Wa}}{V} v_{Feed}$$

$$\frac{dC_{AcAc}}{dt} = r - \frac{C_{AcAc}}{V} v_{Feed}$$

3.4.2.1 The cooling system:

3.4.2.1.1 Cooling jacket:

The coolant temperature and the overall heat coefficient that determines the heat transfer from the reactor to the heat exchanger is assumed to have constant values that's set as:

$U_{VVX} = \ 900 \ [W/m^2K]$

$T_{feed} = 303\ °K$

$T_{cooler} = 303\ °K$

Unlike the previous simulation, the surface area of the cooling jacket is not assumed to be constant. The surface area that's in contact with the liquid inside the reactor is assumed to grow with the volume. The surface area of the cooling jacket is calculated in accordance to the fluid volume under the assumption that the radius and the height of the final reactor volume remains equal.

$Radius_{Reactor} = \left(\frac{V_{Total}}{\pi}\right)^{1/3}$

$Height_{Reactor} = Radius_{Reactor}$

$Area_{Jacket} = Diameter_{Reactor} Height_{Reactor} \pi$

Similarly, to before the differential equation for the reaction temperature can be written as:

$$\frac{dT}{dt} = \frac{rV\Delta H_{reaction}}{mc_p} - \frac{v(T-T_{feed})}{V} - \frac{U_{VVX} Area_{Jacket}(T-T_{cooler})}{mc_p}$$

3.4.2.1.2 Cooling jacket and Thermosyphons:

The same assumptions as was used previously is made. The thermosyphons doesn't provide any heat transfer up until they reach the boiling temperature which they are assumed to do at the same time as the reactor.

$If: T_{reaction} \geq T_{boiling}$

$$\frac{dT}{dt} = \frac{rV\Delta H_{reaction}}{mc_p} - \frac{v(T-T_{feed})}{V} - \frac{U_{VVX} Area_{Jacket}(T-T_{cooler})}{mc_p} - Number * \frac{Q_{Pipe}}{mc_p}$$

$Q_{Pipe} = k_{Pipe} Area_{Pipe}\left(T - T_{boiling}\right)$

$Area_{Pipe} = \pi 2 r_{outer} l_{evap}$

$l_{evap} = \frac{V}{\pi Radius_{Reactor}^2}$

$If: T_{reaction} < T_{boiling}$

$$\frac{rV\Delta H_{reaction}}{mc_p} - \frac{v(T - T_{feed})}{V} - \frac{U_{VVX} Area_{Jacket}(T - T_{cooler})}{mc_p}$$

3.4.3 Fine Chemicals:

In processes that produces bulk chemicals and fine chemicals there is several common differences. Fine chemicals rely not as heavily on catalysis as bulk chemicals do and the processes usually involves several side reactions that can result in the formation of large amounts of by-products such as inorganic salts. Besides this the purity of the fine chemicals is also of great interest which means that the by-products need to be removed through several separations steps following the reactor. The reaction rate of the side reactions increases often in correlation with the temperature which means that a large portion of the by-products is produced during a hot-spot period if the process occurs in a batch or semi-batch reactor. The by-products can also bring a potential risk to the process in case they are strongly exothermic, which is quite often the case. By using the additional cooling that's supplied by the pipes the reaction rate of undesired side reactions can be halted which would result that the reactor produces a product of higher purity which could potentially decrease the amount of separation steps that's necessary afterwards. Besides this the decreased reaction rate of the side reactions could also limit the energy that's being released within the reactor and increase the loss prevention of the process.

A simulation of a relatively simple theoretical process is to be used as a test to see the result of the additional cooling of the pipes. The process is set up as a desired reaction of first order followed by an undesired side reaction of the product, for instance a decomposition reaction. The component named A, P and S is the reactant, the desired product, and the undesired product. Both the reactions are highly exothermic and the first reaction is relatively slow while the second is faster.

$$Reaction\ 1:\ \ A \rightarrow P$$

$$Reaction\ 2:\ \ P \rightarrow S$$

Table 8. A table displaying the reaction kinetics, the physical parameters and the as the parameters for determining the heat transfer of the cooling jacket.

Parameter	**Value**
$k_{0,1}$	0.5 s^{-1}
E_1	20 000 J/mol
$\Delta H_{r,1}$	-300 000 J/mol
$k_{0,2}$	10^{11} s^{-1}
E_2	100 000 J/mol
$\Delta H_{r,1}$	-250 000 J/mol
ρ	1000 kg/m^3
c_p	4000 J/kg*K

V	6.3 m^3
Area$_{\mathbf{Jacket}}$	16.38 m^2
U$_{\mathbf{Cooling\ Jacket}}$	500 $W/m^2 * K$
T$_{\mathbf{Cool}}$	305 K

The reaction kinetics of the two reactions is taken into the Arrhenius equation to determine the different reaction rates.

$$k_i = k_{0,i}\, e^{\left(\frac{-E_i}{RT}\right)}$$

$$r_1 = k_1 C_A \quad , \quad r_2 = k_2 C_P$$

Since the reaction is performed in a batch reactor the differential equations are only effected by the reactions and not by feeding or volume changes.

$$\frac{dC_A}{dt} = -r1$$

$$\frac{dC_P}{dt} = r1 - r2$$

$$\frac{dC_S}{dt} = r2$$

Considering that there is more than one reaction in this process the selectivity of the reaction can be examined. The selectivity functions as a measurement of how many reactants or products that was wasted by the undesired side reactions.

$$Stoichiometric\ factor = 1 \rightarrow \ Selectivity = \frac{Desired\ Product\ Produced}{Reactants\ Consumed\ in\ the\ Reactor}$$

Another difference with this simulation from the previous ones is that the radius and height of the reactor isn't the same anymore. The reactor will have a much larger height instead of radius which will aid both the cooling of the surface jacket as well as the pipes.

Table 9. The initial conditions of the simulated model.

Parameter	**Initial Condition**
C$_{\mathbf{A,0}}$	1000 mol/m^3
C$_{\mathbf{P,0}}$	0 $kmol/m^3$
C$_{\mathbf{S,0}}$	0 mol/m^3

T_0	295 K

3.4.3.1 The cooling System:

3.4.3.1.1 Cooling Jacket:

The reactor is assumed to be adiabatic and isothermal. This allows the following equation to be used to determine the temperature for a reactor that’s cooled by a cooling jacket:

$$\frac{dT}{dt} = \frac{r_2 V \Delta H_{reaction,1}}{mc_p} - \frac{r_2 V \Delta H_{reaction,2}}{mc_p} - \frac{U_{VVX} Area_{Jacket}(T - T_{cool})}{mc_p}$$

Since the reaction is performed in a batch reactor instead of a semi-batch reactor the energy lost to heat the cold feed is no longer in the equation. There are also now two exothermic reactions that can release energy within the reactor.

3.4.3.1.2 The Cooling Jacket + Thermosyphons

When the additional cooling of the thermosyphons is added to the process the differential equation can be written as:

$$\frac{dT}{dt} = \frac{r_2 V \Delta H_{reaction,1}}{mc_p} - \frac{r_2 V \Delta H_{reaction,2}}{mc_p} - \frac{U_{VVX} Area_{Jacket}(T - T_{cool})}{mc_p} - Number * \frac{Q_{Pipe}}{mc_p}$$

The working fluid within the thermosyphon is water with a vapor pressure at 70 mbar, which gives the water a boiling temperature of 313 degrees Kelvin. This allows the heat transfer that each pipe performs to be calculated as:

$$Q_{Pipe} = k_{Pipe} Area_{Pipe} (T - T_{Boil})$$

$$Area_{Pipe} = \pi 2 r_{outer} l_{evap}$$

$$l_{evap} = \frac{V}{\pi Radius_{Reactor}^2}$$

One difference between this model and the previous two is however that the temperature within the pipe is going to be examined as well. This is mainly to observe the time that’s required to bring the working fluid up to its saturation temperature. The starting temperature of the working fluid is assumed to be the same as the temperature of the feed. Before the working fluid has reached its boiling temperature, the heat transfer will be much lower since there is no forced convection inside the pipe without the evaporation. This means that the convective heat transfer within the pipe is first in the form of a free convection before it’s turned into a forced convection. To simulate this an adjustment to the calculation of the overall heat transfer coefficient is required since before the boiling initiates the heat transfer coefficient within the thermosyphon is going to be dominant.

The overall heat transfer coefficient is calculated using the following equation. (Alveteg, 2013)

$$\frac{1}{k_{total}} = \frac{\left(\frac{d_{inner}}{d_{outer}}\right)}{\alpha_{within}} + \frac{d_{outer}\ln\left(\frac{d_{outer}}{d_{inner}}\right)}{2\lambda_{copper}} + \frac{1}{\alpha_{outside}}$$

The inner diameter is determined using the inner and outer radius of the thermosyphon that's used in the simulation. The heat transfer coefficient from outside the thermosyphon is calculated using the Chilton-Colburn Analogy and the thermal conductivity of the pipe material (copper) is assumed as a constant. The heat transfer coefficient of the working fluid within the pipe is given two constant values. The first constant is used during the boil up period and when the saturation temperature is reached the second constant is taken in as the new heat transfer coefficient. The values of the constants that has been chosen can be seen in Table 10.

Table 10. The constant heat transfer coefficients of the working fluid along with the thermal conductivity of the pipe metal.

Heat transfer coefficient	
$\alpha_{\text{Boil up}}$	300 W/m^2*K
α_{Boiling}	15 000 W/m^2*K
Thermal Conductivity	
λ_{copper}	394 W/m*K

$$T_{within} < T_{Boiling\ point}$$

$$\frac{dT_{within}}{dt} = \frac{k_{tot}Area_{evaporator}(T - T_{within})}{m_{thermosyphon}c_{p,water}}$$

$$T_{within} \geq T_{Boiling\ point}$$

$$\frac{dT_{within}}{dt} = 0$$

The amount of water that's suitable to be within the thermosyphon is assumed in accordance to a study that indicated that lower filler ratios of the evaporator region resulted in an improved heat transfer. Though since not very many different filler ratios were tried out a slightly larger ratio has been selected for this simulation. The reason for this is that the larger amount of water should slow the boiling up process and that if the boiling up period is acceptable at high filler ratios it should be also be reasonable at lower ones. (Dr. Ahmad, 2013)

$$m_{thermosyphon} = 0.45V_{Pipe}\rho_{water}$$

$$V_{Pipe} = l_{evap,final}\pi r_{outer}^2 = h_{reactor}\pi r_{outer}^2$$

3.5 A Worst-Case Scenario

As was mentioned previously in chapter 3 a simulation test would be performed where the cooling jacket is no longer operational yet the heat pipes continues to function. This will be referred to as a worst-case scenario and will be simulated for the models involving semi-batch reactors. The entirety of the scenario is that it's based on a situation where the cooling of the thermal jacket is no longer functional yet no emergency actions (such as stopping the feed flow) is taken. The thermal stability of the process will then be analyzed and it shall be evaluated whether thermosyphons can prevent the thermal runaway.

