TU Delft Delft University of Technology

CDP Group 3381
Conceptual Design Project

New Oxidizer for Advanced Propellants

Final Report

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Preface

The report that you have in your hands is the result of 12 weeks of work on a course for the TU Delft called Conceptual Design project. This design course is part of the curriculum for master students Chemical Engineering at the TU Delft and has as a goal to let students develop essential skills in the design field.

Of course this report could not have been made without some help. We would therefore like to thank a few people that made this possible. First, Dr.ir. J.F. Zevenbergen for making this project interesting by giving us a great assignment. Next, we would like to thank our technical supervisor Ir. drs. G. Bierman and our creativity and group coach Ir. P.L.J. Swinkels for their help in finishing this project.

We would also like to thank Kostis Tzanetis for his help and his company during the long hours in the basement. Furthermore we would like to wish Dirkjan Journée the very best and we hope he recovers quickly. We would also like to thank him for providing us with music and laughs during the project.

Furthermore, without the multiphase reactors, the slow clap processor (at least we still have that), the awful music and the burn shots this project would not have been possible (and would have been a lot less fun)!

Delft, 15-07-2011

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Summary

Currently the Ariane 5 rocket uses solid rocket fuel with ammonium perchlorate as oxidizer. It has been proposed that this oxidizer is changed to a new oxidizer: ammonium dinitramide. This oxidizer has 6-7% more thrust and is environmentally friendlier. However, only lab scale production has been attempted. The goal of this project is to design a process to produce ADN on an industrial scale with a production capacity of 2075 t/a, the amount needed to supply the Ariane 5 rockets.

In order to achieve this, the reaction option best suited for bulk production is selected from several options found in patents. This reaction uses H_2SO_4, HNO_3 and ammonium sulfamate (a commonly available fertilizer) as the main reactants. No kinetics are known, but it is assumed that the reaction rate for this highly exothermic reaction is faster than the cooling rate. This means that the heat removal rate to keep the reactor vessel at the required temperature of -50°C will be the limiting factor in the design. A yield of 50% is taken from literature.

Based on the selected patent, a process is designed that consists of the following three general steps: reaction, neutralization and separation. Only the reaction is within the scope of this project and the other steps are not designed in detail.

The reactor chosen is the spinning disc reactor with a set-up of 12 reactors in parallel to achieve the required cooling rate of 1188 kW. These reactors are especially good at handling viscous liquid and solids and have a high heat transfer coefficient, making them well suited to this process. To provide cooling, a refrigeration cycle is designed. Propylene is chosen as the refrigerant because it is cheap and has the right thermodynamic properties. The refrigerant will have a cooling temperature of -70°C.

Process flow schemes are given for the complete process and the refrigerant cycle. These are both accompanied by stream tables, which give an overview of the process. The reactor unit, heat exchangers and refrigerant cycle have detailed design specifications.

Using the method of the Dow Fire and Explosion Index, the degree of hazard for the reactor unit has been classified as heavy, while the degree of hazard for the refrigeration unit is moderate. After performing a HAZOP, care was taken to control the valves of each stream separately and to install a spare compressor unit for the refrigeration cycle.

An economic evaluation is performed using the several economic criteria: the payback time, return on investment and internal rate of return. When using the equipment costs for just the reactor and refrigeration units, these indicators proved favorable. If a preliminary downstream cost was included of up to €M 15 (this is an extreme case) the project is still economically favorable.

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Chapter 1: Introduction

Currently in the Ariane 5 rockets solid rocket propellant is used. These solid rocket motors (SRM's) use a mixture of an oxidizer and a fuel. Currently ammonium perchlorate (AP) is used in the Ariane 5 rockets. This oxidizer has as a disadvantage that it produces HCl when used in rocket fuel. However, a new alternative is available: ammonium dinitramide (ADN). This oxidizer has as a main advantage that it produces 6-7% more thrust and as a second advantage that it is less harmful to the environment, producing NO_x rather than HCl when used in rocket fuel. However at this point in time, ADN nowadays is only produced on lab scale, resulting in very high prices, of around €1000,- per kg,.

The lab synthesis of ADN consists of a couple of steps. In general the synthesis works with a double nitration on a starting chemical, yielding dinitramidic acid (DNA), which then has to be neutralized with ammonia to form ADN. After this synthesis, one ends up with needle like ADN crystals, which need to be recrystallized to form spherical particles. After this step the ADN undergoes a microencapsulation to protect the ADN from moisture in the air.

The goal of this design project is to design an industrial scale process that can produce ADN at a competitive price, focusing on the reaction step that yields the dinitramidic acid. At the start of the project nothing was known about producing this compound on industrial scale. The first part of the project focused on finding different ways that ADN could be synthesized on lab scale, and choosing one that was viable for scaling up to a larger scale. For this the synthesis route that was chosen was the synthesis route starting with ammonium sulfamate (AS) which is nitrated twice, with a mixture of nitric acid and sulfuric acid as a nitrating agent.

For the reaction very little information was available. The reaction temperature is -50°C, and the reaction is very exothermic. However kinetics, such as reaction rates are unavailable, as is the heat of reaction. This was an issue with the design of the process. However from the used patents it could be found that the heat removal rate was rate liming. So the assumption is made that the reaction is fast, and the design should be based on the heat removal rate. Also a yield and decomposition are assumed, based on yield of the patents. This assumption is made so that the heat of reaction is maximized for the chosen yield, giving a conversion of 100% and a yield of 50%.

After this reaction step dinitramidic acid (DNA) is formed and needs to be neutralized with ammonia to form the desired ADN. After this the ADN needs to be crystallized, forming ADN crystals. These crystals are recrystallized in an emulsion crystallization for form the ADN crystals which are used as the oxidizer for the solid propellants.

The scope of this project is the design of the first step of this process, the reaction at -50°C to form the DNA. The process designed will also show process options of subsequent process steps for producing crystallized ADN. However, the steps after the reaction to DNA are not designed in detail.

To realize a process that produces the ADN on an industrial scale, the first essential part is to assess the market, determine the production capacity. For this project, the market was set to the Ariane 5 rockets, which use solid oxidizer. The capacity was calculated using the amount of rocket launches, and the ADN usage of one launch. This yielded a capacity of 2000 ton annually if full replacement of the AP oxidizer is realized.

The next step is to look at the chosen process option and scale this up to a process, again with a focus on the first part. For this, the basis of the reactor design is the ability to remove heat from the reactor. The solution for this problem is to use spinning disc reactors, which can handle heat and mass transfer very well. In the end, 12 spinning disc reactors are needed, with 2 spare reactors installed. For the cooling of the flows to the reactor, and the reactor itself, a refrigeration cycle is designed. This is an essential part of the process, as it keeps the reactors at the desired temperate. The rest of the flow scheme is made, but not designed in detail.

Process control is also an important aspect, so time has been devoted to design a preliminary control system for the process. This includes different types of controllers to keep the process in check.

Safety, health and the environment have also been taken into account. A Fire and Explosion Index study has been performed and a HAZOP was done for the reactor unit. Furthermore, the economics of the project have been studied. For this economic indicators are used to estimate the viability of the project as it has been designed.

Chapter 2: Concept Options & Selection

This chapter will discuss significant decisions in this project with respect to concept options. For each decision criteria, advantages and disadvantages of concept options are identified and weighed against each other to reach a final decision.

This chapter contains three sections. The first section describes what strategy has led to the synthesis method chosen for the scaled up process. The second section discusses whether a batch or continuous process is more suitable for the large scale production of ADN. These decisions lead to the construction of a block scheme diagram shown in Figure 3. The final section will then touch upon the choice of raw materials. The results of this chapter and alternatives considered are shown in the decision tree diagram below (Figure 1).

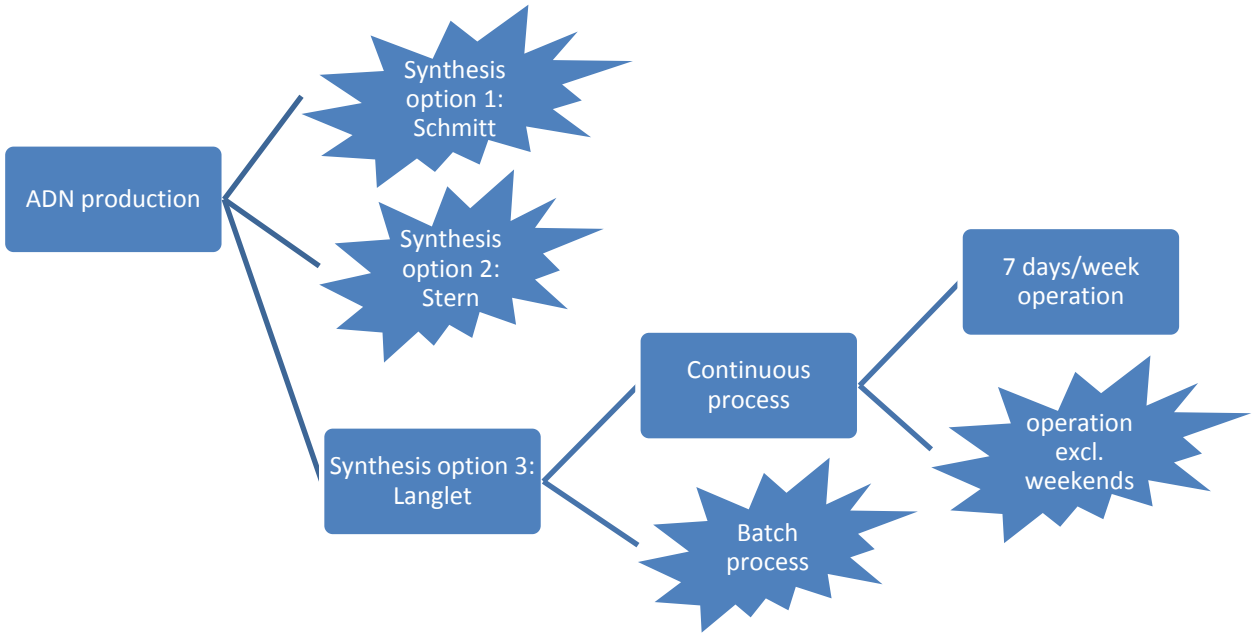

Figure 1: Decision tree on synthesis methods and process types

Synthesis methods

Based on the project objectives presented in the Introduction, a literature study is conducted on the production of ADN. Barely any documentation on the industrial scale production of ADN is available. However, a large number of synthesis methods on lab scale are reported in (mostly) patents. In order to design a process for the production of ADN, a synthesis method has to be selected for scale up.

All syntheses have in common that they require nitrating agents that attack the reactant. Also, all reactions occur at low temperatures. One important difference in the synthesis methods are the different yields that each method gives (Venkatachalam, Santhosh et al. 2004). A first selection is made using this criterion to limit the synthesis methods to three options (Schmitt, Bottaro et al. 1994; Stern, Koppes et al. 1998; Langlet, Östmark et al. 1999). For more information on the chemical reactions see Appendix C: Description of chemical reactions. Another difference in the methods are the types of nitrating agents and the different chemicals used as reactants. The required chemicals differ largely in their availability, which is the reason that the availability of raw materials is chosen to

be another key selection criterion. The advantages and disadvantages of the three reaction options are analyzed and summarized in Table 1.

Table 1: Summary of advantages and disadvantages of the three reaction options for making ADN.

	Advantages	**Disadvantages**
Reaction 1 Schmitt	Some reactants available as bulk chemicals	Low reaction temperature (-78°C)
		Low yield (~ 15%)
		Low availability of nitrating agent
		Complicated nitration step
Reaction 2 Stern	Regeneration of reactant is possible	Low yield (~ 40%)
		Multiple nitration steps
		Low availability of nitrating agent
		Complicated nitration step, N_2O_5 is difficult to apply on a large scale
		Large amount of byproduct formed
		Low reaction temperature (-78°C)
		Large amount of solvent is necessary
Reaction 3 Langlet	Good yield (~ 60%)	Harmful acids used in the process
	Non-explosive reactants	Low reaction temperature (-40°C)
	Reactant and nitrating agent available as bulk chemicals	

Based on the most important specifications, yield and availability of raw materials, it is clear that reaction three gives the highest yield of ADN while using raw materials that are available as bulk chemicals. This as opposed to the other two reactions that have lower yields and require more difficultly available nitrating agents. Furthermore, the first two reactions require much lower process temperatures. When taking other aspects into account, the third reaction is also more favorable than the other two reactions. Therefore, the decision is made to scale up synthesis method three.

The chemical reaction is given below in Figure 2. The reactant used is ammonium sulfamate, which is a commonly used herbicide produced in bulk quantities. The nitration is performed with a mixture of nitric and sulfuric acid and produces dinitramidic acid (DNA). The second reaction step is a neutralization reaction of the acid with ammonia producing ADN. For more detail on the nitration step, a reaction mechanism is given in Chapter 3: Concept stage as proposed by Santhosh in his thesis (Santhosh 2005).

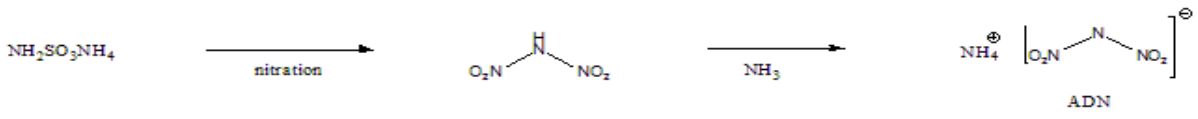

Figure 2: Chemical reaction formula for reaction three (Langlet et al.)

Batch vs. continuous process

For scaling up the process, two main modes of operation are compared globally: continuous operation and batch wise operation. At this point, a number of process properties are relevant. First of all, 2000 tons of ADN is required every year. It is also known that the chemical reaction is highly exothermic and takes place at a low temperature.

Based on the ADN production requirements, rules of thumb state that when production capacity is <500 ton/y, batch operation is favored, whereas when production capacity is >5000 ton/y, continuous operation is favored. The production capacity for ADN lies exactly in between these two ranges. Therefore, based on the production capacity, no preference is given to either batch or continuous operation. (Seider, Seader et al. 2010)

In terms of market demand, ADN needs to be supplied for six rocket launches, spread out irregularly over a year. Since there is no seasonality in the demand, a batch process is not necessarily favorable either. In the case of unexpected peaks in demands, both batch and continuous processes will face inventory issues.

However, with respect to the safety and ease of operation, a continuous operation is preferred. Especially since the reactor needs to be at low temperatures and a lot of heat needs to leave the reactor, repeatedly starting-up and shutting down a batch process and its respective cooling system presents more operating difficulties and risks. Therefore, it is decided to design a continuous process.

Based on the selected synthesis method, a continuous process is designed. This block scheme is developed based on a brainstorm session, where group members individually interpret the lab scale synthesis method described in the literature (Langlet, Östmark et al. 1999). The process is described in Figure 3 below.

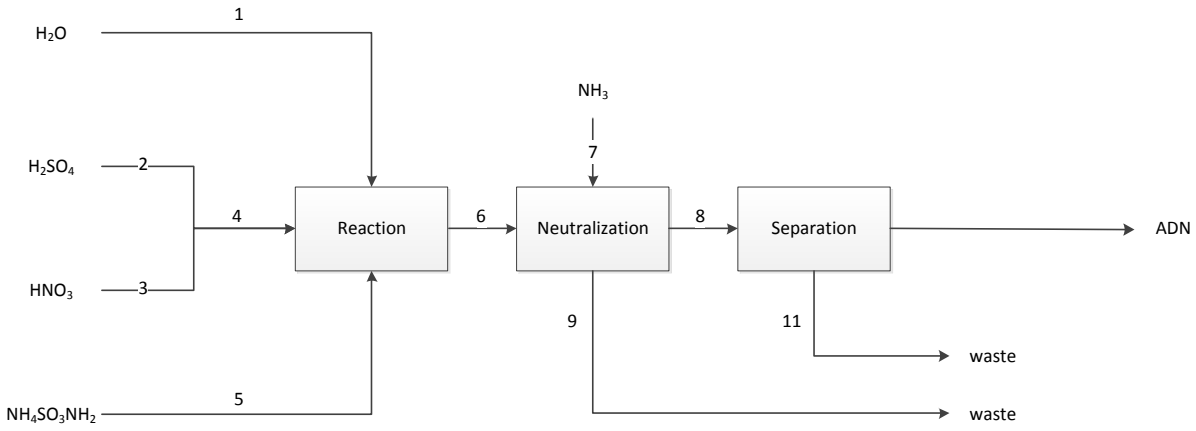

Figure 3: Block scheme of the process

Ammonium sulfate (5), the nitrating acids (2&3) and water (1) are fed to the first reaction black box. The product (6) then leaves to the neutralization section, where ammonia is used to neutralize the acids, producing waste and product. Finally, the product is purified in the separation stage.

Fully continuous vs. periodically continuous

After having advanced to more specific design of the process, it has also been considered to shut down operation of the continuous process in the weekends since it could be a cheaper solution. The

most important factors influencing this choice are the costs and safety. First of all, by operating on weekdays only, labor costs in the weekends can be avoided. However, initial investments are roughly 2 million Euros higher due to the additional reactor capacity required. Furthermore, energy loss from the cooling system due to shut down and start-up will drive up costs. Also, since a higher reactor capacity is required during normal working days when the plant is closed in the weekends, more labor will be required during normal working days. Finally, additional start-ups and shut downs bring along more risks with respect to process operation safety. Considering the process streams contain very aggressive acids, operation at steady state is desired. Also, process streams will be significantly larger, resulting in a more hazardous process. Generally, it can then be concluded that a fully continuous process is the desired option.

Raw materials

The consequence of choosing a synthesis method is that most of the important raw materials are also determined. The most important criterion for choosing raw materials is their availability, which cause the choices to be made relatively straightforward. In the case of the type of nitrating agent for example, a mixture of sulfuric and nitric acid will be used. Alternatives, such as N_2O_5 and NO_2BF_4 are rejected due to their low availability. Moreover, the chemical reaction described by Langlet does not consider the use of other nitrating agents, which means that if alternative chemicals are chosen, the patent cannot be used as the basis for the design of this process anymore (Langlet, Östmark et al. 1999). Furthermore, the ratio of sulfuric and nitric acid content is also investigated. The decision on this matter is made swiftly, when looking at the yield dependence on the acid ratio (Santhosh 2005). The process of choosing raw materials has therefore been simple, requiring little brainstorming or creativity.

Conclusion

A few consequential process concept selections are made in this chapter: (1) synthesis route and (2) continuous vs. batch operation. With respect to the synthesis route, it has been decided to scale up the lab scale synthesis of ADN because no literature is available on the industrial scale production. A number of patents are examined as concept options. In the end, the patent that synthesizes ADN on lab scale with the highest yield, simplest nitration reaction and most readily available chemicals is chosen. Selection of this synthesis method has for a large part also determined the choice of raw materials.

In deciding between a continuous or batch process it is found that based on production capacity neither is more advantageous than the other. However, when considering market demands and the importance of operating this process safely, the continuous process seems more favorable. Hereafter, a continuous plant but shut down in the weekends versus a fully continuous process is also considered briefly. Rough economic estimates, but mainly safety considerations determine that the fully continuous process is more favorable.

Chapter 3: Concept stage

In the basis of design report some key data for the design are presented. This chapter will focus on summarizing those key data and provide some background to clarify the findings. The concept stage process description and overall block scheme and mass balances will first be treated. Then the heat of reaction and viscosity estimates will be discussed. Following that the battery limit as used in this project will be discussed. Lastly the initial economic study and plant location will be covered.

Overall block scheme and Process Description

The block scheme shown in Figure 3 is further specified. The system has been designed for a production capacity of 2075 t/a of ADN, the amount needed for the Ariane 5 rocket, which resulted in the block scheme shown in Figure 4. In the diagram, the component streams are calculated and given in tons per year. The process is roughly divided into three sections:

1. Reaction section: Here the acids and ammonium sulfamate are brought together and react to form ADN.
2. Neutralization section: Here the acid solution containing dinitramidic acid is neutralized to form salts using ammonia.
3. Separation section: In this section the ADN is separated from the waste products.

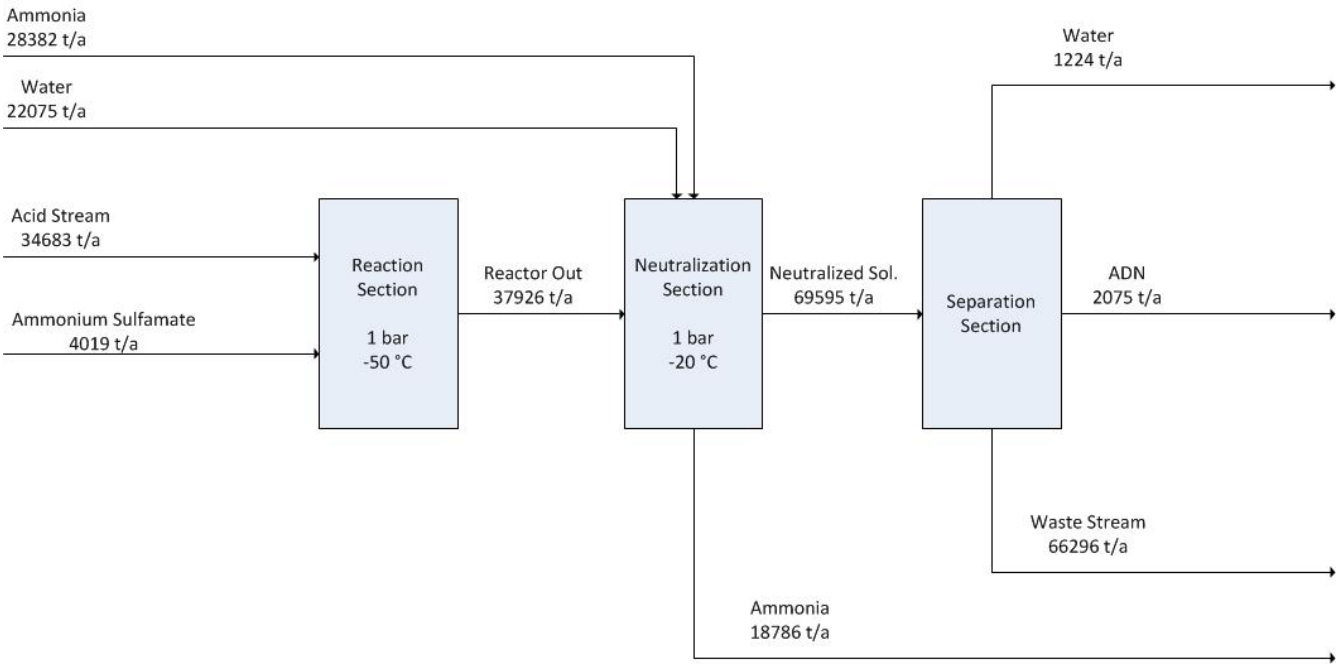

Figure 4: A generalized block scheme with streams in tons per year

Due to time constraints focus of this project is on the reaction section. The process in more detail can be found in the Chapter 4: Process design and description. Now the key data about the different sections will be briefly discussed.

Reaction

In this section the reaction to ADN takes place. The mechanism for this reaction can be seen in Figure 5. This is the reaction mechanism from H_2SO_4, HNO_3 and ammonium sulfamate to dinitramidic acid.

It starts with nitration of ammonium sulfamate by the nitronium ion that is formed by the H_2SO_4 and HNO_3 solution. The intermediate product of this step can now react via two pathways. The first possibility is first a reaction with water and then a second nitration step with a nitronium ion. The other pathway starts with a second nitration and reacts to dinitramidic acid after another reaction with water. Both pathways end up with the same product formed.

As can be seen from the reaction scheme, decomposition reactions also take place. Again, there are two possibilities. The first is a decomposition of the intermediate product that is formed after the reaction with water in the first pathway. However, due to the fact that in this step an intermediate decomposes, and no kinetic data is known, this step is disregarded in further calculations. The second decomposition takes place after DNA is formed and is catalyzed by the acid solution. Because of the acidic nature of the reaction environment it is therefore essential that the acid solution is neutralized swiftly.