To compare the probability of a thermal runaway between an ordinary semi-batch reactor and one that's additionally cooled by thermosyphons a fault tree analysis has been made. Considering that no statistics have been gathered and that the scenario that has been set up is purely theoretical the exact frequency cannot be evaluated yet a comparison is still possible.

The ordinary semi-batch reactor is estimated to come with several safety precautions such as emergency cooling as well as both an automatic and a manual possibility of stopping the dosing. A fault tree has then been made to estimate what kinds of events that is required to trigger a thermal runaway, see Figure 10.

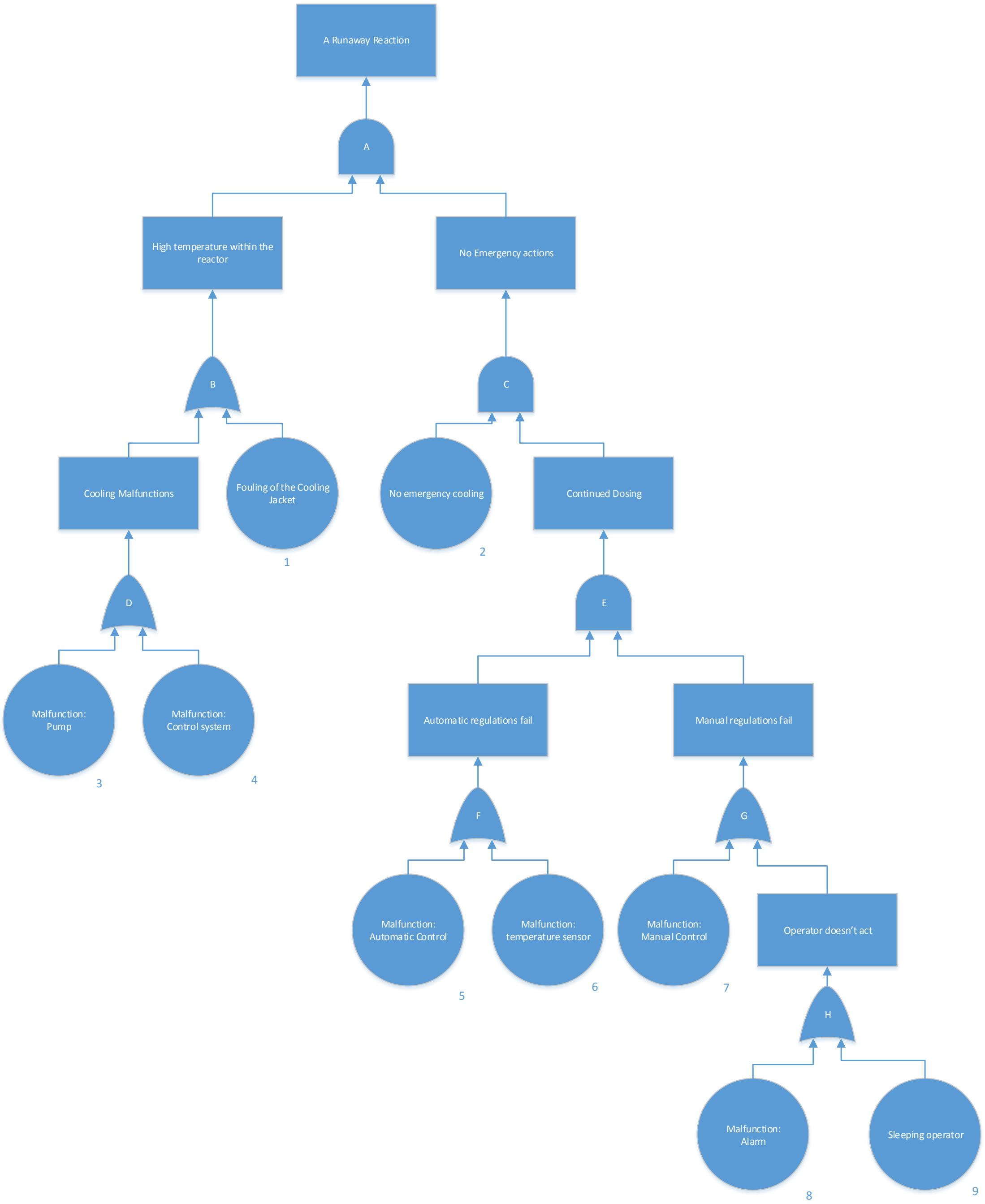

Figure 10. A fault tree that displays the base events that can trigger a thermal runaway for an ordinary semi-batch reactor.

A Minimal Cut Set (MCS):

To evaluate the most frequent and thereby the most dangerous set of events that can trigger a thermal runaway all the cut sets from the fault tree above needs to be determined. A cut set is the determination of the number of basic events that needs to occur to reach the final event, in this case a runaway reaction. One example of a cut set would be in case the following base events would happen:

- The fouling in the cooling jacket causes the temperature to rise to a dangerous level (Base event 1)
- There is no emergency cooling that can be applied (base event 2)
- The automatic and manual regulations fail because of two separate malfunctions (base event 5 and 7)

Together these four base events create a situation where a runaway reaction could be possible and the possibility is named CS1. All the cut sets that can trigger the final event has been calculated and named in Table 10.

Table 11. A display of all the cut scenes that can lead to a thermal runaway.

CS1=1,2,5,7	**CS2=1,2,5,8**	**CS3=1,2,5,9**	**CS4=1,2,6,7**	**CS5=1,2,6,8**	**CS6=1,2,6,9**
CS7=3,2,5,7	**CS8=3,2,5,8**	**CS9=3,2,5,9**	**CS10=3,2,6,7**	**CS11=3,2,6,8**	**CS12=3,2,6,9**
CS13=4,2,5,7	**CS14=4,2,5,8**	**CS15=4,2,5,9**	**CS16=4,2,6,7**	**CS17=4,2,6,8**	**CS18=4,2,6,9**

The cut sets are then ranked in accordance to the number of base events that’s required and the possibility of each base event. In the table above all the cut sets consist of four base events and thereby it’s the possibility of the separate base events that’ll determine the MCS.

Without any direct experiments or statistics, the base events will be ranked in possibility in accordance to the kind of error it is. Human errors are most common and besides this the frequency of errors in active components (such as pumps) is also more common than errors among passive components (such as tanks). (Karlsson, 2012)

Therefor the frequency is ranked as:

Frequency: **Human errors** > **Error in an active component** > **Error in a passive component**

Through this CS3, CS9, CS15 along with CS6, CS12 and CS18 can be evaluated as the minimal cut set and therefor the events that has the highest risk of triggering the runaway reaction. The reason for this is simply that they all involves the possibility of a human error and the only difference between them is their errors in an active component.

If now a new scenario is visualized. It’s a semi-batch reactor just like in the previous scenario yet beside the cooling jacket it’s also cooled by installed thermosyphons. The condensation region of the thermosyphons is cooled by a heat exchanger that is driven by a separate pump and a different regulation system than the cooling jacket. In case the thermosyphons would be able to provide the cooling that’s required to prevent a runaway reaction a new fault tree could be written, see Figure 11. The difference with the previous one is that this fault tree now involves two actions that’s required for the reactor temperature to reach a dangerous level. Both the cooling jacket and the thermosyphons needs to be out of order or there will be enough cooling capacity of the process will be enough to prevent the runaway.

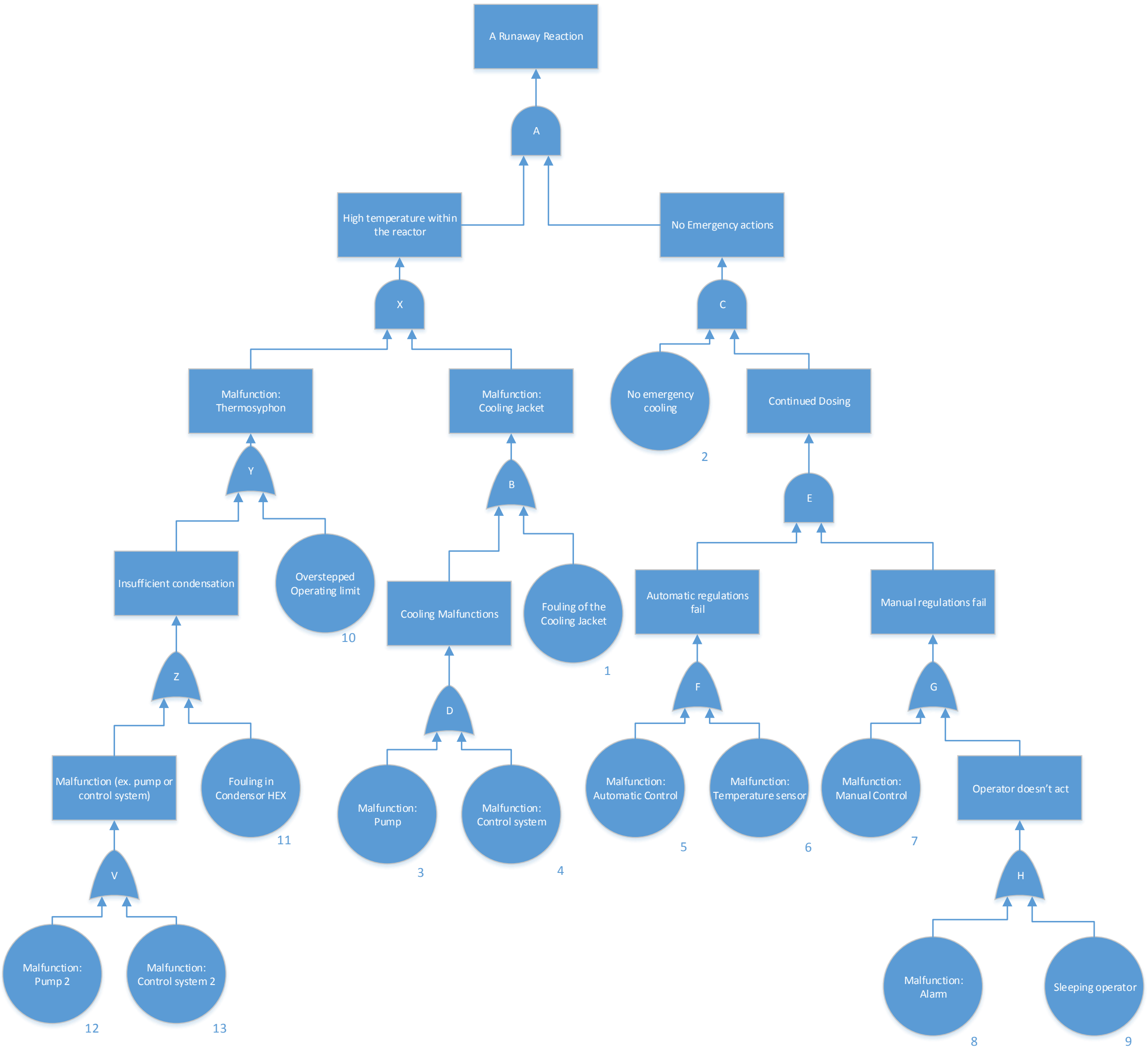

Figure 11. A fault tree presenting the base events that can cause a thermal runaway to occur in a semi-batch reactor that's cooled with both a cooling jacket and thermosyphons.