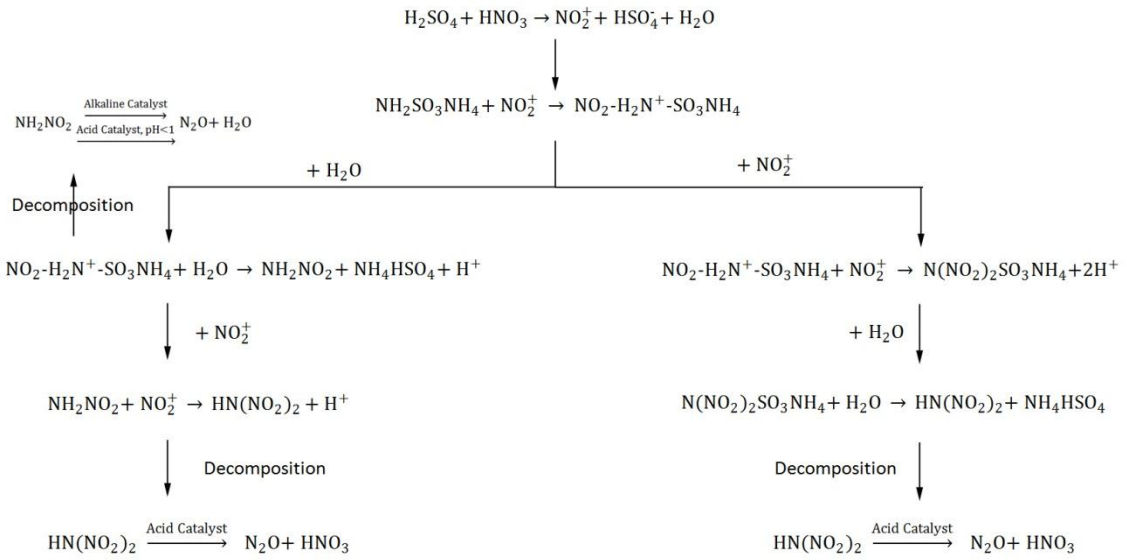

Figure 5: Reaction scheme for the formation of DNA including decomposition reactions

If then 100% conversion and 50% decomposition are assumed based on a yield of 50%, the overall reaction becomes as follows:

$$NH_2SO_3NH_4 + 2\,HNO_3 + 2\,H_2SO_4 \rightarrow 0.5\,HN(NO_2)_2 + 2H^+ + NH_4HSO_4 + H_2O + 0.5\,N_2O + 0.5\,HNO_3 + 2\,HSO_4^- \qquad \text{Eq. (3.1)}$$

In literature it has been found that the best yield is achieved with a reactant molar ratio of:

AS : water: H_2SO_4 : HNO_3 = 1 : 1.8 : 2 : 12

The relative large amount of HNO_3 used, is because it acts as a diluting agent, thus lowering the viscosity of the solution without compromising the reactivity of the mixture. Water is added because it is found that the reaction of intermediates to DNA runs better with addition of a small amount of water. (Santhosh 2005)

The reaction is highly exothermic and has been found to produce the highest yields when the reaction is carried out at temperatures between -45°C and -55°C. An estimate for the heat of reaction can be found in the next paragraph, in the section Heat of reaction.

Neutralization

In the neutralization step, the acid solution is neutralized using ammonia to form salts. All the diluted acids and DNA are neutralized in this way. The salts that are formed are:

- ADN
- $(NH_4)_2SO_4$
- NH_4NO_3

For a more detailed treatment of the neutralization step, see Chapter 4: Process design and description.

Separation

The reactant stream coming from the neutralizer will have to be processed further to obtain pure ADN crystals. The ADN has to be separated from the salts (and residual water). For more information on the separation process, see Chapter 4: Process design and description.

Heat of reaction and viscosity

Heat of reaction

Not much is known about the heat of reaction for the reaction scheme that is used to design the process besides the fact that it is a highly exothermic reaction. In order to design the process however, it is very important that an estimate is made so that the exothermicity can be taken into account and the reactor can be designed accordingly.

One way to estimate the heat of reaction is to use bond energies. Each bond within a molecule has an energy that is the amount of heat required to break the bond in one mole of molecules. If the bond energies of all the bonds in the molecule are added together, the bond energy of a molecule is found. The heat of reaction is then estimated by adding all the bond energies of the product molecules together and subtracting all the bond energies of the reactant molecules (keeping in mind stoichiometry of course).

Using this method, the following values were found, for the complete bond energy calculations see Appendix D: Bond energy calculations.

Table 2: Heat of reaction estimation for the reaction and decomposition of DNA

	Products	Reactants	Heat of Reaction	
Reaction	4743	5949	-1206	kJ/mol
Decomposition	5018	4743	275	kJ/mol

This estimate can then be used to determine the amount of heat that needs to be taken away from the reactor in order to maintain the low temperatures needed for the reaction.

It is assumed that the reaction time is very fast and that the cooling rate is the rate limiting step in this process. This is in accordance with literature where the reactant is added slowly to prevent heating up of the reaction mixture. Looking at the mass balance for a continuous process (more information can be found in Chapter 2: Concept Options & Selection) and a production rate of 2075 ton/year ADN, the addition rate (and thus reaction rate) for AS is 0.127 kg/s. (Langlet, Östmark et al. 1999; Santhosh 2005)

Another assumption is that the reaction has a conversion of 100% and that the product decomposes for 50%, leading to a total yield of 50%. The heat of the total reaction can then be calculated using the molar flow of ammonium sulfamate as reaction rate. The results of this can be seen in Table 3.

Table 3: Heat produced in the reaction with 100% conversion and 50% decomposition

Mol. Weight AS	**114.14**	**kg/kmol**
Flow	0.127	kg/s
Molar flow	1.112669	mol/s
Reaction (100% conversion)	-1341.878	kJ/mol
Decomposition (50%)	152.9919	kJ/mol
Total:	**-1188.886**	**kJ/mol**

This means that with a fully continuous operation, -1.2 MW needs to be transported away from the reactor to prevent the reactor temperature from rising. The reactor design is therefore focused on being able to transport the heat as can be read in Chapter 7: Equipment and unit design. The refrigeration cycle that is designed is therefore capable of cooling this amount of heat plus the cooling load needed to cool the reactant streams going into the reactor. This design can be found in Chapter 7: Equipment and unit design.

Viscosity

Since one of the reactants is highly viscous, it is important to estimate the viscosity for the reactor mixture. However, since the viscosity at the operating temperature is not tabulated, an estimation is made. A range of viscosity values from literature is extrapolated as a function of temperature so that the viscosity of the pure compounds at -50°C is approximated. The overall viscosity of the mixture is then calculated based on the mass fractions. This resulted in a mixture viscosity of 0.032 Ns/m^2 in the reactor at -50°C, which is not extremely viscous. For more detailed calculations, see Appendix E: Viscosity estimates.

Solubility

It has been stated that the reaction is extremely fast and only limited by the cooling rate in the reactor. However, since ammonium sulfamate is added to the reactor as a solid, it is important to

know if dissolving is not the limiting step. In order to determine this, the solubility rate of AS is determined so that the assumption that the cooling rate is limiting can be verified.

The dissolving time is approximated by setting up a mass balance over a (spherical) AS particle in a moving flow, with a bulk AS concentration of zero The mass transfer coefficient is given in the transport phenomena data companion(Janssen and Warmoeskerken 2006). For a complete derivation see Appendix F: Solving the particle.

$$\frac{dD}{dt} = -2k \qquad \text{Eq. (3.2)}$$

With mass transfer coefficient k:

$$k = 2.0 + 0.66 * Re^{1/2} Sc^{1/3} * \frac{\mathbb{D}}{D} \qquad \text{Eq. (3.3)}$$

Solving this leads to:

$$\frac{2}{3} * \left(D^{3/2} - D_0^{3/2} \right) = -1.32 * \frac{M}{\rho} * \frac{P^*}{RT} * \mathbb{D}^{2/3} * \nu^{1/2} \qquad \text{Eq. (3.4)}$$

If this equation is filled in using the calculated viscosity of 0.032 Pa s, a diffusion coefficient of $1*10^{-9}$ m^2/s (this is the diffusion coefficient of salt, which is similar in size to AS), Reynolds 200, Schmidt $3*10^{7}$, a starting diameter of $1*10^{-4}$ m we find that the time to dissolve AS is $9*10^{-4}$ seconds. This is so fast that the assumption that the cooling rate is limiting holds.

Battery limit

The battery limit of a plant is everything that is included in the direct manufacturing of the product. Auxiliary units such as producing steam, cooling towers, etc. are usually outside the battery limits. In this paragraph, the battery limits for the production process will be set.

It is assumed that all storage of raw materials is outside the battery limit. Also excluded are the pumps and compressors required to transport the materials to the process site at the required pressures. These raw materials are listed in Table 4. Furthermore, all downstream processing of ADN is presumed to happen outside the battery limit, which includes further processing of ADN and treatment of the waste streams.

Table 4: Raw materials as supplied in the ADN process

Raw material	Pressure [bar]	Temperature [K]
NH_3	10	298
Water	1	298
H_2SO_4 (98%)	1	298
H_2SO_4 (80%)	1	298
HNO_3 (98%)	1	298
N_2	10	298
$NH_4SO_3NH_2$	1	298
Cooling Propylene	10	298
Cooling Water	1	288
Steam	3	463

Initial economic study and plant location

Important factors in the opportunity assessment of this project are the economic viability and location of the ADN plant. The next paragraphs will briefly summarize the preliminary findings as seen in the basis of design. In Chapter 9: Economic analysis the financial side of this project is evaluated in more detail.

Initial economic study

In order to determine the maximum possible investment the discounted cash flow rate of return method is used. In the preliminary stage this uses the financial margin as cash flow. The financial margin is defined as the difference between the selling price of ADN and the cost of raw materials, assuming 2000 tons of ADN per year are sold. The selling price of ADN should not be higher than its current competitor ammonium perchlorate, which means that a maximum price level of €21 should be used.

It is determined that the margin of ADN is €16 per kg leading to a yearly cash flow of M€ 34 . Using the DCFROR method the maximum allowed investment has been determined to be in the order of M€ 260. This assumes a plant lifetime of 15 years. More detail on these calculations can be found in Appendix G: Economic evaluation using DCFROR. However, this excludes utility costs, equipment costs, etc. A far more detailed treatment of economics can be found in Chapter 9: Economic analysis.

Plant location

There are two options for the location of the ADN plant. The first is French Guiana which has as advantage that it is close to the launch site, which means the product would not have to be transported far to the point of use. The second option is France, also the location of the current oxidizer (AP) plant. France has many advantages, such as better infrastructure, better access to raw materials and more skilled labor. Since ADN is quite stable to transport, the advantage of placing the plant in French Guiana is limited. Therefore, France is selected as location for the manufacturing process.

Conclusion

To summarize this chapter the block scheme for the overall process consists of three parts: reaction, neutralization and separation. Of these parts the focus will be on the reaction section. The total amount of material has been determined in order to produce 2075 tons of ADN per year.

The reaction mechanism leads to an overall reaction, taking into account 100% conversion and 50% decomposition:

$$\begin{gathered} NH_2SO_3NH_4 + 2\,HNO_3 + 2\,H_2SO_4 \\ \rightarrow 0.5\,HN(NO_2)_2 + 2H^+ + NH_4HSO_4 + H_2O + 0.5\,N_2O \\ + 0.5\,HNO_3 + 2\,HSO_4^- \end{gathered} \qquad \text{Eq. (3.5)}$$

This reaction is highly exothermic and runs best between -45°C and -55°C.

The heat of reaction is estimated using bond energies to be -1206 kJ/mol for the reaction and 275 kJ/mol for the decomposition. The total rate of reaction is limited by the cooling rate as dissolving rate and reaction rate are both very fast.

The battery limit is taken to exclude the storage and delivery of raw materials and downstream processing of ADN.

The initial economic study using the DCFROR method proved to be favorable, however only raw material cost was taken into account here. In this report a more detailed economic study has been done. The plant location is chosen to be in France as this is an option with more advantages than French Guiana.

Chapter 4: Process design and description

In this chapter, the process is designed in more detail, so that the block scheme is transformed into a process flow scheme. Different technologies are considered for the process and decisions for specific unit operations are made as well. The design decisions are discussed first in the section on unit operation options. After the unit operations have been determined, the process flow schemes are developed, which can be found in Appendix H: Process flow schemes. A step by step description of this process is provided in the process description section.

Unit operation options

Based on the block scheme formulated in Chapter 2: Concept Options & Selection, the process is designed in more detail. The objective is to develop the block scheme into a fully equipped Process Flow Scheme with suitable unit operations. From the Basis of Design Meeting it followed that priority should be given to the design of the first “reaction” black box in the block scheme diagram. Therefore, design options for the reaction step are considered much more extensively compared to the neutralization and separation steps.

The decision tree that summarizes the design options considered and chosen is presented in Figure 6 below. In the next paragraphs, the design process for each black box step is explained in more detail.