Table 12. All the separate cut sets that can trigger a runaway reaction in the system that's presented. The minimal cut scenes are marked out as red.

CS1= 1,2,5,7,10	**CS2= 1,2,5,8,10**	**CS3= 1,2,5,9,10**	**CS4= 1,2,6,7,10**	**CS5= 1,2,6,8,10**	**CS6= 1,2,6,9,10**
CS7= 3,2,5,7,10	**CS8= 3,2,5,8,10**	**CS9= 3,2,5,9,10**	**CS10= 3,2,6,7,10**	**CS11= 3,2,6,8,10**	**CS12= 3,2,6,9,10**
CS13= 4,2,5,7,10	**CS14= 4,2,5,8,10**	**CS15= 4,2,5,9,10**	**CS16= 4,2,6,7,10**	**CS17= 4,2,6,8,10**	**CS18= 4,2,6,9,10**
CS19= 1,2,5,7,11	**CS20= 1,2,5,8,11**	**CS21= 1,2,5,9,11**	**CS22= 1,2,6,7,11**	**CS23= 1,2,6,8,11**	**CS24= 1,2,6,9,11**
CS25= 3,2,5,7,11	**CS26= 3,2,5,8,11**	**CS27= 3,2,5,9,11**	**CS28= 3,2,6,7,11**	**CS29= 3,2,6,8,11**	**CS30= 3,2,6,9,11**

CS33= 4,2,5,7,11	**CS34= 4,2,5,8,11**	**CS34= 4,2,5,9,11**	**CS135= 4,2,6,7,11**	**CS36= 4,2,6,8,11**	**CS37= 4,2,6,9,11**
CS38= 1,2,5,7,12	**CS39= 1,2,5,8,12**	**CS40= 1,2,5,9,12**	**CS41= 1,2,6,7,12**	**CS42= 1,2,6,8,12**	**CS43= 1,2,6,9,12**
CS44= 3,2,5,7,12	**CS45= 3,2,5,8,12**	**CS46= 3,2,5,9,12**	**CS47= 3,2,6,7,12**	**CS48= 3,2,6,8,12**	**CS49= 3,2,6,9,12**
CS50= 4,2,5,7,12	**CS51= 4,2,5,8,12**	**CS52= 4,2,5,9,12**	**CS53= 4,2,6,7,12**	**CS54= 4,2,6,8,12**	**CS55= 4,2,6,9,12**
CS56= 1,2,5,7,13	**CS57= 1,2,5,8,13**	**CS58= 1,2,5,9,13**	**CS59= 1,2,6,7,13**	**CS60= 1,2,6,8,13**	**CS61= 1,2,6,9,13**
CS62= 3,2,5,7,13	**CS63= 3,2,5,8,13**	**CS64= 3,2,5,9,13**	**CS65= 3,2,6,7,13**	**CS66= 3,2,6,8,13**	**CS67= 3,2,6,9,13**
CS68= 4,2,5,7,13	**CS69= 4,2,5,8,13**	**CS70= 4,2,5,9,13**	**CS71= 4,2,6,7,13**	**CS72= 4,2,6,8,13**	**CS73= 4,2,6,9,13**

Just like before all the cut sets share the same number which means that they can only be ranked according to the kind of base event. Among the four new base events that's been presented in the fault tree the following three can are errors among active components:

- Malfunction: Pump 2
- Malfunction: Control System 2
- Fouling in the condenser heat exchanger

The last one that refers to the possibility that the heat transfer limit of the thermosyphon have been crossed can be seen from two different perspectives. Firstly, the calculation of determining the limit of the thermosyphon can be a human error. This is in case the designer made any errors when designing the process for this kind of scenario. Besides this the thermosyphon is a passive device and thereby the error could be classified as an error of a passive component. It is though assumed that the process has been designed properly and that the base event can be seen as an error of a passive component. With this information, the minimal cut scenes can be determined and the events where the process provides insufficient condensation becomes part of the MCS. All the minimal cut scenes have been marked out in Table 11.

The minimal cut scenes from the two different scenarios can now be compared with each other. The minimal cut scenes from both the fault trees contains one human error while the remaining ones are an error of an active component. Therefore, the only real difference is the number of base events that the two scenarios require to trigger a thermal runaway. The second scenario when a semi-batch reactor is cooled by both a cooling jacket and a thermosyphon contains one more active error than the first scenario. This proves that as long the thermosyphons is designed to be capable of handling worst-case scenarios use of them can lower the risk of thermal runaways.

4 Results & Discussions:

4.1 The Steinbach Case

The primary reason for this study is to observe the pipes effect on the reactor temperature and determine if a thermal runaway can be avoided as well as if a hot spot can be lowered. The process consists of a semi-batch reactor cooled with a cooling jacket and a different amount of thermosyphons. The dosing time is 18000 seconds and reactant B is fed into the reactor during the entire dosing period. The simulations that was performed using the equations mentioned in the chapter 3.4 presented the following results. Thermosyphons was selected to perform the additional cooling and between one to eight pipes was added to the reactor, each with the same inner radius, 5 cm.

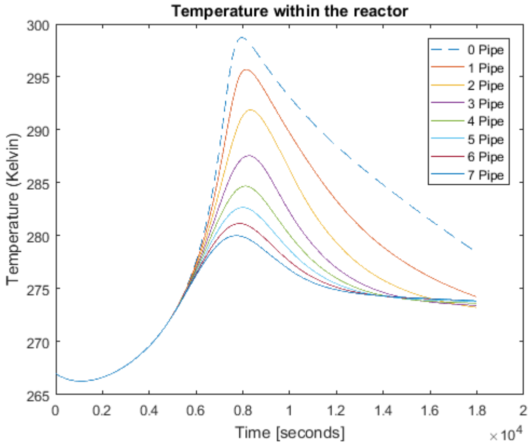

Figure 13. A graph displaying the temperature within the reactor during the cycle time. A different number of thermosyphons was tested yet they all had the same inner radius of 5 cm.

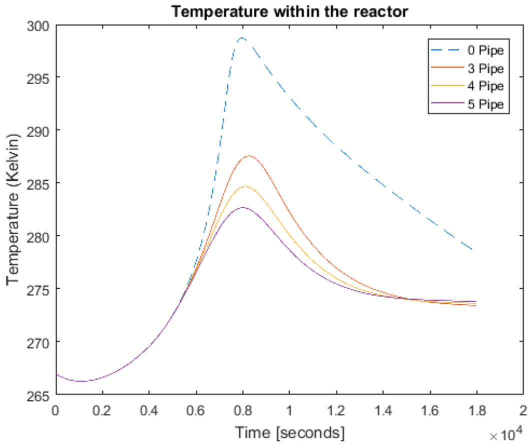

Figure 12. A graph showing the reactor temperature during the cycle when three, four or five thermosyphons is used. [r_{inner}= 5 cm]

Table 13. The highest temperature that's reached during the process cycle.

Number of Thermosyphons	**0**	**3**	**4**	**5**
T_{max}	298.72 ºK	287.57 ºK	284.70 ºK	282.68 ºK

Figure 13 displays that thermosyphons can clearly lower the reactions hot spot and bring a much lower temperature difference during the cycle. The effect of the cooling pipes starts to appear when the reactor temperature reaches about 275 degrees Kelvin. It can also be seen that the effect is lowered when too many pipes is used for cooling. One of the reason for this is that the hot spot doesn't reach a significant temperature difference from the boiling point of the working fluid. This means that there is only a small temperature difference that will create the driving force of the heat transfer. Secondly it was also seen in Figure 7 that the heat coefficient of the pipe increased with higher temperatures. This means that the maximal heat coefficient will decrease if the process reaches a lower hot spot for both of these reasons.

Three to five thermosyphons was determined to be used to study the effect of the pipes on the reaction process. The number was chosen since the pipes lowers the hot spot considerably and that there is a clear difference between each of them, as can be seen in Figure 12.

To begin with the concentration of the reactants within the reactor is examined. The reaction rate is lower due to the temperature decrease. In Figure 14 it can be noted that there is a slope decrease of reactant A at the same time as the hot spot reaches its peak. When the pipes is installed and the hot spot is lowered the reaction rate becomes more constant and the concentration of reactant A is lowered more stably.

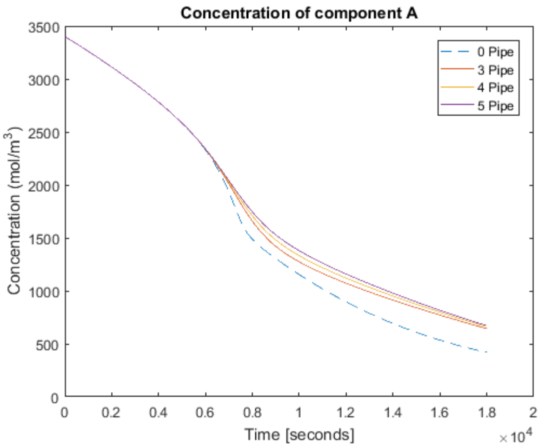

Figure 14. The concentration of reactant A within the reactor during the cycle time

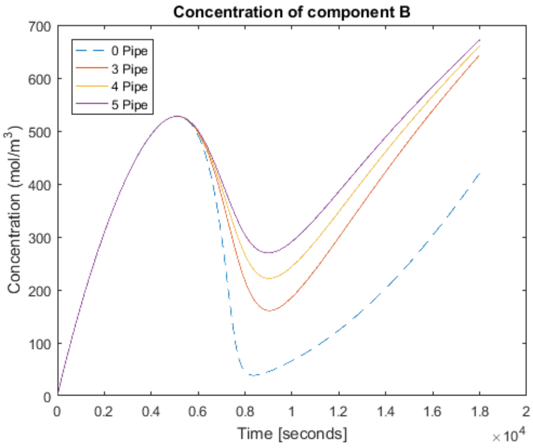

Figure 15. The concentration of the reactant that's being fed into the semi batch reactor, reactant B, under the reaction cycle.

In Figure 14 and 15 the concentrations of the reactants can be seen and the decrease in temperature brings with it a growing accumulation of the reactants, especially component B. Until about one third of the dosing time has ended the concentration of reactant B increases since the reaction rate is lower than the incoming flow. This accumulation of the reactant results in an increased reaction rate. The new reaction rate causes a large energy release and the hot spot begins to grow up until the accumulated concentration of component B has decreased. The difference between the two kinds of cooling system that was examined can first be seen after the accumulation of the reactant has reached its peak. This is because the temperature within the reactor hasn't reached the boiling point of the working fluid and therefor the heat transfer hasn´t initiated yet. When the hot spot begins to grow the effect of the thermosyphons can be seen. Firstly, the accumulated concentration of component B doesn´t decrease to the same level as when only a cooling jacket is used to cool the reactor. It can also be noted that concentration decreases less when more thermosyphons is used. The reason for this is the correlation of the temperature and the reaction rate. The more thermosyphons that's installed the lower the temperature increases and therefor the reaction rate and the feeding rate becomes equivalent at different concentration levels.