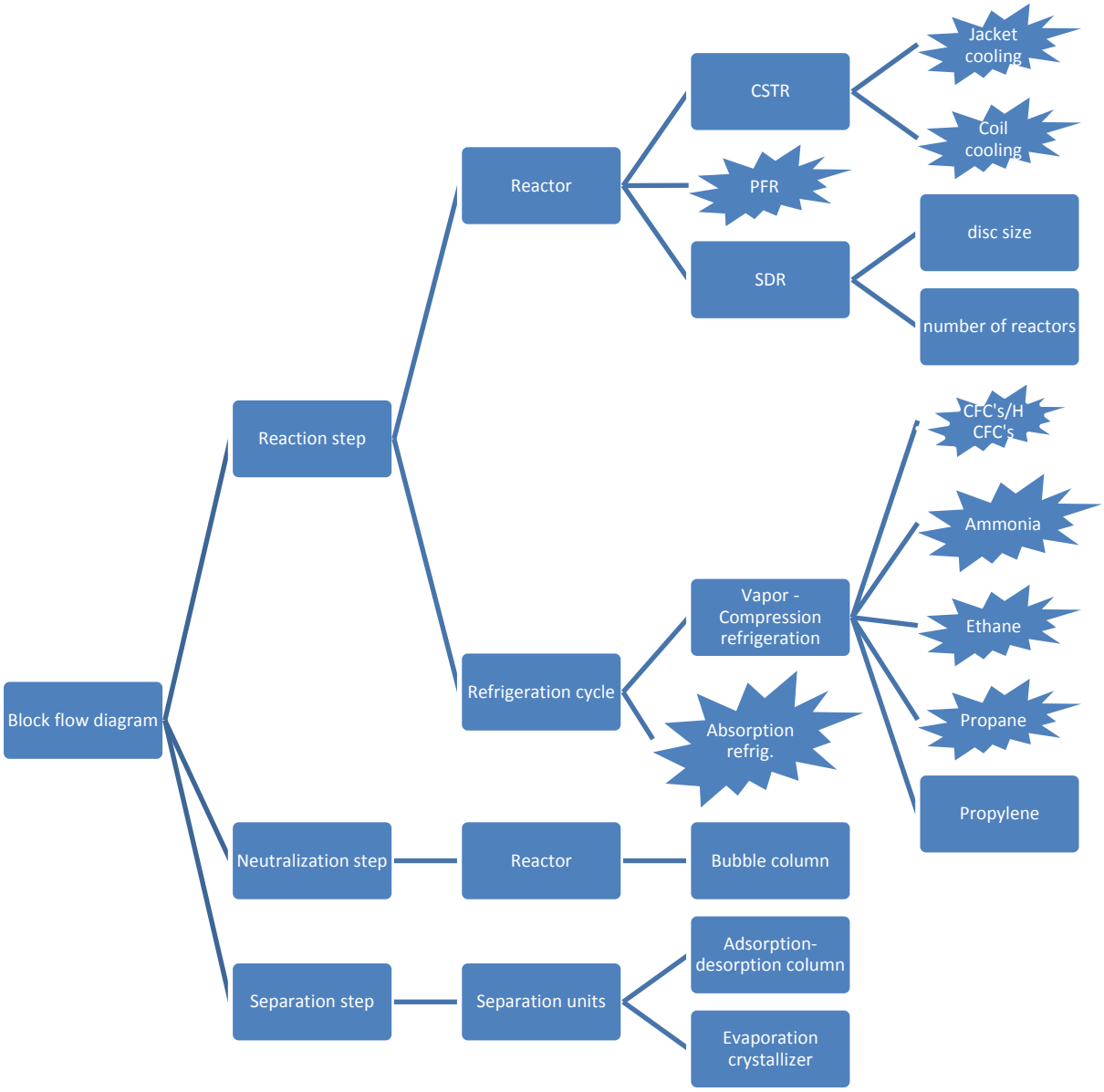

Figure 6 Decision tree on process design

Reaction step

For a reaction step, a reactor (or multiple reactors) will be required. Again the highly exothermic nature of the reaction is an important factor. Heat needs to be removed sufficiently fast to maintain a constant temperature. It is assumed that this rate for cooling the reaction will be the limiting rate in the reactor(s). Assumptions are that both the reaction rate as well as the dissolving rate of ammonium sulfamate are slower than heat removal rate necessary. The assumption for the reaction rate is based on the patent where drop wise addition of ammonium sulfamate to the reaction mixture is described to control the reaction, which implies that the reaction occurs very fast. Also, the dissolving time of ammonium sulfamate in the reaction mixture is estimated by setting up a micro balance over a spherical solid particle (see Appendix F: Solving the particle). Consequently, heat removal is a main design criterion.

Another important property that has consequences for the reactor choice is the viscosity of the reaction mixture. In Langlet's patent, it is described that the reaction became increasingly viscous as

the reaction proceeded, so that vigorous stirring was required. This implies that in an industrial process, good mixing properties are another design criterion.

Based on these two criteria three types of reactors are investigated:

- The continuous stirred tank reactor (CSTR)
  Stirring and mixing are assumed to be ideal in the CSTR. A few calculations are made to inspect whether cooling of this reactor is realistic. The heat of reaction is estimated Chapter 3: Concept stage. For an agitated tank, and a stirred tank with a cooling coil, relations can be found in (Rase 1977) to calculate the heat transfer. Using these equations, and with the estimated values as given above, it is possible to estimate the required area to achieve the cooling. This is for the agitated reactor of ~ 1.5m^3 around 330 m^2, and for the cooling coil, an area of the coil inside the reactor should be around the 500 m^2. These values are quite high, so other options are considered. More detailed calculations can be found in Appendix I: CSTR calculations.

- The plug flow reactor (PFR)
  To ensure ideal mixing, the flow within the pipe needs to be turbulent. A realistic estimate for the velocity through a PFR is around 1 m/s, and a diameter of 0.15 m, yielding a Reynolds number of 7500. The flow is turbulent, so enough mixing happens in the reactor. The heat transfer of a plug flow reactor can be estimated by using the Nusselt relations for flow turbulent flow through a pipe (Janssen and Warmoeskerken 2006). When using these relations, the required area of the reactor has to be larger than 300 m^2. More detailed calculations can be found in Appendix J: PFR calculations.

- Spinning disc reactor (SDR)
  To determine whether a SDR is a suitable reactor for this purpose, a brief description about the SDR is necessary. A SDR is a closed reactor, in which a rotating disc is the basis for the reactor, as can be seen in Figure 7. In this reactor a feed enters at the center of the disc, and will go onto the disc. Here the liquid achieves the angular velocity of the disc, and starts moving to the end of the disc due to the centrifugal forces. In this way the liquid spreads over the entire disc, and forms a very thin liquid layer. At the end of the disc the liquid falls of the disc, and is collected underneath the disc, and will flow out of the reactor. It is also possible to add a gas flow in countercurrent, so that comes in contact with the liquid film. This can be done to use the reactor for gas liquid reactions, or just as a sweep gas.

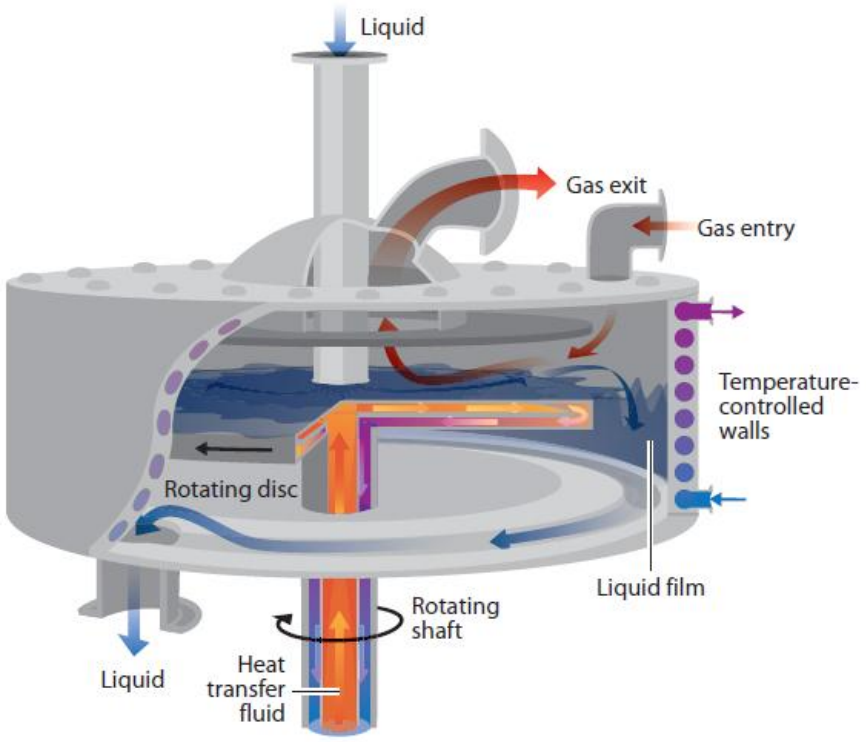

Figure 7: The spinning disc reactor

Due to the centrifugal forces, the liquid forms a very thin sheared film, which has ripples. These ripples enhance the surface area of the liquid, which results in better contact between the gas and the liquid. These ripples can be seen in Figure 8, which shows the ripples inside a spinning disc reactor. This combined with the fact that the film is very thin, makes the reactor ideal for heat and mass transfer. Heat transfer coefficients of 45 $W/m^2/K$ have been achieved. (Ramshaw 2004) When dealing with a very exothermic reaction, it is possible to use coolant inside the disc, as well as inside the walls of the reactor, to keep the entire content of the reactor on the desired temperature. The centrifugal forces also make sure that even if the liquid is viscous mixing is still obtained, and the liquid will still easily flow through the reactor.

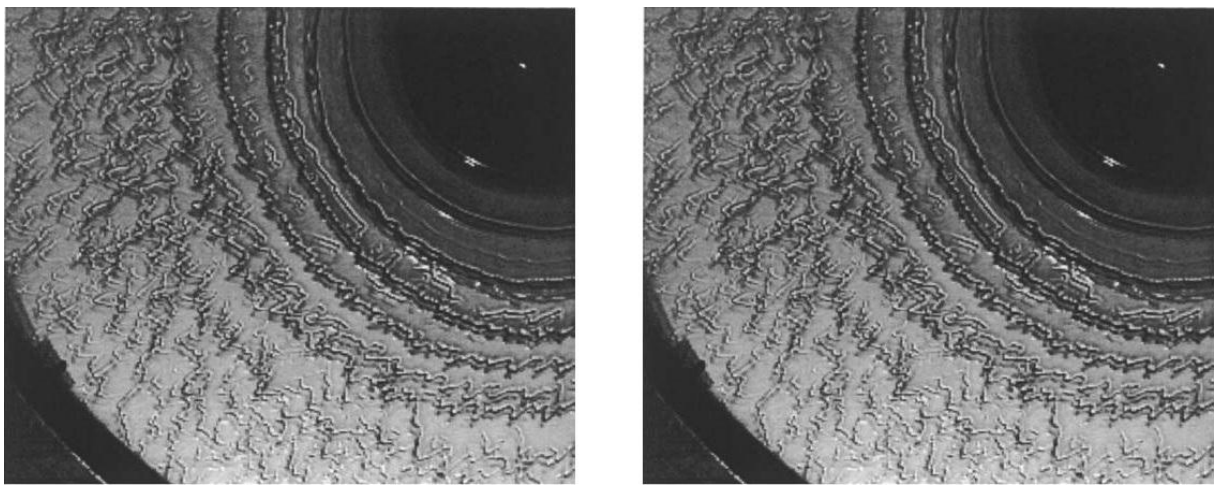

Figure 8: Ripple patterns inside a spinning disc reactor

The residence time inside the reactor is the time the liquid spends on the disc. This is dependent on different properties of the liquid, such as the viscosity and the density, as well as on the flow through the reactor, and the spinning speed of the disc. In most cases the residence time does not exceed more than a couple of seconds.

All of the above make this reactor very suitable for very fast exothermic reactions, even if the involved liquid is viscous. Due to the assumption that the reaction goes infinite fast, and the limiting step is the heat transfer, this reactor should be ideal for producing DNA.

Based on the above reactor descriptions, it has been decided to choose the SDR as the for the reaction step. In Chapter 4: Process design and description, more elaborate information is specified, such as the number of reactors required and calculations for the total heat flow leaving the SDR.

Refrigeration cycle

During the design of the reaction step, the issue of how the reactor will be cooled arises. An elaborate study has yielded that propylene is the best choice for refrigerant.