The second thing to note is that the final accumulation of reactant B increases when thermosyphons is added to the cooling system. The number of thermosyphons that was installed doesn't seem to affect the final concentration of component B very much yet clear differences is easy to during the rise of the hot spot. The reason for this is most likely that while the temperature is being decreased the reaction rate recovers due to an increased accumulation of reactants. The high accumulation of the dosed component, reactant B, at the end of the reaction cycle comes from that the reaction rate decreases due to a low concentration of the loaded reactant. To prevent the accumulation from growing so large the reaction rate could be increased either with a temperature adjustment (such as turning off the cooling jacket) or with a temporary dosing of the reactant A.

The growing accumulation of unused reactants that has been observed could be noted as a disadvantage and potentially a safety risk. The reasoning for this is simply that either the reaction cycle or reactor size needs to be increased to uphold the previous production per cycle and that the accumulation could. To observe the progress of the process the conversion rate of the loaded reactant is calculated according to the equation below.

$$Conversion\ of\ reactant\ A\ (\%): \quad X = 100\frac{C_{A,0}V_0 - C_A V}{C_{A,0}V_0}$$

The conversion is calculated when various numbers of thermosyphons is installed and the results is displayed in Figure 16. The clearest difference can be seen when the reactor temperature reaches the boiling temperature of the working fluid. The difference between using three to five thermosyphons is very low. However, when examining the difference between the two cooling systems the difference is obvious, which is displayed in Table 14. The lower reaction rate has resulted in a conversion decrease of a least 10 %. This means that the additional cooling requires a longer cycle time to reach the same conversion as the original process. To counter the new cycle time the reactor size could be altered to increase the production during the cycle time.

Table 14. The final conversion rate of the loaded reactant, component A.

Cooling system	Cooling Jacket	Cooling jacket + 3 Thermosyphon	Cooling jacket + 4 Thermosyphon	Cooling jacket + 5 Thermosyphon
Conversion of reactant A	79.03 %	67.85 %	67.00 %	66.47 %

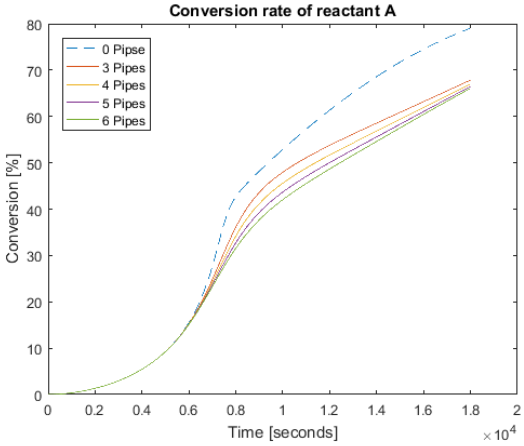

Figure 16. The difference of conversion of reactant A during the process cycle when using a different number of thermosyphons.

To observe the process more closely and to evaluate potential risks the changes of four factors is analyzed:

- The reaction rate
- The released energy
- The heat transfer coefficient
- The heat transfer of a thermosyphon

Three of these factors is calculated out of the results from the differential equation according to the equations beneath and the overall heat transfer coefficient is determined according to the same equations that was presented in chapter 3.2.

$$Reaction\ Rate: r = kC_AC_B$$

$$Released\ Energy: E = r\Delta H_{reaction}V$$

$$Heat\ transfer\ of\ the\ thermosyphon: Q_{Pipe} = k_{pipe}Area_{Evaporator}(T - T_{Boil})$$

As was previously mentioned when the conversion was analyzed the additional cooling that the thermosiphons apply decreases the reaction temperature and thereby also the reaction rate. In Figure 19 the reaction rate can be compared and it's clear that the high peak that the hot spot provides is lowered by at least 40 % when three or more thermosiphons is used.

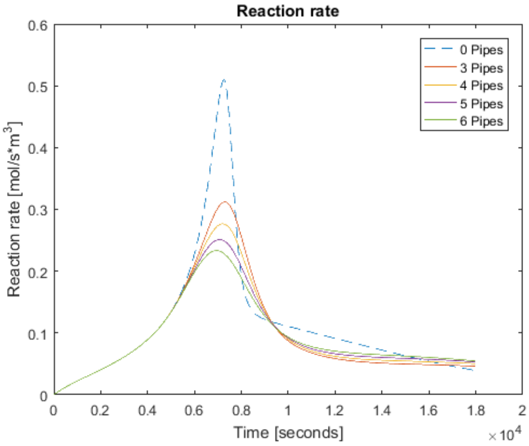

Figure 18. A graph displaying the reaction rate during the process cycle.

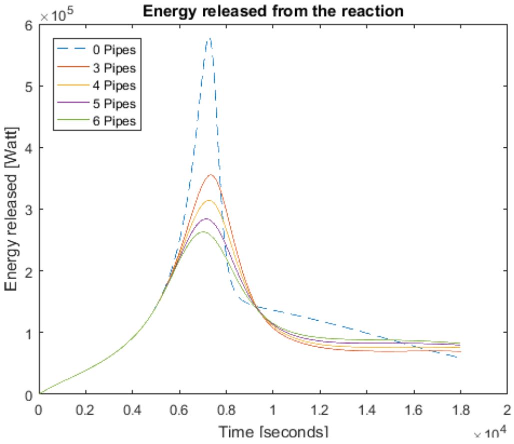

Figure 17. The energy that's being released due to the exothermic reaction.

Since the reaction rate is one of the factors that determines the heat generation that the exothermic process provides a clear correlation can be seen in Figure 20 where the released amount of energy that's released every second is compared under the same circumstances. Since the only difference between the two parameters is the adding of a constant reaction enthalpy the curves shape is identical. When it comes to the differences between the two cooling systems the biggest change can be seen during the hot spot period. The reaction rate of the process that's only cooled by a cooling jacket grows dramatically due to the temperature peak before it begins to decline thanks to the low concentration of the dosed reactant. When the second cooling system is examined the reaction rate reaches its maximal level during the hot spot period yet the growth is much lower in response to the decreased temperature rise. When five thermosyphons is installed in the reactor the highest reaction rate and energy release is roughly half when compared to the original cooling system. Another interesting difference that the second cooling system provides is that the reaction rate is almost constant during the final part of the reaction. The thermosyphons can thereby help with decreasing the changes of the reaction rate during the process. That the hot spot can be controlled and adjusted like this can prove to be very useful considering it’s then that the risk of a thermal runaway is at its highest level and that most undesired products is usually produced. Since the process that’s being observed in this simulation doesn’t involve any unwanted reactions the second statement can’t be examined more closely yet it will be discussed later.

Since a thermosyphons has heat transfer limitations and that the overall heat transfer coefficient is crucial to determine the number of pipes that’s required to use these parameters needs to be examined. As displayed previously (Figure 7) the heat transfer coefficient increases with temperature and thereby it’s clear to see that the peak value is reached as the cycle is at its hot spot (see Figure 21). Since the temperature rise of the hot spot decreases when more thermosiphons are used for cooling the heat transfer coefficient decreases as well yet the changes is not of bigger scale.

The theoretic heat transfer that the thermosiphon is supposed to perform during different moments of the process cycle is easy to compare with the dominating limit of the pipe. The dominating limit of the thermosiphon that’s been used for the simulation is the boiling limit. When the limitation is compared to the energy that’s being transferred through the pipe when three pipes (and less of course) is being used the heat transfer oversteps the boiling limit. To overcome this at least four pipes needs to be used. Depending on potential risks for increased reaction temperature such as jacket fouling or malfunctions of the regulation system it can be recommendable to use even more thermosyphons to minimize the risk that the boiling limit is reached.

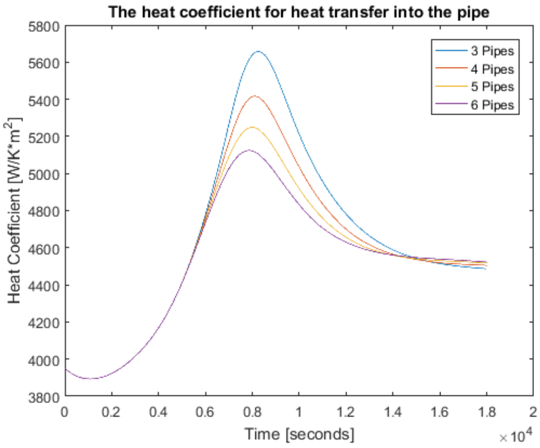

Figure 20. The heat transfer that each thermosyphon performs during the cycle time.

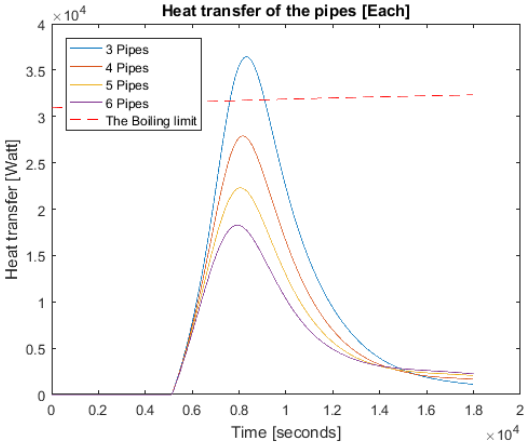

Figure 19. The changes of the heat coefficient during the process.

4.1.1 A pipe with a rough outer surface:

As was discussed in chapter 3.2 an efficient way to improve the heat transfer coefficient is to use pipes with a rough surface. Figure 8 displayed that a roughness of 1 mm could at least double the heat transfer coefficient of a pipe that was of the same size as those that was used for the simulations above. Since this can increase the amount of energy that the thermosiphons can transfer away from the reactor such an increase would be most desirable yet it comes at the cost that the boiling limit will be reached at even smaller temperature differences. Since the boiling limit is directly connected to the radial area of the pipe, thermosyphons of a slightly larger scale was determined to be put to the test. The effect of various number of thermosiphons with an inner radius of six centimeters and a rough surface of 1 mm was tested for the process simulation.

$$\varepsilon = 1\,mm \qquad r_{inner} = 6\,cm$$

As was expected, due to the increased heat transfer coefficient the pipes cooling effect was improved. In Figure 17 it can be seen that the hot spot of the process was greatly diminished when two or more thermosiphons was used and that when four thermosiphons are used the hot spot didn't go even five degrees above the boiling temperature of the working fluid within the pipe.

Table 15. The highest temperature that's reached during the process cycle.

Number of Thermosyphons	**0**	**2**	**3**	**4**
T_{max}	298.72 ºK	282.89 ºK	279.11 ºK	277.56 ºK

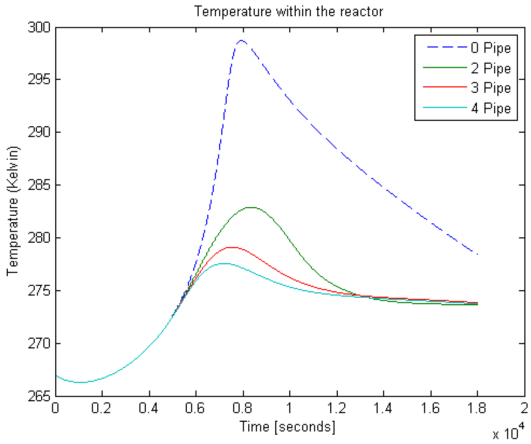

Figure 21. The reactor temperature during the process cycle when various numbers of thermosyphons is installed to provide additional cooling

Figure 24 and 23 displays the concentration and the conversion of the loaded reactant, component A. Just like before the additional cooling of the thermosyphons have a negative effect of the conversion. The low temperature decreases the reaction rate and the production is lowered. The conversion is also displayed in table 15 where the exact amount of decrease can be seen. Considering an even more impressive temperature control with the rough-surfaced thermosyphons the disadvantages can be assumed to point in the same direction. When observing the conversion rate the difference is still very clear between the two cooling systems. Something that's worth to note is however that the different number of pipes still doesn't affect the end results very much. The conversion rate is lowered by almost 15 % when four surface treated thermosyphons is installed and the production is thereby lowered as well. It can also be observed that the conversion is lower when using four treated thermosyphons than when five ones with a smooth surface was used.

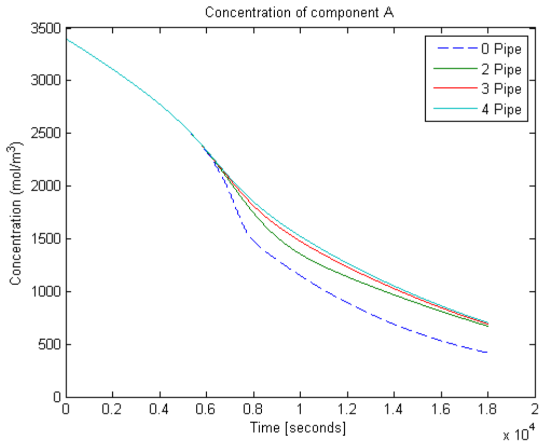

Figure 23.The concentration of the loaded reactant, component A, during the dosing time.

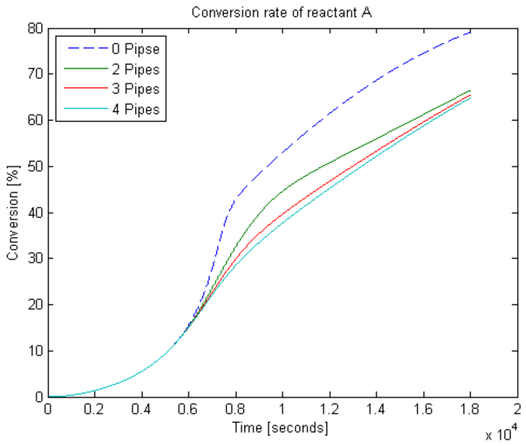

Figure 22. The conversion rate of the loaded reactant, component A, during the simulation.

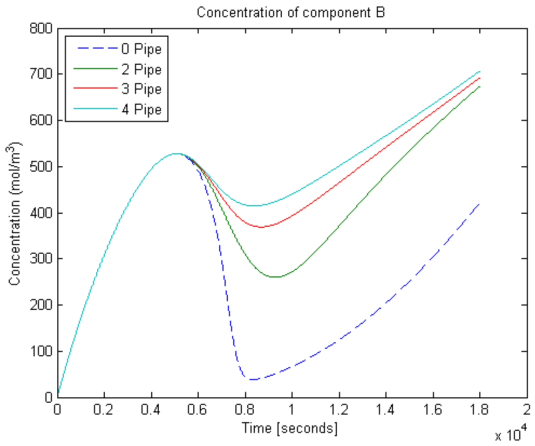

Figure 24. The concentration of the dosed reactant, component B, during the reaction.

Table 16. The final conversion rate that's reached during various simulations of the model.

Cooling system	Cooling Jacket	Cooling jacket + 2 Thermosyphon	Cooling jacket + 3 Thermosyphon	Cooling jacket + 4 Thermosyphon
Conversion of reactant A	79.03 %	66.41 %	65.44 %	64.76 %

In Figure 20 the concentration of component B within the reactor is displayed. Just as in the previous simulation it's clear that the accumulation of the component grows when the additional cooling is used yet that the difference between the numbers of pipes isn't overwhelming. The reasons behind the results should still be the same as before since the only thing that has been altered between the two simulations is the heat coefficient.

Just like previously the process is analyzed more closely by examining the following parameters:

- The reaction rate

- The released energy
- The heat transfer coefficient
- The heat transfer of a thermosyphon

There is a considerable change in the heat transfer coefficient when a roughed surface pipe is used instead of a smooth. The heat transfer coefficient that determines the heat transfer into the pipe is displayed in Figure 25.

In Figure 26 the heat transfer of a thermosyphon is compared with the dominating limit, the boiling limit. When two pipes are being used the heat transfer oversteps the limitation due to the growing heat transfer coefficient and the temperature difference. If four thermosyphons is being used the heat transfer reaches its peak at a level of about 50 % of the limit. It's also worth to mention that the high heat transfer coefficient enables this to occur even though the reaction temperature is less than 5 K above the boiling temperature of the working fluid.

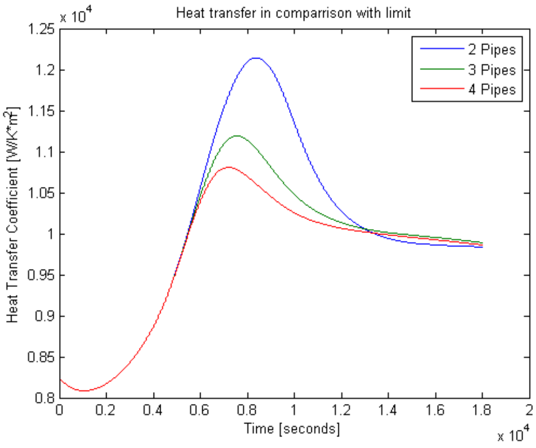

Figure 25 The overall heat transfer coefficient that determines the amount of heat that's transfered from the reactor to the heat pipes.

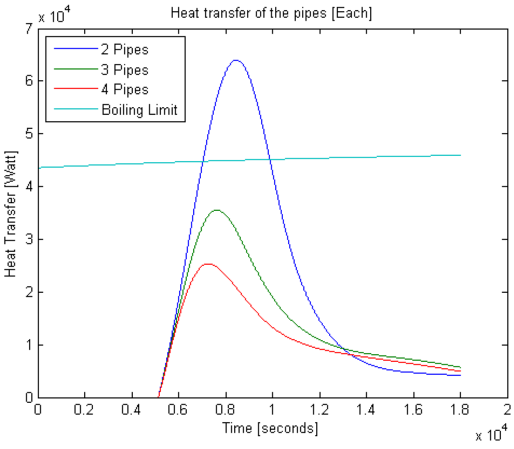

Figure 26. The heat that's transfered from the reactor by each thermosyphon in comparison with their dominating limit, the boiling limit.

When it comes to the reaction rate and the energy released into the reactor the curves is very similar to before with only a difference in the number of pipes that's required.

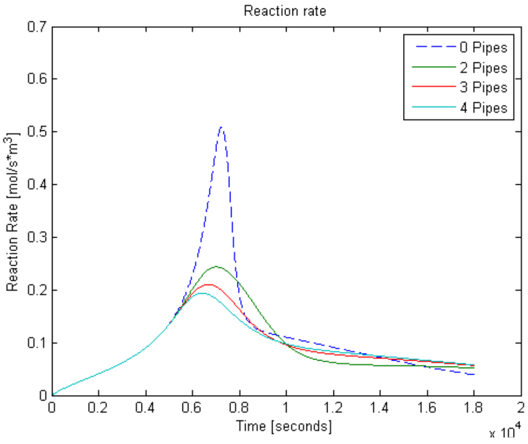

Figure 27. A display of the different reaction rates between the two cooling systems.

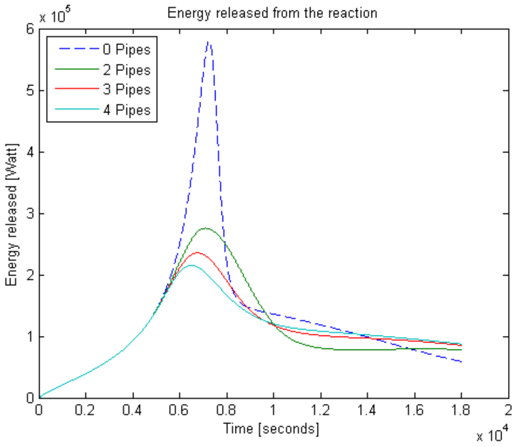

Figure 28. The energy amount that's released during the process.

4.1.2 In case of fouling or a malfunction:

The simulations have given a taste that a thermosiphon can be of good use for lowering the hot spot that's generated by an exothermic reaction in a semi-batch reactor yet what would happen in case of an accident? As was mentioned before a thermal runway is often caused due to either fouling or a malfunction. What effect would the additional cooling have if the worst accident would happen and that a malfunction in the regulation system or an accident would cause the flow within the cooling jacket to be stopped completely and yet the dosing wasn't ceased?

The simulation is performed under the same circumstances as before except that the cooling of the cooling jacket is completely removed. Thermosyphons with a rough surface was chose to be tried due to their promising results in the previous simulation. This means that the pipes have an inner radius of six centimeters and a roughness of 1 mm.

$$\varepsilon = 1\,mm \qquad r_{inner} = 6\,cm$$

As can be seen in Figure 29, the reaction temperature increased with more than 100 degrees if no cooling process was installed which could have become a major accident if for example a decomposition reaction would have been initiated. Without the cooling jacket, at least three thermosyphons is required to keep the temperature under control. In Figure 30 a very clear difference between using either three or four thermosyphons can be seen. If less than three thermosyphons is installed a thermal runaway is initiated and the temperature continues to rise during the entire dosing time. When using three the temperature reaches up to 300 K and remains relatively constant for the remainder of the cycle. If four thermosyphons is applied the temperature within the reactor doesn't even go above the previous hot spot of the original process that was only cooled by a cooling jacket. Thereby, even if the cooling jacket is completely useless three or more thermosyphons can provide the required cooling to control the reaction.

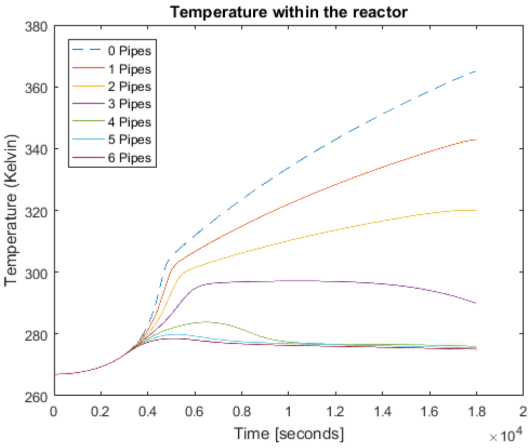

Figure 29. The temperature within the reactor in case the cooling jacket isn't functionable during the cycle.