Before choosing a refrigerant, the first choice is made between different possible refrigeration systems. The two most common refrigeration cycles are compression refrigeration and absorption refrigeration. (ASHRAE 2010) Compression refrigeration makes use of the phase change from liquid to vapor and the fact that it takes energy for this change to take place and after this phase change mechanical work is used to compress the vapor to liquid again. With absorption refrigeration the same principle is used but the recovering part is done by absorbing the gaseous compound into a liquid and thereby reducing the partial pressure in the evaporator.

In the case of this design, compression refrigeration is the more valid option because it is currently more developed for industrial applications. Also, absorption refrigeration is especially useful when direct energy sources (such as burning of oil, solar energy, etc) are available, which is not the case for this process. Compression refrigeration makes use of electricity (in order to drive the mechanical systems) which is available as a utility on the chemical plant. (Dincer 2003)

Another very important point is the refrigerant used. This choice should be made so that the refrigerant is safe, environmentally friendly and has the right thermodynamic properties for the refrigerant cycle. It is widely known that the classes of refrigerants known as CFC's (or chlorofluorocarbons) are damaging to the environment and are therefore regulated. The potential damage done to the ozone layer by a refrigerant is classified by its Ozone Depletion Potential (or ODP) (EPA 2011). Alternatives for these harmful compounds are hydrochlorofluorocarbons (HCFC's) or hydrocarbons such as ethane and propane. However, HCFC's still deplete the ozone layer and will be phased out in the future, so it has been decided to choose a hydrocarbon refrigerant. The biggest downside of this class of refrigerant is the fact that they are flammable, but they are inexpensive and have no ozone depletion potential.

Within the hydrocarbon class the most used refrigerants are methane, ethane, propane, n-butane and isobutene. In order to decide which refrigerant fits our system best, the thermodynamic properties of these refrigerants are studied. When looking at these refrigerants, only three have the right thermophysical properties: ethane, propane and propylene. In order to compare these three refrigerants so that the best can be chosen, the pressure enthalpy diagrams are used to calculate

their respective coefficients of performance (COP). The COP is a measure for efficiency of the cycle and the refrigerant and is defined as:

$$COP = \frac{Refrigerating\ Capacity}{Compressor\ Power} \qquad \text{Eq. (4.1)}$$

Calculations of the COPs show that propylene is the best choice for refrigerant as it has the highest COP (and requires the lowest mass flow and compressor work). Therefore, it will be used as the refrigerant in the refrigeration cycle for this process.

Neutralization and separation steps

As mentioned before, priority is given to the reaction step and it is decided that the neutralization and separation steps are outside the scope of this project. However, some design is done for these two steps. The unit operations of these steps are the result of a single group brainstorm session. No in depth alternatives are considered for these steps.

For the neutralization step, the product leaving the spinning disc reactor becomes the feed for the neutralization. The feed for the neutralization is a viscous liquid, which needs to react with ammonia, which is a gas at standard conditions. Consequently, the reaction will be a gas-liquid reaction. Furthermore, the reaction needs to run at -16 °C. In the neutralization step, additional water needs to be added, to make sure that all the compounds dissolve completely, and no solids form in the column.

However it must be noted that the column as it is in the process includes mixing of strong acids with ammonia and water, which will cause a highly exothermic reaction. The following reactions take place:

$$H_2SO_4 + 2NH_3 \rightarrow (NH_4)_2SO_4 \qquad \text{Eq. (4.2)}$$

$$HNO_3 + NH_3 \rightarrow NH_4NO_3 \qquad \text{Eq. (4.3)}$$

$$HN_3O_4 + NH_3 \rightarrow NH_4N_3O_4 \qquad \text{Eq. (4.4)}$$

It was decided to use a 3 times excess of ammonia to make sure that all the reaction will go to completion. To show that the neutralization is highly exothermic, an estimation has been made for the heat balance of this neutralizer, which can be found in Appendix K: Cooling neutralization, and shows that the neutralizer will need a cooling of about 3 MW. So it is highly recommended to look at other ways to neutralize the acid flow.

The separation steps are directly scaled-up from the lab scale operations described in Langlet's patent (Langlet, Östmark et al. 1999). In his patent, the product stream from the neutralization step is flushed through an activated coal adsorber, and desorbed using hot water. Hereafter, the product is separated from the water by evaporation crystallization, yielding pure ADN.

Process description

Following the decisions made on unit operation design, two Process Flow Schemes are developed. One for the general ADN production process and a second PFS for the refrigeration cycle is designed.

In this section, the PFSs are explained step by step for all streams and all unit operations: first for the general ADN production process and then for the propylene refrigeration cycle. The PFSs and stream tables can be found in Appendix H: Process flow schemes.

ADN production process

To start with the SDR (R01) feed streams, the reactants are the sulfuric acid, nitric acid and ammonium sulfamate. The sulfuric acid streams <3, 4> and the nitric acid stream <5> are combined to produce the nitrating agent for the reaction, stream <9>. Two sulfuric acid streams are used, to regulate the water content in the reactors. Mixing is assumed to be ideal after the acid streams are combined. The acid stream <9> is in fact the nitration mixture. After cooling to -50°C with cooling propylene (E03) it enters the SDRs through stream <12>.

Parallel to this feed, solid ammonium sulfamate <7> is added to nitrogen, which acts as the carrier fluid <6> of ammonium sulfamate. Nitrogen is assumed to be available at 10 bar, and will be controlled to atmospheric pressure <10> (since the whole process is intended to operate at 1 bar). The nitrogen flow will be cooled to -50°C with cooling propylene (E02) similar to the nitration mixture stream <9>. Then, ammonium sulfamate is added to the cold nitrogen flow <11> using a solid addition unit (X01). The resulting flow <13> will be the other feed stream that enters the reactor.

The reactor feeds <12> and <13> are fed in twelve parallel continuous SDRs (R01). In the reactors, ammonium sulfamate will dissolve in the liquid nitrating mixture that is present as a thin film on the spinning discs. Ammonium sulfamate is nitrated to dinitramidic acid with nitrous oxide and ammonium bisulfate as by-products. The reactor is cooled with cooling propylene to remove the heat caused by the reaction as well as to maintain the reactor at -50°C. To prevent pressure build-up in the reactor by nitrous oxide, the nitrogen used as carrier fluid for ammonium sulfamate also has the role as a sweeping gas. Nitrogen and nitrous oxide will then exit the reactor at stream <14>. Assuming reactant conversion at 100%, the liquid product contains the nitration mixture with dinitramidic acid and ammonium bisulfate <15>. Furthermore, two spare reactors are kept stand-by and are available in case of reactor failure.

The liquid product <15> leaving the SDRs is then fed to the bubble column reactor (R02), where dinitramidic acid will be neutralized using ammonia gas <1>. Prior to feeding the ammonia to the bubble column, the stream is cooled to -20°C with a heat exchanger using cooling propylene (E01), which is the desired operating temperature of the bubble column reactor. The liquid feed then, is <15> and the bubble feed is stream <20>. In the reactor, counter current flow of ammonia bubbles and acids will neutralize the acid solution, producing ADN and other acid salts in solution. The solution will leave the column as bottom product <22> and unreacted ammonia will leave the column as top product <21>. An additional cold water stream <19> is fed to the bubble column in order to prevent the salts from precipitating. The water is cooled with propylene to 5°C. The bubble column also needs to be cooled due the exothermic neutralization reaction. The cooling of this reactor will be coupled to a different refrigeration cycle than the propylene cycle that is used for earlier mentioned cooling purposes, because the cooling load of the bubble column is estimated to be very large.

The bottoms product <22> of the bubble column is fed to an adsorption column (C01) with activated carbon. In this column, ADN is adsorbed and the waste streams containing the other acid salts in water will leave as waste streams <23>. After the adsorption process, the ADN will be desorbed by flushing hot water <18> through the column, as shown for (C02). Hot water is heated with steam to 80°C in E04. Adsorption and desorption flows are alternated by opening and closing valves. In the PFS, (C01) adsorbs ADN, while in (C02) ADN is desorbed. Regulation with valves will result in

adsorption in (C02) and desorption in (C01). It is assumed that multiple adsorption and desorption columns will be available. However, a calculation of the actual amount columns required and the development of cycle diagrams for the columns falls outside the scope of this project.

Finally, after desorption of ADN by hot water, the product stream <24> containing water and ADN, is fed to an evaporation crystallization unit (S01). Here, water is evaporated at 0.47 bar and 80°C. The compressor for the crystallizer is assumed to be in the crystallizer, and not designed. The heat required for evaporation is supplied by steam. After water is evaporated and leaves through flow <25>, ADN will crystallize and is obtained in the final product stream <26>.

Propylene refrigeration cycle

Propylene acts as refrigerant for the heat exchangers (E01), (E02), (E03) and (E05), and cools the SDRs (R01). In other words, propylene is used to cool ammonia gas <1> with (E01), nitrogen gas <10> with (E02), the nitration mixture <12> with (E03), and water <17> with (E05). Also, it removes the heat generated by the nitration reaction in the SDRs (R01).

In the refrigeration cycle, propylene <1> is split into five parallel streams <2, 5, 8, 11, 14>. Thereafter, it will pass through an expansion valve, which cause both pressure and temperature to drop <3, 6, 9, 12, 15>. This allows absorption of heat in the heat exchangers by evaporation of the cooling fluid <4, 7, 10, 13, 16>. After taking up heat from the ADN production process the refrigerant streams are combined again <17> and are compressed (K01), resulting in a rise of temperature and pressure <18>. The compressed refrigerant vapor will then pass through a condenser (E06), which is a heat exchanger that causes the vapor to condense isothermally and isobarically. This results in the initial stream <1>, closing the refrigerant cycle.

Furthermore, propylene can be refreshed by opening valves in propylene feed and exit streams <19,20>. At standard operation, these valves will remain closed. Finally, a bypass stream <21> is added to the parallel flows. This flow is designed for process control purposes; more information on this flow is given in Chapter 5: Process control.

Conclusion

In this chapter it is discussed how the process steps are translated into unit operations. The reaction will run in SDRs, the neutralization reaction takes place in a bubble column reactor and separation will happen through adsorption and desorption columns and evaporation crystallization. Cooling of the system is identified to be an important aspect of the process, which is why a refrigeration cycle is designed as well. Using these unit operations, a PFS on the general production process is designed. Another PFS is developed for the refrigeration cycle. Both can be found in Appendix H: Process flow schemes.

Chapter 5: Process control

In this chapter the process control will be described. The first part of the chapter will focus on the production process flow scheme, while the second part will focus on the refrigeration cycle. The process control is essential to make sure that the process can be operated and can run continuously in a safe manner. The process should be able to operate continuously, which is in general a complex procedure. For this the process control is essential, and all the vales should be controlled by flow controllers, which can be operated from an operating room. Also for a safety point of view it should be possible to operate the vales manually, so an operator can always interfere when something tends to go wrong.

The process flow diagram can be found in Appendix H: Process flow schemes for the process as well as for the refrigeration cycle.

Production process flow scheme

For the process flow scheme the flow, temperature, pressure and level controllers will be discussed briefly.

Flow controllers

All spinning disc reactor feed streams that enter the process are controlled with flow controllers that are coupled to their respective valves. To run the reactor at optimal conditions, which includes the stoichiometric ratios required, the flow controllers are essential. Besides the reactor feed streams, the water streams are also controlled with flow controllers. This will prevent precipitation of the acid salts in the neutralization reactor as well as to ensure that enough water is used for desorption of the product in the desorption column.

An additional flow controller that measures the flow of the product stream of the SDRs will be coupled to the ammonia feed stream. Both of these streams are feeds of the neutralization reactor. This flow controller will ensure that in case the product stream leaving the SDRs deviates from the specified amount, the ammonia flow is adjusted to accordingly.

Temperature controllers

Temperatures are specified for all streams and unit operations. This implies that many unit operations as well as a number of streams need to be cooled/heated - the SDRs, the nitration reactor and the evaporation crystallization unit. All these streams and units are cooled by heat exchangers. At these points, deviations from the specified temperature can lead to major complications. For example, if the SDR temperature rises too much, the reaction will run away. Therefore, whenever temperature plays a role, controllers measure temperatures at operating points and will forward their signals to the heat exchangers.

Pressure controllers

In this process, pressure control is relevant whenever a gas plays a role in a unit operation. In the SDRs, N_2O gas is produced as a by-product. Buildup of this gas in the reactor will lead to an increase in pressure resulting in dangerous situations. A pressure controller then allows the gas to be purged at faster rates. The same arguments are relevant for ammonia gas build up in the bubble column reactor and water vapor in the evaporation crystallizer, so in respective units pressure control is also necessary.