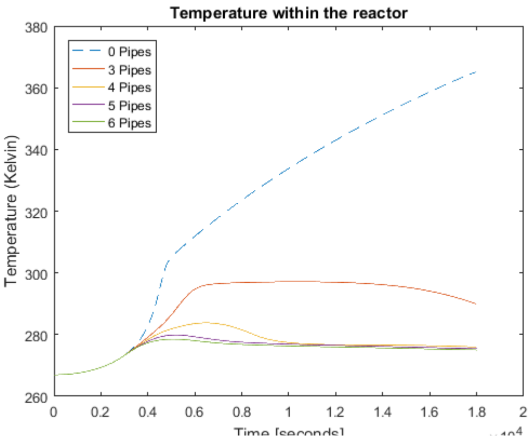

Figure 30. The effect that three, four, five and six thermosyphon has on the reaction temperature during a worst case scenario.

Table 17. The highest temperature that's reached in the reactor if the cooling jacket is out of order.

Number of Thermosyphons	0	3	4	5	6
T_{max}	365.06 ºK	297.14 ºK	283.82 ºK	279.89 ºK	278.53 ºK

From the previous simulation, it was noted that a very small temperature difference was enough to bring the heat transfer of the thermosyphon up to the boiling limitation. In Figure 31 a graph comparing the heat transfer and the limitation is displayed and even though three or four thermosyphons is only required to cool the reaction it takes at least six to bring it underneath the boiling limitation. This is important to note and it gives a good indication that for safety measures it's best to install at least six thermosyphons into the reactor to keep their functionality safe. It can also be observed that even when using six thermosyphons the boiling limitation remains fairly close to the maximal heat transfer and thereby it might be wise to install even more.

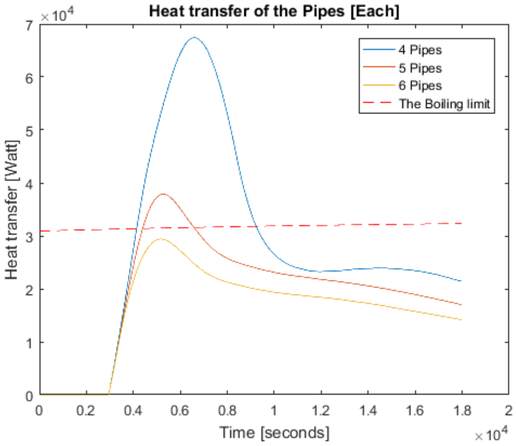

Figure 31. The heat transfer that each thermosyphon provides in comparison with their dominating limit.

4.2 Hydrolysis of Acetic Anhydride

The process was simulated following the model of the hydrolysis process that was presented in chapter 3. It's an adiabatic semi-batch reactor that's loaded with a high volume of water and dosed with a continuous flow of acetic anhydride during a dosing time of twenty minutes. The results that's presented is the outcomes when a cooling jacket performs all the cooling as well as a reactor with both a cooling jacket and thermosyphons. Due to the improved heat transfer coefficient, thermosyphons with rough surfaces was determined to be used for the first simulation test of the process. Pipes with an inner radius of five centimeters and a roughness of 1 mm was simulated as an additional cooling of the process. The saturation temperature of the working fluid within the thermosyphons is 313ºK which results that no bigger differences in the results can be seen until the reaction temperature has reached this point.

In Figure 32 the reaction temperature during the cycle time is displayed. When a cooling jacket is installed there is a clear temperature increase during the entire dosing time. The reason for the quick temperature decrease that follows the end of the dosing period can be seen in Figure 34 where the concentration of acetic anhydride is displayed. The concentration doesn't build up to any large amounts of the reactant due to the relatively fast reaction rate and the reaction ends after 25 minutes due to reactant shortage. One thing that's worth pointing out is that when two or more thermosyphons is added then the hot spot is drawn out. Table 18 displays that the thermosyphons provides a very decent control of the reaction temperature since the hot spot doesn't even go above 3 degrees over the boiling point of the working medium.

Table 18. A display of the maximal reaction temperatures that's reached when different numbers of thermosyphons is used to cool the process.

Number of Thermosyphons	0	1	2	3	4
T_{max}	331.4 ºK	319.9 ºK	317.3 ºK	316.1 ºK	315.5 ºK

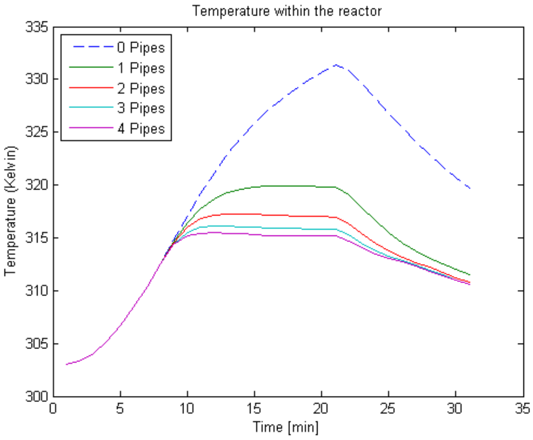

Figure 32. The reaction temperature within the semi-batch reactor when various numbers of thermosyphons is used.

When the reaction temperature is compared with the reaction rate it can be seen that the reaction rate is relatively similar when using one to four thermosyphons. That the reaction rate isn't more effected by the temperature differences is however reasonable when the concentration of acetic anhydride is considered. The accumulated amount of the reactant increases with the number of thermosyphons and the concentration increase makes up for the temperature loss, keeping the reaction rate at a reasonably fast and constant speed.

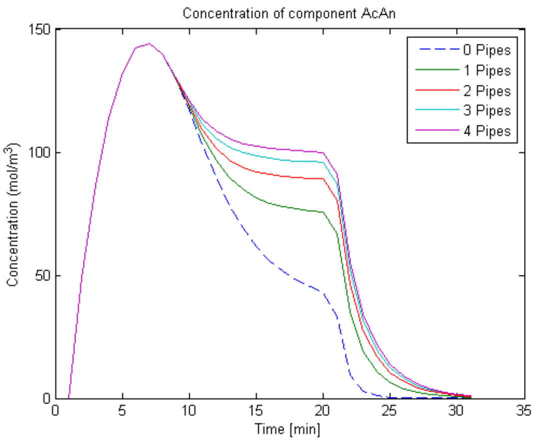

Figure 34. The concentration of the fed reactant, acetic anhydride.

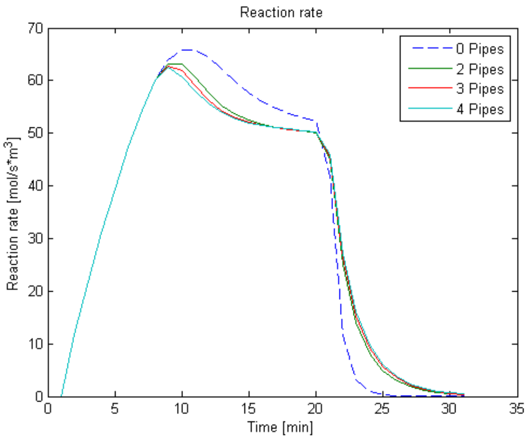

Figure 33. The rate of the hydrolysis reaction when different numbers of thermosyphons was used.

The energy that's released during the reaction is more similar to the reaction rate than it was in the previous simulations. This is due to that there is less volume changes in this reactor than it was in the previous semi-batch reactor. The heat coefficient has already been noted as being strongly effected of the reaction temperature and as can be seen the heat transfer of the thermosyphons decreases when larger numbers of pipes is used due to the temperature decrease. The differences isn't however of any larger scale. Due to the small temperature rises the heat transfer that each pipe is able to perform is also beneath the dominating limit, the boiling limit, when two or more thermosyphons is put to use.

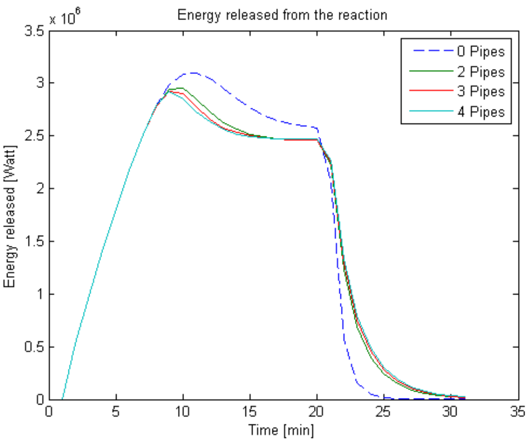

Figure 36. The energy that's released from the hydrolysis reaction during the process cycle.

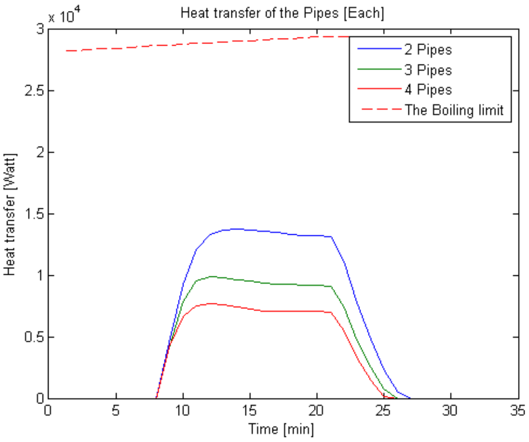

Figure 35. The heat transfer that a thermosyphon performs during the process in comparison with its operating limit.

4.2.1 In case of fouling or a malfunction:

Just like in the previous malfunction simulation (Chapter 4.1.2), the worst case of a scenario would be if the cooling of the cooling jacket would stop while the dosing couldn't be ceased. What would the result be in case a malfunction in the equipment or the automation would stop the cooling stream yet retain the cooling of the thermosyphons?

In Figure 37 the reaction temperature is displayed in a semi-batch reactor where the cooling jacket doesn’t provide any heat transfer at all. When there is no cooling whatsoever the temperature increases during the entire dosing time up to about 350ºK. The boiling points of each component within the reactor is above 373 degrees Kelvin yet considering the small size of the reactor the temperature rise is quite noticeable. When two or more thermosyphons (r_{inner} = 5 cm, ε= 1 mm) is used the reaction temperature remains much more stable. The maximal temperature that is reached when using two or more thermosyphons is almost the same as when the cooling jacket was installed.

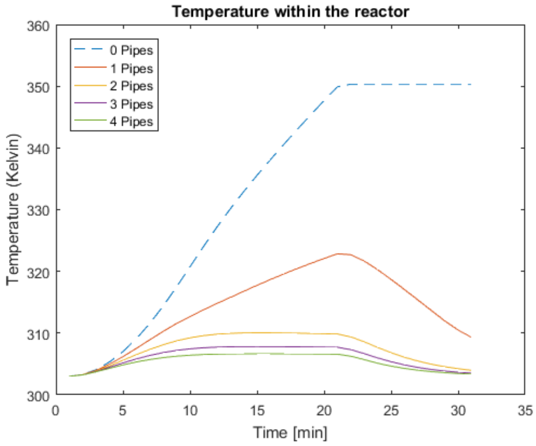

Figure 37. The reaction temperature within the semi-batch reactor when various numbers of thermosyphons is used and the cooling jacket is not providing any cooling of the process.

Table 19. The maximal temperature that is reached during the cycle time when the cooling jacket is out of operation.

Number of Thermosyphons	0	1	2	3	4
T_{max}	350.33 ºK	322.84 ºK	310.06 ºK	307.82 ºK	306.65 ºK

The reason for not using less than two thermosyphons is that when one is used the temperature within the reactor rises too high and the heat transfer exceeds the boiling limit. As can be seen in Figure 39 the heat transfer is far from the boiling limit when two or more are installed. This is very good for the safety of the reaction since it indicates that the thermosyphons will be efficient during the entire cycle in case such a malfunction would occur.

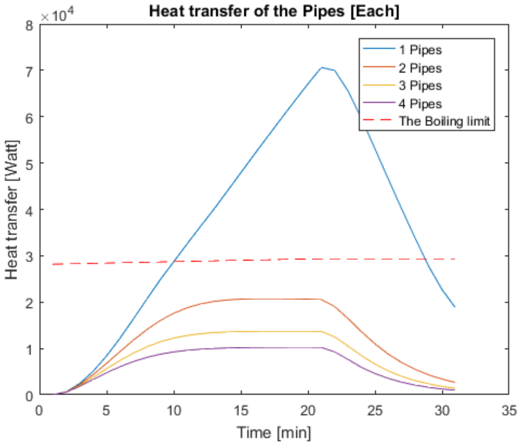

Figure 38. The heat transfer of each thermosyphon during the malfunction cycle in comparison with the pipe’s dominating limit.

4.3 Fine Chemicals

The results from the previous two simulations has indicated that the thermosyphons can bring a benefit to the temperature control and therefor to the thermal safety. Considering that both the simulations didn't involve any side reactions they can't be used to examine the selectivity improvement that the temperature control enables.

When using the model that was presented in chapter 3.4.3, a batch reactor that involves a desired reaction along with an undesired side reaction the effect of the thermosyphons on the reaction efficiency can be observed. The batch reactor has a volume of 6.3 cubic meters and is surrounded by a cooling jacket with a constant cooling temperature of 305°K. The thermosyphons that's being tested is partially filled with water with a boiling temperature of 313 degrees Kelvin. For the following results thermosyphons with a rough surface (1 mm) and an inner radius of six centimeters were simulated as an additional cooling system.

In Figure 39 and 40, the thermosyphons effect on the reaction temperature can be witnessed. The different shape of the curves when compared with the previous simulations models is due to the reactor type. As this is a batch reactor there is no slow reaction rates in the start as the concentration of the dosed reactant builds up, instead a more linear reaction rate is achieved. The reason is most likely that the temperature rise makes up for the decrease of reactants. The differences of adding additional pipes becomes relatively small when five or more is used and thereby the results of using two to five thermosyphons will be focused.

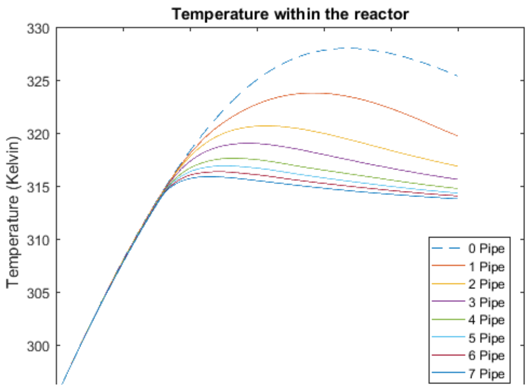

Figure 39. A display of the reaction temperature when the two cooling systems is compared with various numbers of thermosyphons installed.

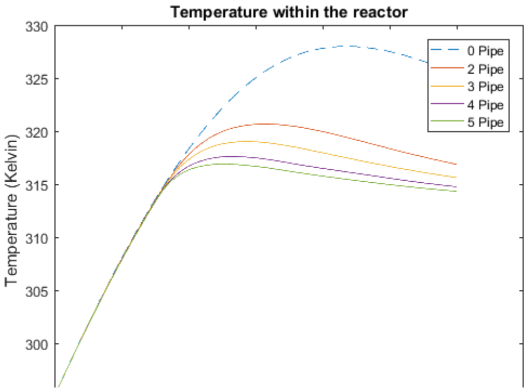

Figure 40. The temperature within the reactor when two to five thermosyphons is installed in comparison with the original cooling system

The temperature within the reactor is strongly affected by the thermosyphons due to lower reaction rates and heat transfer. When two or more thermosyphons is used to cool the process the reaction temperature becomes much more linear after the evaporation within the pipes have initiated. By adding five thermosyphons the maximal temperature that's reached after about one third of the cycle time is hardly changed at all during the remaining process. The temperature within the reactor can most likely be lowered even more if the boiling temperature of the working fluid is adjusted. As was mentioned previously the temperature within the pipes were examined during this process. By comparing the reaction temperature and the temperature within the thermosyphon it can be noted that it requires 120 seconds longer for the working fluid within the thermosyphons to reach the boiling point. Considering that 120 is only 2 % of the cycle time this shouldn't be of any concern.

Table 20. A display of the maximal temperature that's reached during the cycle and the time required for the reactor and the thermosyphons to reach the boiling point of the working fluid.

Number of thermosyphons	**0**	**2**	**3**	**4**	**5**
T_{max}	328.00°K	320.67°K	319.02°K	317.61°K	316.91°K
$\text{Time}_{\text{Reactor}}$ *($T_{reaktor}$=313°K)*	-	1459 s	1464 s	1468 s	1473 s
$\text{Time}_{\text{Thermosyphon}}$ *(T_{Pipe}=313°K)*	-	1576 s	1578 s	1584 s	1590 s
ΔTime	-	117 s	114 s	116 s	116 s

Another of the main reasons for performing this simulation was to examine the efficiency of the reactor when the two cooling systems was used. To begin with the concentration levels of each component is presented in the following graphs. In Figure 41 the concentration of the reactant, component A, is displayed. Similarly, to the previous models that has been simulated the additional cooling provides a decrease in the reaction rate and therefor a larger amount of the reactant remains at the end of the reaction cycle. The differences that the number of thermosyphons that's installed isn't of any larger scale yet a small increase in remaining reactants can be seen when more pipes were used.

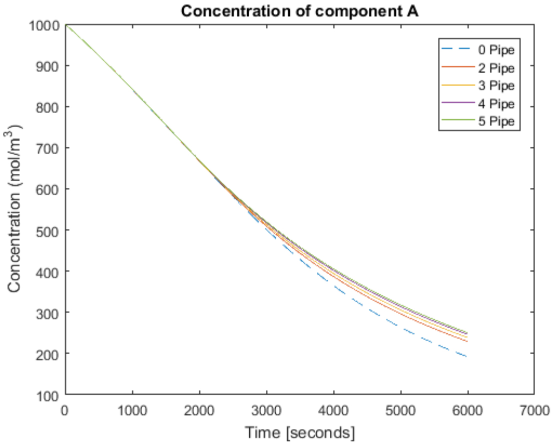

Figure 41. The concentration of reactant A during the cycle time of the batch reactor when different numbers of thermosyphons was used.

When examining Figure 41 which presents the concentration of the desired product, component P, a similar result can be seen. The lower reaction rates have led to a production decrease. As was mentioned previously this can be countered by either prolonging the cycle time or increasing the reactor volume.

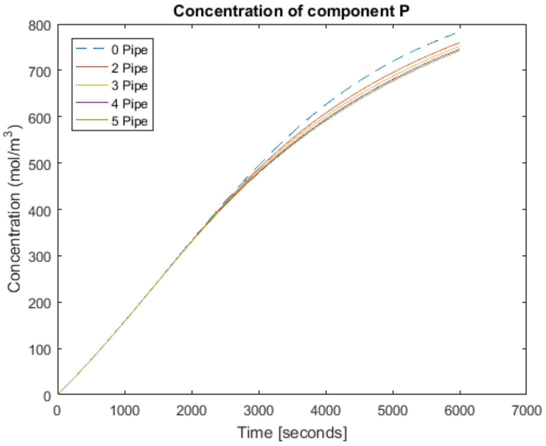

Figure 43. The concentration of the desired product, P, during the cycle time of the batch reactor when different numbers of thermosyphons was used.

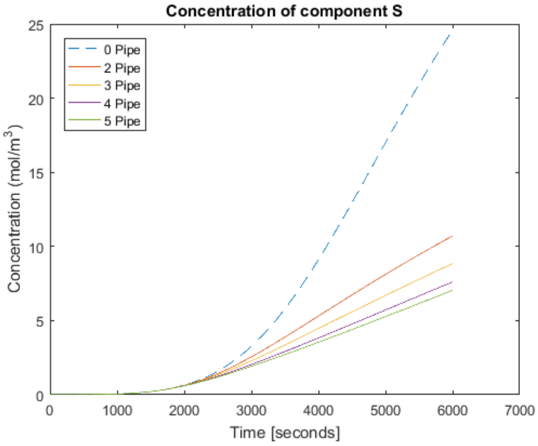

Figure 42. The concentration of the undesired product, S, during the cycle time of the batch reactor when different numbers of thermosyphons was used.

The main difference between this simulation model and the ones that’s been tested previously can be seen in Figure 42. The undesired reaction consumes the desired product and creates an unwanted product, component S. The concentration of the unwanted product doesn’t reach any high amounts during this simulation though it can be observed that the temperature control decreases the production.

To examine the effect that the thermosyphons brings to the process the conversion rate and selectivity is analyzed. The selectivity displays a measurement of how well controlled the reaction is by examining the number of used reactants and the production of the desired product. Considering that the stoichiometric factor is one, the selectivity of the process can be calculated with the following equation:

$$Selectivity: Y = \frac{C_P}{C_{A,0} - C_A}$$

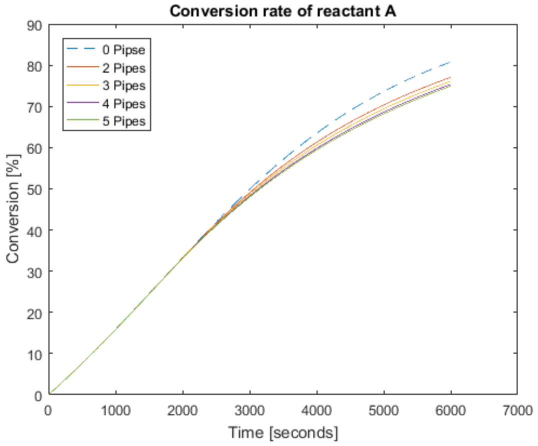

Figure 44. A comparison between the two cooling systems effect on the conversion rate of the reactant, component A, during the process.