Level controllers

In both the bubble column reactor as well as the evaporation crystallizer, a mixture of liquid and gas is present. A constant liquid-gas level is important. Amongst one of the issues is that at increasing liquid levels, the reactor could leave the unit at the top, where the gas product is supposed to leave. Another example is when the liquid level is too low, the heat exchanger will start cooling the gas. This is not what the heat exchanger is designed for, which could lead to disturbances in the system.

Refrigerant cycle

Similar to the production process flow scheme, the refrigerant cycle also requires a control system to ensure that the heat exchangers have the correct cooling loads. The cooling loads of each heat exchanger depend on the extent of refrigerant expansion that is allowed prior to heat exchange. A flow controller measures the flow and gives feedback to the expansion valve, thereby regulating expansion. The set point of the flow controller is determined by the temperature controller, which measures the temperatures of the streams or unit operations that require cooling (or heating).

In actual operation, cooling loads and flows through the heat exchangers are likely to deviate from specifications. Therefore, a bypass is designed in the cycle that will measure the additional or reduced amounts of flow through the heat exchangers. The flow measured in this bypass will correct the amount of compression and cooling that is necessary for the refrigeration cycle. If for example less cooling is needed in one of the heat exchangers, less refrigerant will flow through the respective heat exchanger and flow through the bypass back to the compressor. This means that less energy is needed for as well the compression as for the condensation, because the mass flows are in that case less than specified, so less energy is needed for compression or condensation.

Conclusion

The ADN production process is mainly controlled by flow and temperature controllers. All streams that contain valves have flow controllers looped back to the valves. At many points in the process, maintaining or reaching a certain temperature is essential. Here, temperature measurements are coupled to the amount of heating or cooling that is required. Finally, unit operations where vapor–liquid mixtures are present also require pressure and level controllers to prevent pressure build up and overflow.

With respect to the refrigeration cycle, propylene is allowed to enter a bypass in case more or less heat duty is required. The flow measurer of this bypass will feedback to the valve of this stream as well as to the compressor and condenser. This way the refrigeration cycle is adjusted to the cooling demands, which are monitored by the temperature controllers in the general process flow scheme.

Chapter 6: Material and energy balances and utility requirements

This chapter summarizes the main results of the material and energy balance calculations. Material balances of unit operations, the overall mass balance of the whole process and the heat duties required are presented. Finally, the utility requirements are also summarized in this chapter. The material balances shown in this chapter are based on the process summary streams, which can be found in Appendix H: Process flow schemes.

Material balances

In Table 5, mass balances of all unit operations are shown. All in- and outflows of the unit operations are shown with their corresponding streams. It can be seen that all material flows balance as all inputs and outputs are equal to each other.

Table 5: Material balances of unit operations

Equipment	**Streams in**		**Streams out**	
	(kg/s)	stream #	(kg/s)	stream #
R01	1.100	<12>	0.192	<14>
	0.295	<13>	1.203	<15>
subtotal	**1.395**		**1.395**	
R02	1.203	<15>	0.596	<21>
	0.700	<19>	2.207	<22>
	0.900	<20>		
subtotal	**2.803**		**2.803**	
C01	2.207	<22>	2.141	<23>
C02	0.039	<18>	0.105	<24>
subtotal	**2.246**		**2.246**	
S01	0.105	<24>	0.039	<25>
			0.066	<26>
subtotal	**0.105**		**0.105**	

Table 6 shows the plant wide component balance. The mass flows of all chemical materials entering and leaving the process are tabulated in this table with their respective streams in mentioned as well. The overall mass balance is correct, as total mass streams in and out of the process are 3 kg/s.

Table 6: Total balance of the plant in terms of chemical components

Component	Streams in		Streams out	
	(kg/s)	stream #	(kg/s)	stream #
Water	0.77	<2>	0,80	<23> & <25>
H_2SO_4	0.22	<3> & <4>		
HNO_3	0.84	<5>		
Ammonium Sulfamate	0.13	<7>		
N2O			0,02	<14>
NH3	0.90	<1>	0,60	<21>
ADN			0,07	<23> & <26>
(NH4)2SO4			0,44	<23>
NH4NO3			0,94	<23>
Nitrogen	0.17	<6>	0,17	<14>
Total	**3.03**		**3.03**	

Energy balances

The enthalpies of many streams are not calculated for this process due to the lack of tabulated heats of formations. Also, many compounds (i.e. the nitronium ion) are not known in modeling software such as Aspen. Otherwise, the process could be modeled. Instead, since this process cooling intensive, the focus is on the heat duties that are required for cooling and heating. The cooling duty of the nitration reaction in the SDRs (R01) are assumed equal to the heat of reaction of the respective reaction. The estimation for the heat of reaction is given in Chapter 3: Concept stage. The neutralization reaction (R02) requires cooling as well. Its cooling duty is also directly related to the exothermicity of the reaction. The heat of reaction is estimated in Chapter 3: Concept stage. For the evaporation crystallization (S01), the duty is determined by estimating the evaporation heat:

$$\mathrm{Q} = H_{evap}\ \phi_n \qquad \text{Eq. (6.1)}$$

where Q (J/s) is the duty, H_{evap} (kJ/mol) is the heat of evaporation (at standard conditions) and φ_n is the molar flow. Finally, the cooling duties for the process streams are estimated by heat capacities and temperature differences:

$$\mathrm{Q} = c_p\ \Delta T\ \phi_n \qquad \text{Eq. (6.2)}$$

where Q is the duty (J/s), c_p (J/mol K) is the molar heat capacity, ΔT (K) is temperature change and φ_n (mol/s) is the molar flow. c_p is assumed to be temperature independent. The results of the cooling duties required are given in Table 7 below.

Table 7: Equipment heat duties

Equipment	Heat duty (kW)
E01	-84
E02	-13
E03	-145
E05	-59
E06	-2411
R01	-1189
R02	-3139
Total cooling	**7040**

Equipment	Heat duty (kW)
S01	90
E04	9
Total heating	**99**

Utility requirements

For the process as designed a number of utilities are required. In Table 8 below, the utilities requirements are listed. In the overall production process, a lot of cooling is necessary. The majority of this cooling is done with cooling propylene, for which the refrigeration cycle is designed. This is also the reason why most of the utilities required are for the refrigeration cycle. First of all, condensation of propylene in the refrigeration cycle (E06) is done with a relatively large amount of cooling water, 168 t/h. Another significant utility is electricity consumption due to compression of the refrigerant by the compressor (K01). A last utility concerning refrigeration is that the refrigerant needs to be refreshed, so some propylene is required.

Furthermore, a negligible amount of electricity is also required for running the SDRs (12 kWh/h). And finally, a small amount of low pressure steam is included for the heating of water stream <16>. A more elaborate table of utility requirements can be found in the Appendix R: Utilities.

Table 8: Utility requirements

Utility	Requirement
Cooling water (t/h)	168
Electricity (kWh/h)	1365
Low pressure steam (t/h)	0,1
Propylene (t/h)	21

Conclusion

In this chapter, material balances of the unit operations as well as material balances of the whole process are presented and shown to be “balanced”. The heat duties of heat exchangers and unit operations show that a relative large amount of cooling is necessary for the process. It should be mentioned that enthalpy streams could not be calculated due to insufficient data in literature. Finally, cooling plays the most important role in utility requirements when looking at the cooling water and electricity requirements for the refrigeration cycle.

Chapter 7: Equipment and unit design

This chapter will focus on the design of the different units in the process flow scheme. Because the focus of this design project is mainly on the first part of the process, not every column in the process flow scheme is designed in this chapter. This chapter will include design of the heat exchangers, the spinning disc reactors, and the global design of the refrigeration cycle. The other units are not designed in more detail. In Appendix L: Equipment summary and specification sheets, the equipment summary is given for all the units, while the specification sheets are only available for the units that are designed in more detail.

Spinning disc reactors

This part of the report will focus on the calculations of the SDR. initially, some calculations will be done about the flow in the reactor. After that, the calculations will go on to calculate the heat transfer, and the corresponding number of reactors that are thus needed.

Nusselt flow model

To do calculations concerning the heat transfer of the liquid to the disc, some assumptions have to be made. Firstly, the flow can be approximated with a Nusselt flow of a condensate film. With this assumption, the flow should be stable, ripple free, and not have circumferential slip at the interface between the disc and the liquid. This also implies that there is no shear at the gas liquid interface. The real reactor will deviate from this, in the sense that there will be ripples, and some slip at the disc liquid interface. (Ramshaw 2004)

With these assumptions, a force balance can be set up between $r = r$ and $r = r + dr$, which will give the radial acceleration for the fluid between $y = y$ and $y = s$. Here *r* is the radial distance on the disc, and *y* is the height in the film, and *s* is the thickness of the film.

$$\omega^2 r\rho(s - y) = \mu\frac{du}{dy} \qquad \text{Eq. (7.1)}$$

With the following boundary conditions:

- $u = 0$ at $y = 0$ (no fluid slip at disc liquid interface)
- $\frac{dy}{du} = 0$ at $y = s$ (no shear stress at gas liquid interface)

This equation can be solved to yield the film velocity, U.

$$U = \frac{\omega^2 r\rho}{\mu}\left(sy - \frac{y^2}{2}\right) \qquad \text{Eq. (7.2)}$$

The average velocity can be found by integrating the velocity between *0* and *s*, and dividing by *s*, yielding:

$$U_{av} = \frac{1}{s}\int_0^s U\,dy = \frac{\omega^2 r\rho s^2}{3\mu} \qquad \text{Eq. (7.3)}$$

The maximum film velocity at $y = s$ is given by

$$U_{max} = \frac{\omega^2 r\rho s^2}{2\mu} = 1.5U_{av} \qquad \text{Eq. (7.4)}$$

If the liquid enters the reactor at r_i with a mass flow φ_m, and achieves the angular velocity of the disc immediately, the mass flow rate at a certain radius r is given by:

$$\varphi_m = \rho U_{av} s 2\pi r \qquad \text{Eq. (7.5)}$$

Combining the previous two equations an equation can be formed for the thickness of the film, which can be used to get an equation of the average velocity, independent of the film thickness.

$$s = \left(\frac{3\mu\phi_m}{2\pi\omega^2\rho^2}\right)^{1/3} r^{-1/3} \qquad \text{Eq. (7.6)}$$

$$U_{av} = \left(\frac{{\phi_m}^2\omega^2}{12\rho\pi^2\mu}\right)^{1/3} r^{-1/3} \qquad \text{Eq. (7.7)}$$

With this the average time for the liquid to travel to the end of the disc can be calculated, and is given by (Ramshaw 2004):

$$t = \int_{r_i}^{r_o} \frac{dr}{U_{av}} = \frac{3}{4}\left(\frac{12\pi^2\rho\mu}{\varphi_m^2\omega^2}\right)^{1/3}\left({r_0}^{4/3} - {r_i}^{4/3}\right) \qquad \text{Eq. (7.8)}$$

Heat transfer

The heat transfer in the disc is about 100 times higher than the mass transfer. The mass transfer can be described with a penetration theory. However, the Fourier numbers concerning heat transfer are approximately 100 times higher than the Fourier numbers of mass transfer. This is because mass diffusivity is in the order of 10^{-9} m^2/s, compared to liquid thermal diffusivity, which is in the order of 10^{-7} m^2/s. Also, it is mentioned that the liquid film on the disc is very thin.

For these reasons it is safe to assume that the temperature profile in the disc can be described by a quadratic equation. If this is done, one will achieve the following temperature profile:

To calculate the heat transfer coefficient for the heat flow through the disc, the assumption can be made that the temperature gradient perpendicular to the disc is greater than the gradient in the radial direction. With this assumption the local heat flow into the film from the disc will be controlled by *dT/dy* at the disc surface.

$$Q = \lambda\left(\frac{dT}{dy}\right)_{y=0} = \frac{2\lambda}{s}(T_w - T_s) \qquad \text{Eq. (7.10)}$$

The effective heat transfer coefficient h is given by the formula:

$$h = \frac{Q}{\Delta T} = \frac{\frac{2\lambda}{s}(T_w - T_s)}{(T_w - T_s)} = \frac{2\lambda}{s} \qquad \text{Eq. (7.11)}$$

This effective heat transfer coefficient holds reasonably well, as long as the disc is fully wetted. This also means that film “dry-out” is not allowed, so the liquid should not break up in rivulets (Ramshaw 2004).

The SDR for the ADN process

When using the formulas as stated above, it is possible to calculate a heat transfer of the disc to the liquid film, and see if this type of reactor can achieve the desired cooling. For these calculations, the values are used as stated in Table 9. With these values it is possible to calculate the time on the disc, the film thickness, the liquid velocity, and the heat transfer. Then with the area of the disc, it is possible to see if the SDR can achieve the desired cooling. For the calculation of heat transfer, the

disc is split up in multiple sections, which each have their own heat transfer coefficient, and area. This is because the thickness of the disc is dependent on the radial position on the disc.