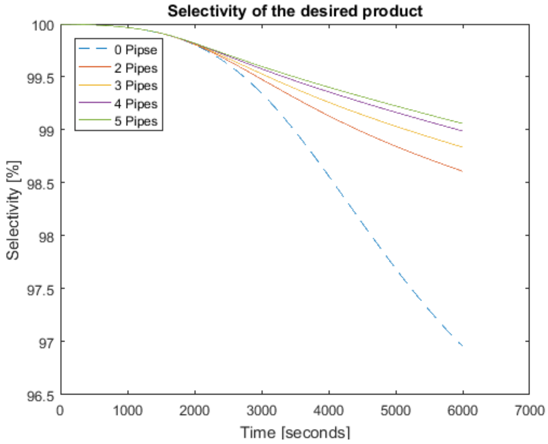

Figure 45. A display of the selectivity changes that the thermosyphons provides.

When observing the results in Figure 44 and 45, it can be concluded that the additional cooling can be seen as both an advantage and a disadvantage. The lower temperature results in a lower production yet as well with a more selective process. By using five thermosyphons which caused the temperature within the reactor to remain almost constant after the low hot spot the selectivity is above 99 percent. However, at the cost of the selective process comes a decrease of production of almost 6 percent. For industries that produces bulk chemicals the conversion decrease could be of more importance yet the thermal safety could perhaps make up for the loss since. The high flexibility of the thermosyphons makes it most likely possible to create an extremely effective process with a very low production of undesired by-products. The selectivity and control of the multiple reactions that occur is often of very high importance in industries producing fine chemicals and therefor this cooling system could be most suitable for such operations.

Table 21. An evaluation of the process efficiency through conversion and selectivity when two to five thermosyphons is used in comparison with the original design.

Number of thermosyphons	**0**	**2**	**3**	**4**	**5**
Conversion$_{\mathbf{final}}$	80.77 %	77.05 %	76.11 %	75.35 %	74.95 %
ΔConversion$_{\mathbf{final}}$	-	-3.72 %	-4.66 %	-5.42 %	-5.82 %
Selectivity$_{\mathbf{final}}$	96.95 %	98.61 %	98.83 %	98.99 %	99.06 %
Δ Selectivity$_{\mathbf{final}}$	-	1.66 %	1.98 %	2.04 %	2.11 %

Figure 47 shows a graph that displays the heat transfer that is performed by each thermosyphons during the different simulations. The heat transfer is initially not very impressive during the boil up yet after the boiling temperature is reached the heat transfer increases which corresponds with the overall heat transfer coefficient that’s presented in figure 46. Two thermosyphons is enough to bring the heat transfer underneath the limit yet it’s very close and more pipes would be recommendable.

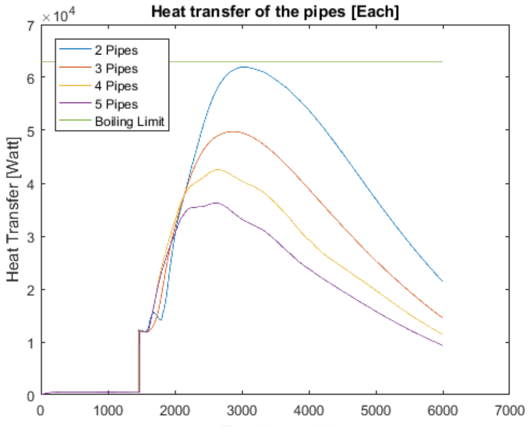

Figure 47. A display of the heat transfer that each thermosyphons displays in comparison with the boiling limit.

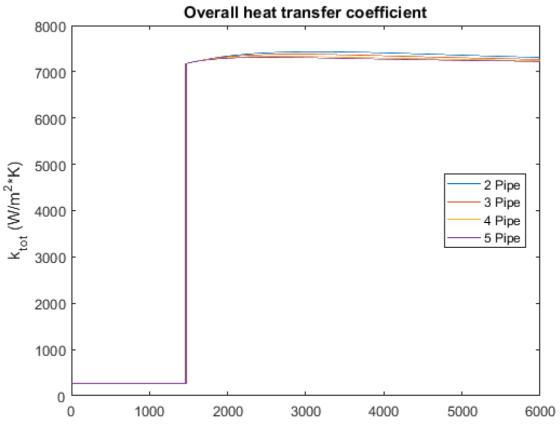

Figure 46. The overall heat transfer coefficient during the reaction cycle.

5 Conclusion

According to the theoretical simulations that has been performed in this work the thermosyphons can be of good use to ensure the safety and efficiency of a chemical reactor. By adding thermosyphons to cool the temperature within a batch or semi-batch reactor hosting an exothermic reaction the temperature control has increased significantly. Hot spots that's classically displayed during a batch reaction can be considerably lowered with an acceptable number of medium sized thermosyphons. By lowering the hot spot the safety of the process is increased and a more efficient control of the reaction rates can be achieved. Thermosyphons might also be a better alternative to wicked heat pipes considering that they are capable of transferring more heat and comes at a cheaper price. Since heat pipes have proven to have a superior overall heat transfer coefficient in previous studies this might be debatable and something that requires experiments and consideration.

During the simulations it was also noted that less thermosyphons were required to be used if the surface wall of the evaporator region were rough instead of smooth. The rough surface gave a significant improvement to the heat transfer coefficient of the reactor fluid which improved the pipes the heat transfer capabilities. Something that speaks against the surface treatment could be that they come at a higher economical cost and that it might be more economical to install a few more smooth pipes than a couple of less rough one.

Thermosyphons is generally considered to be relatively cheap yet the golden rule of the lower the number the lower the cost still stands. The simulations have however indicated that thermosyphons is very sensitive to temperature differences and that the impressive overall heat transfer coefficient enables the limitation to be reached at low temperatures differences. To counter this and ensure that the thermosyphons stays below their dominating limit a higher number of pipes can be installed. This will make sure that during fouling or malfunctions their heat transfer capabilities will not be lost or decreased dramatically. Another way to lower the temperature sensitivity is to not give the evaporator regions a rough surface. The rough surface gave a significant improvement to the heat transfer coefficient of the reactor fluid and by lowering this a higher temperature difference is required to reach the heat transfer limitation.

To summarize the conclusion the theoretical simulations have indicated that a cooling system that contains heat pipes in the form of thermosyphons is capable to improve the reaction selectivity and the thermal stability of exothermic reactions. The simulations have even gone so far as to show that it's theoretically possible to avoid thermal runaways during worst case scenarios such as a complete regulation malfunctions. The effect that the cooling have had on the production capabilities of the reactor is not desirable yet logical considering that the majority of exothermic reactions speeds up by increased temperatures. This makes thermosyphons a notable tool to be used in processes that requires high selectivity due to factors such as expensive reactants. Another beneficial situation to use the additional cooling system is when the process contains undesired exothermic reactions such as decompositions since they can lower the runaway risk.

6 Further work

To further evaluate how precious thermosyphons can be to the thermal safety and efficiency of chemical process more studies, experiments and simulations is required. The overall heat transfer coefficient that’s being used in this study is simplified and a more advanced model should be used where the process isn’t cooled by thermosyphons with ideal temperature and pressure. This is especially important since the heat transfer coefficient during a phase change is very dependent on the temperature of the heating medium. Since only a small temperature rise above the boiling temperature of the working fluid was obtained during most of the simulations the heat transfer coefficient within the pipes might not be high enough to be neglected.

Something that’s also required to be examined is the cooling of the condensation region of the pipes. In this study, the cooling has been assumed to be ideal and thereby there is not much that indicates the cooling requirements that’s necessary to achieve this.

Besides this it’s also worth to note that thermal runaways also tend to occur in storage facilities where the stored components is heated up to dangerous levels. Heat pipes could maybe prove useful in minimizing the risks of such events. Pipes could be in contact with the stored component while having their condensation regions within a container of a safe fluid.

7 References

Abdollahi, M. A. (2015). Water Boiling Heat Transfer in Vertical Jacketed Pipe: A CFD Model. *International Conference on Chemical, Civil and Enviromental Engineering*, p. 28-31.

Alveteg, M. (2013). *Handbook, Physical properties, correlationa and equations in Chemical Engineering.* Lund: MediaTryck.

Bjerle, I , Berggren, J-C och Karlson, H. (1977). Kemiska reaktorer - del 1: Dimensionering och Simulering av Satsreaktorn. *Kemiska Tidsskrifter*.

Dincer, I. (u.d.). Chapter 7 - Heat Pipes. i *Refrigeration Systems and Applications* (s. 405). John Wiley & Sons.

Dincer, I. (u.d.). Chapter 7 - Heat Pipes. i *Refrigeration System and Applications.* John Wiley & Sons.

Dr. Ahmad, H. (2013). Comparison between a Heat Pipe and a Thermosyphon Performance with variable evaporator length. *Al-Rafidain Engineering*, Vol. 21 p. 1-12.

García, M. (2016). Thermal stability and dynamic analysis of the acetic anhydride hydrolysis reaction. *Chemical Engineering Science*, p. 269-276.

Grewer, T. (1999). Prediction of thermal hazards of chemical reactions. *Journal of Loss Prevention in the Process Industries*, Vol. 12, p. 391-398.

Guinand, C. (2016). Thermal Process Safety Based on Reaction Kinetics and Reactor Dynamics. *AIDIC, Vol. 48 2016*, Vol 48. p. 19-24.

(2002). *Hazard Investigation - Improving Reactive Hazard Management.* U.S. CHEMICAL SAFETY AND HAZARD INVESTIGATION BOARD.

Heat Transfer Limitations of Heat Pipes. (den 14 February 2017). Hämtat från Thermal-Fluids Central: http://www.thermalfluidscentral.org/encyclopedia/index.php/Heat_Transfer_Limitations_of_Heat_Pipes

Karlsson, H. (2012). *Processriskanalys.* Lund: Mediatryck.

Khalid, J. (2000). Improvements of gravity asssited wickless heat pipes. *Energy Conversion & Management*, p. 2041-2061.

MAHBulletin. (2016). *Chemical Accidents Prevention and Preparedness.* European Commission.

Mas, E. (2006). Safe Operations of Stirred-Tank Semibatch Reactors Subject to Thermal Hazard. *American Institute of Chemical Engineers Journal*, 3570-3582.

Moulijn, J. (2008). Chapter 10. Fine Chemicals. i *Chemical Process technology* (p. 307-330). John WIley & Sons.

Reay, D. (2013). Appendix 1, Working fluid properties. i *Heat Pipes: Theory, Design and Applications* (p.228, 232). London: Elsevier.

Reay, D. (2014). Chapter 2 Heat transfer and fluid flow theory. i *Heat Pipes Theory, Design and Application.* Elsevier.

Reay, D. (2014). Chapter 4 Design Guide. i *Heat Pipes Theory, Design and Applications.* Elsevier.

Stoessel, F. (2008). Chapter 1 – Introduction to Risk Analysis of Fine Chemical Processes. i *Thermal Safety of Chemical Processes* (p. 3). Wiley-WCH.

Stoessel, F. (2008). Chapter 2 – Fundamentals of Thermal Process Safety. i *Thermal Safety of Chemical Processes* (p. 34-35.). Wiley-WCH.