Table 9: Values for the SDR calculations

Parameter	Symbol	Value	Units	Details
Total mass flow	M	1.224 2.246	kg/s Kg/s	Fully continuous Weekend shut down
Viscosity	μ	0.032	Ns/m^2	Appendix E: Viscosity estimates
Density	ρ	1600	kg/m^3	Estimate
Entrance radiance	r_i	0.05	M	Estimate
Diameter disc	d	0.7	m	Bigger SDR to reduce amount of SDR's needed
Radius disc	r_0	0.35	m	
Speed		3500	rpm	Must be between 200 and 4000
Angular velocity	ω	366.52	rad/s	Calculated from the rpm
Heat transfer coefficient	λ_f	0.2853	W/m/K	Estimate by mass fractions of H_2SO_4, HNO_3 and H_2O combined with their own heat transfer coefficients (Janssen and Warmoeskerken 2006)

Here, the two possible options are investigated; the fully continuous, and the shut down during weekend's option. In both cases the number of reactors was minimized which were needed to achieve the desired cooling. It is determined that for the case of the weekend shutdown about twice as much reactors are needed as for the fully continuous. Due to the fact that the price of extra reactors is more than the salary for the employees to operate the plant, the choice was made for the latter of the two options.

As can be seen in Table 9 the speed of the spinning disc is $3500\ rpm$, which is near the maximum that can be achieved in a SDR. This is to improve the heat transfer, the higher the speed of the disc, the higher the achieved heat transfer, due to the smaller film thickness. Operating at $4000\ rpm$ does not affect the total number of reactors needed, so $3500\ rpm$ is preferred (a lower rpm results in less energy use and less chance of breakdown.)

In this case a single reactor must achieve the cooling of the 1188 kW divided by the number of reactors needed. The mass flow per reactor is then equal to the total mass flow divided by the number of reactors. Using these assumptions the values as shown in Table 10 are calculated, and the complete detailed calculations can be found in Appendix M: SDR calculations.

Table 10: Obtained values for the SDR's

Parameter	Symbol	Values	Units	Details
Number of reactors	-	12	#	Optimized to achieve cooling
Mass flow per reactor	M	0.102	kg/s	Total mass flow divided by number of reactors
Liquid transit time	t	0.279	s	Calculated
Film thickness at disc edge	s	3.33E-05	m	Calculated
Average speed	U_{av}	0.870011294	m/s	Calculated
Total heat transfer per reactor	Φ_q	102	kJ/s	Calculated
Total heat transfer	Φ_q	1220	kJ/s	Number of reactors times heat transfer per reactor

With the 12 reactors as mentioned in Table 10 the system is slightly overdesigned, being able to cool 2 kW extra per reactor. However, the SDR's are reactors with a spinning disc, which is the essential, moving, part of the reactor. This gives a higher risk of mechanical failure of the reactors. For this reason it was decided to install 14 reactors in parallel. This way the reactors are always able to operate with the desired cooling, and the capacity can still be met if one or two reactors need to shut down due to maintenance as another reactor can then be brought online as a replacement.

As can be seen in Table 10 the residence time of the liquid is around 0.3 seconds. In this time the solid particles need to dissolve, and the reaction needs to take place. For the reaction, a typical fast reaction time is fast enough, so it is essential to know if the particles are fully dissolved before the liquid leaves the reactor, and leave time for the solid to react. Calculations are done, and they show that the dissolving of the particles takes significantly less time than the residence time of the liquid in the reactor. Calculations of the dissolution time can be found in Appendix F: Solving the particle.

It is also possible to introduce a countercurrent sweep gas flow, which will have a big transfer area with the liquid, due to the ripples that the liquid surface will have in the reactor. This way the SDR can be used as a reactor for gas liquid reactions. In this process however, the reaction is no gas liquid reaction, meaning that this flow is not necessary. However the solid AS particles need to be transported to the reactor. This is done by a nitrogen flow, which will also act as a cocurrent sweep gas to remove the N_2O that the reactor produces.

Material selection

For the spinning disc reactors it is also essential to look at the material used. The choice for the material has to be made, based on the fact that the reactor needs to operate at -50°C, and the chemicals in the reactor are acidic. For this reason it has been decided to use glass lined stainless steel as material for the spinning disc reactors.

Conclusion

With the use of spinning disc reactors, it is possible to achieve the desired cooling for the exothermic reaction that takes place. A total number of 12 spinning disc reactors are needed, which have a disc that spins at $3500\ rpm$. With the use of these reactors, the residence time inside the reactors is 0.28 seconds. Also because the reactors contain a very fast moving part, it is decided to install two spare

reactors, which can be used in case of maintenance or breakdown of one or two of the reactors, making sure that the desired capacity is always met.

Heat exchangers

The heat exchangers are also designed in some more detail. For all of these heat exchangers the same procedure is used by first determining the load that the heat exchanger needs to cool or heat. Next a heat transfer coefficient is estimated for the type of heat exchanger, with the specific compounds. Then, the required area can be calculated with the formula below:

$$\phi_q = A * H * LMTD \qquad \text{Eq. (7.12)}$$

where A is the area needed for the transfer of the heat flow ϕ_q. H equals the overall heat transfer coefficient, and LMTD is the log mean temperature difference. Also, the materials used for these heat exchangers are specified. All the detailed values can be found in Appendix L: Equipment summary and specification sheets. The overall heat transfer coefficients are estimated using chapter 8 of (Couper, Penney et al. 2010).

E01 – Neutralization feed cooler

This cooler needs to cool the ammonia flow which goes into the neutralizer. The ammonia needs to be cooled to -20°C, and for this the propylene refrigerant cycle is used. The load to cool the ammonia is 83.59 kW, and the calculated log mean temperature difference is -70.1 °C. Using an estimate for the overall heat transfer coefficient of a pipe and tube heat exchanger, for gas-liquid heat transfer, the area needed can be calculated. The area needed for this heat exchanger is 19.87 m^2.

The materials chosen for this heat exchanger are stainless steel, which can resist the acidic nature of the components, as well as the low temperature.

E02 – Inert cooler

The inert cooler needs to cool the flow of nitrogen, which will be the gas that caries the AS into the reactor. The nitrogen needs to be cooled to -50°C, again by use of the refrigerant. The duty to cool the nitrogen is 13.05 kW. The design is again a shell and tube heat exchanger, with the same estimate for the overall heat transfer coefficient. The LMTD is -43.13 °C, which results in an area of 4.52 m^2. Again the materials that are chosen are stainless steel.

E03 – Acid cooler

This heat exchanger is a cooler to cool the acid flow to the desired -50°C before it enters the reactor. The capacity for this cooling is 144.81 kW. The cooling will be done with the refrigerant, yielding again a LMTD of -43.13 °C. With a shell and tube design, and a conservative estimate for the overall heat transfer coefficient, because of the viscous acids, the area needed is 15.04 m^2. For this cooler normal stainless steel is not sufficient in the tube side, due to the acids. For his reason the choice has been made to use glass lined stainless steel and normal stainless steel on the shell side.

E04 – Water heater

The water heater is used to heat up the water that will be used for the desorption step. For the heating, 9.12 kW is needed, which can be achieved by the use of steam that is available as a utility. By using steam, and setting the steam exit temperature on 140°C, in which case it is still steam, the LMTD becomes already 112.48°C, meaning that the area needed for the heat transfer is quite small. Thus the choice has been made to use a double tube heater. Using an estimate for the overall heat

transfer coefficient, the area needed comes to 2.38 m^2. As material choice, carbon steel should be sufficient.

E05 – Water cooler

This cooler cools the water that goes into the neutralization step. This water is cooled to 5°C, to cool it, without letting it freeze. Again the refrigerant is used, which must cool 58.66 kW. For this again a double pipe cooler is used, because the very high LMTD (-84.6 °C) results in an area of only 2.31 m^2. Due to the low temperatures carbon steel cannot be used, so instead stainless steel is used as material.

E06 – Condenser

This is the condenser of the refrigeration cycle, which needs to cool 2410.73 kW at 30°C to condense the refrigerant. This requires a quite large flow of cooling water, which is assumed to enter at 20°C, and leaves at 25°C. With these values, the LMTD becomes -12.33 °C. Using an estimate for the overall heat transfer coefficient, the area needed is 391 m^2. Also a flow of cooling water of 47 kg/s is needed to achieve this cooling. This illustrates that the condenser will by far need the most cooling in the whole factory. The material choice is normal carbon steel, which can be used due to the normal operating temperature and the mild properties of compounds.

Conclusion

Most of the designed heat exchangers are relatively small, except for the heat exchanger with the refrigeration cycle, which in the end needs to cool all the energy that the refrigerant takes up from the cooling of the reactor and the flows to the reactor. The detailed values that are calculated can be found in Appendix M: SDR calculations.

Refrigeration cycle

The process as it has been developed, now requires a cooling capacity of 2 MW. In order to provide this cooling, an appropriate refrigeration cycle has to be designed. As the cooling is one of the more challenging parts of the process, given its high exothermicity and the product decomposing at temperatures higher than -16°C, a refrigeration cycle is essential. As described in Chapter 5: Process control, the choice has been made for compression refrigeration.

The basic refrigeration cycle as used with vapor compression refrigeration can be seen below. The system starts with vapor at point 1 which is adiabatically compressed leading to point 2. This compression requires work put into the system to reduce the volume (this increases pressure and temperature). The high pressure vapor then goes to the condenser where it is liquefied (using air or water as heat sink) leading to the high pressure saturated liquid. The liquid then passes to the expansion valve where it's pressure and temperature drop again to a low pressure liquid refrigerant that is lead into the evaporator. In the evaporator, heat is taken from the medium to be cooled in order for the refrigerant to boil, which provides the cooling effect. This cycle as described now is a perfect refrigeration cycle. In reality the process will also have sub cooling (of the liquid) and superheating of the vapor, causing the cycle to deviate from reality. Also, in most cases were cooling below -30°C is required, a multistage compressor system is used. This is because in these cases the gap between the evaporator discharge temperature (which is the low temperature that is used to cool with) and the condenser discharge temperature (which is high enough so that the refrigerant can use its heat to cooling water or air). The refrigerant is then led in series through multiple compressor potentially with flash gas removal or intercoolers in between. (Stoecker 1988)

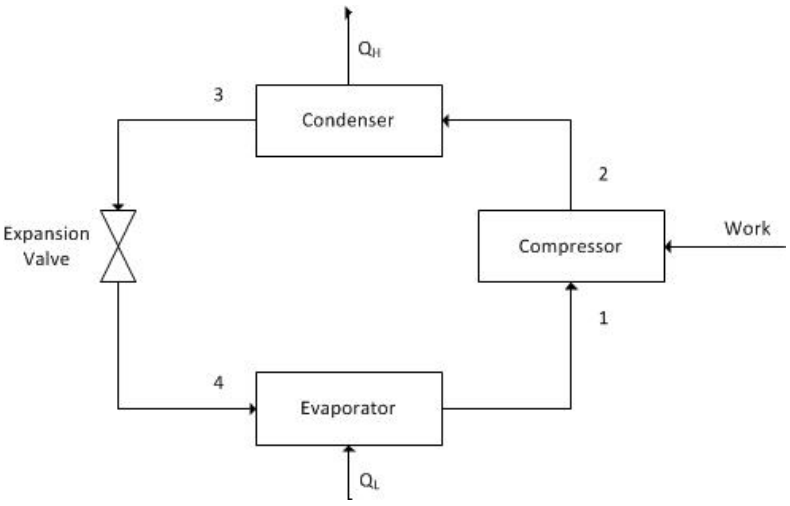

Figure 9: Schematic of a basic vapor compression refrigeration cycle (Koelet 1992)

As described in Chapter 4: Process design and description, the choice of refrigerant is very important, and the choice was already made to focus on the hydrocarbon class, which is better for the environment. Within the hydrocarbon class the most used refrigerants are methane, Eethane, Ppropane, Nn-Butane and isobutene. In order to decide which refrigerant fits our system best the thermodynamic properties of these refrigerants are studied. The refrigerant will have to have an evaporator temperature of around -70°C. This is because there needs to be a driving force between the medium to be cooled and the refrigerant, but this temperature cannot be lower than -70°C due to the nature of the reactor. Additionally, since it is preferable to use air or water as a heat sink in the condenser, the condenser temperature should be approximately 20-30°C. Therefore, when looking at the pressure enthalpy diagrams of the different hydrocarbons it can be determined which refrigerant requires the smallest pressure difference in order to establish these temperatures. The smaller the difference in pressure between evaporator and condenser, the less work the compressor will have to deliver, which means that the refrigeration cycle requires less power input.

A general (idealized) refrigeration cycle in the pressure enthalpy diagram can be seen in Figure 10. Since the condenser temperature is known and the liquid is saturated (and therefore on the black line), the corresponding point in the diagram can be determined as Condenser Out. After the temperature in the evaporator has also been determined (this is the -70 °C) and knowing that the pressure drop takes place with constant enthalpy in the expansion valve, the point for the Evaporator In can be determined. Then, the refrigeration load can be determined as the Evaporator Out point is assumed to be on the saturated vapor line. The refrigeration load is then the difference between Evaporator Out and Evaporator in. Finally, because it is assumed that compression takes place isentropically, the point for Compressor Out can be determined in the pressure enthalpy diagram.

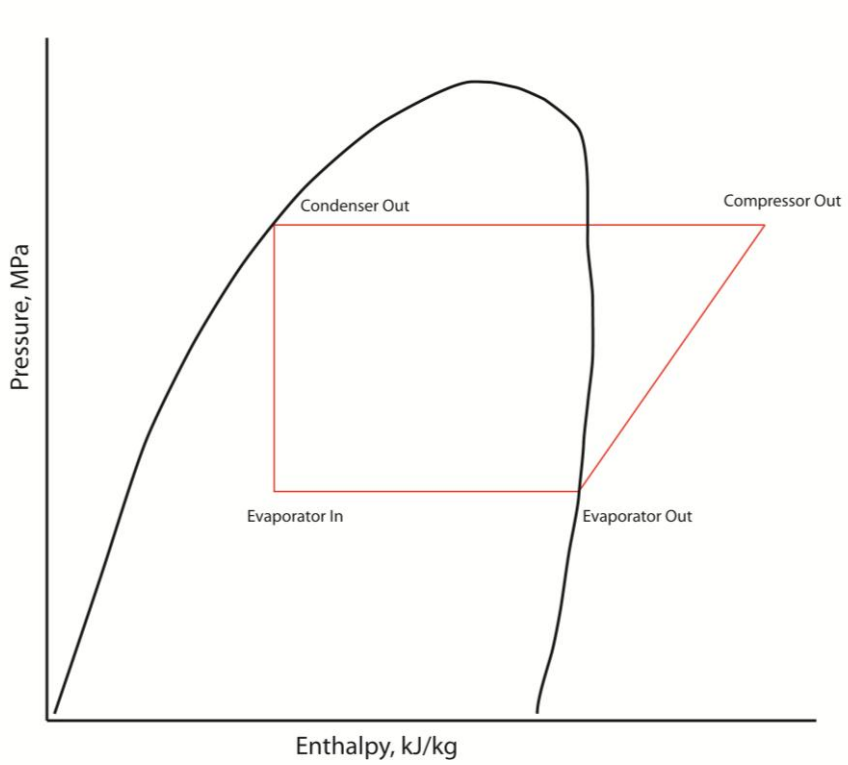

Figure 10: A generalized ideal refrigeration cycle

When looking at the possibilities for hydrocarbon refrigerants, only three have the right thermophysical properties: ethane, propane and propylene. In order to compare these three refrigerants so that the best can be chosen, the pressure enthalpy diagrams are used. With these diagrams as explained above, the enthalpy and pressure at all points can be determined and used to calculate certain decisive values. The diagrams for the three compounds can be found in Appendix N: Pressure-Enthalpy diagrams for hydrocarbons (ASHRAE 2009). The values as found in the pressure-enthalpy diagrams can be used to calculate the mass flow of refrigerant required:

$$\dot{\varphi_m} = \frac{Q}{H_{Evaporator\ Out} - H_{Evaporator\ In}} \qquad \text{Eq. (7.13)}$$

In Chapter 3: Concept stage it has been determined that the required cooling rate is approximately 1200 kW. When the mass flow is known it is also possible to calculate the compressor work rate:

$$W = \varphi_m * (H_{Compressor\ Out} - H_{Compressor\ In}) \qquad \text{Eq. (7.14)}$$

These values can then be used to calculated the so-called coefficient of performance or COP (Stoecker 1988). The COP is a measure for efficiency of the cycle and the refrigerant. In this case it means:

$$W = \varphi_m * (H_{Compressor\ Out} - H_{Compressor\ In}) \qquad \text{Eq. (7.14)}$$

All these parameters have been calculated for the three refrigerant possibilities, the results can be found in Table 11.

Table 11: Parameters for three hydrocarbon refrigerants

		Ethane	Propane	Propylene
H Evaporator In	**[kJ/kg]**	385	280	250
H Evaporator Out	**[kJ/kg]**	509.43	492.41	504.79
Mass Flow	**[kg/s]**	11.96	7.01	5.84
H Condenser In	**[kJ/kg]**	690	670	690
H Condenser Out	**[kJ/kg]**	388.42	278.83	277.21
Compressor Work	**[kW]**	2159.35	1244.07	1081.65
COP	**[-]**	**0.69**	**1.20**	**1.38**

As can be seen in the table, propylene is the best choice for refrigerant as it has the highest COP and the lowest mass flow and compressor work. Therefore, it will be used as the refrigerant in the refrigeration cycle for this process.

The only downside for this refrigerant is that the equipment will have to be sealed very well as the evaporator pressure is 0.032 MPa, which is lower than atmospheric pressure. The reason for the sealing is that air and moisture might leak into the refrigeration cycle which is not good for performance. However, the condenser pressure is 1.308 MPa, which is quite low and easy to reach. The compressor would therefore have to deliver 1082 kW, with a suction pressure of 0.032 MPa and a discharge pressure of 1.308 MPa and a throughput of 5.84 kg/s.

The condenser can be air cooled, water cooled or evaporative cooled. Due to the moderate heat load (2411 kW) the water cooler is the most logical choice, which is designed as E06 Condenser.

Conclusion

To summarize the best type of refrigeration to use is vapor compression refrigeration. The choice has been made to use propylene as the refrigerant, because it has the best coefficient of performance, requires the smallest mass flow, and least compressor work. This has a downside that the evaporator pressure is below atmospheric, which means that the equipment needs to be sealed very well.

Conclusion

This chapter dealt with the design of the reactors, heat exchangers, and a global design of the refrigeration cycle. These units are designed in more detail, while the other units were out of scope of a more detailed design.

In this chapter the reactors are designed as 12 spinning disc reactors, with 2 spare reactors installed. These reactors have a spinning disc inside, making them very capable of handling viscous liquids. Also this spinning disc creates a very thin liquid film, giving these reactors a very high heat transfer coefficient, making them capable of getting rid of the heat produced by the reaction.

Furthermore, the heat exchangers are designed, by estimating the overall heat transfer coefficients, and calculating the area needed. The choice has been made to use 4 shell and tube type heat

exchangers, and two double pipe heat exchangers, were the area needed for heat transfer is very small.

The refrigeration cycle was designed for the use of propylene as refrigerant, and the cooling of the designed heat exchangers: E-01, E-02, E-03, E-05 and the reactors. The mass flow required for the cooling of all these flows totaled 5.84 kg/s. Also the compressor work was calculated to be 1082 kW, and the condenser duty is 2411 kW. The condenser of the refrigeration cycle was designed as the heat exchanger E-06 Condenser, and the design can be found in Chapter 7: Equipment and unit design.

Chapter 8: Safety, health and environment

This chapter focuses on Safety, Health and Environment (SHE) of the ADN production process. Focus will be mostly on safety and health as these are the most pressing issues. In order to quantify the safety of this process the Dow fire and explosion index is used. With this index it is possible to quantify the degree of hazard of a process unit. Another way to raise awareness of safety issues is a Hazard and Operability study (HAZOP). A limited HAZOP is carried out for the most critical pieces of the process. Lastly, the risks of the reactants used are studied, together with the wastes produced by this production process.

Dow fire and explosion index

The Dow fire and explosion index (F&EI) is a step by step way to calculate the degree of hazard, which ranges from light to severe. The F&EI uses a material factor (MF) which is multiplied with the general process hazards factor and the special process hazards factor (DOW 1994). This results in a number which classifies the hazard of the process unit under consideration. The classification can be seen in Table 12.

Table 12: Degree of hazard classification according to F&EI number

F&EI	Degree of Hazard
1 - 60	Light
60 - 96	Moderate
97 - 127	Intermediate
128 - 158	Heavy
159 - up	Severe

The index was made to help engineers to identify and be aware of the risks involved with each process area. This would allow for improvement of potentially harmful situations.

Since the F&EI is set up over a process unit, first the decision has to be made which units will be studied. In this process, the most important units are the reactor, the neutralization vessel, the separation tank and the refrigeration cycle. Because of the scope of this project only the reactor and the refrigeration cycle associated with it will be studied (as two separate units). These units will be treated in the paragraph below. The refrigeration cycle is a potential hazard mostly because the refrigerant propylene is flammable.

Reactor

The determination of the F&EI uses many different hazards. For clarity, only the relevant general and special process hazards are shown in Table 13. For the complete list of hazards see Appendix O: Complete Fire and Explosion Index.

Table 13: Calculation of the Fire and explosion index for the reactor

Process Unit	**Reactor**
Material in Unit	Mixture
Material Factor	**24**
Nh	3
Nf	2
Ni	not known
General Process Hazards	
Base	1
Exothermic Reaction	1.25
Material Handling and Transfer	0.4
Factor F1	**2.65**
Special Process Hazards	
Base	1
Toxicity of the material	0.6
Pressure Penalty	0
Corrosion and Erosion	0.2
Leakage - Joints and Packing	0.1
Rotating Equipment	0.5
Factor F2	**2.4**
Total Factor	**6.36**
Fire and Explosion Index	**152.64**
Degree of Hazard	Heavy

The material factor has been determined using Table 1 in the Fire and explosion index hazard classification guide (DOW 1994). Here it is assumed that the mixture in the reactor undergoes a violent chemical change at high temperatures, giving the mixture an N_r rating of 2 leading to a MF of 24.

The N_h or NFPA Health rating has been determined to be 3, which according to (DOW 1994) corresponds to “Materials that on short exposure could cause serious temporary or residual injury, including those requiring protection from all bodily contact”. Since the reactor mixture contains acid and has a low pH, this classification is considered appropriate.

The reaction is also highly exothermic, which causes the reactor to receive the highest possible penalty of 1.25. Also, some combustible solids are handled which corresponds to a penalty of 0.4. This, together with a base penalty of 1, gives a general process hazard factor of 2.65.

For the special process hazards, the toxicity of the material (with $N_h = 3$) gives a penalty of 0.6. There is no penalty for the low temperature. The guide states that if there is no possibility of achieving

temperatures below the transition temperatures of the reactor material under normal and abnormal conditions, no penalty should be applied. There is also no pressure penalty since the reactor operates at atmospheric pressure. There is a penalty for corrosion because the acid reactor mixture is corrosive, so a penalty of 0.2 is applied. It has also been assumed that there is very little leakage in the joints, giving a penalty of just 0.1. However, due to the type of reactor used (spinning disc reactors) which have a lot of rotating equipment the penalty for rotating equipment is 0.5. This results in a total special process hazard factor of 2.2.

When these factors are multiplied the result is $F_3 = 5.83$. In order to find the fire and explosion index, this number is multiplied with the material factor, resulting in a F&EI of 139.92, which corresponds to a heavy degree of hazard.

Refrigeration Cycle

Again, to determine the degree of hazard the fire and explosion index hazard classification guide is used. For simplicity, only the relevant factors can be seen in the table. For the complete list of F&EI see Appendix O: Complete Fire and Explosion Index.

Table 14: Calculation of the Fire and explosion index for the refrigeration cycle

Process Unit	**Refrigeration Cycle**
Material in Unit	Propylene
Material Factor	21
Nh	1
Nf	4
Ni	1
General Process Hazards	
Base	1
Factor F1	**1**
Special Process Hazards	
Base	1
Toxicity of the material	0.2
Sub-Atmospheric Pressure	0.5
Pressure Penalty	0.49
Combustible & Flammable Materials	0.91
Leakage - Joints and Packing	0.3
Rotating Equipment	0.5
Factor F2	**3.9**
Total Factor	**3.9**
Fire and Explosion Index	**81.9**
Degree of Hazard	Moderate

The material used in the refrigeration cycle is propylene, which has known material factors and properties. They are stated in Table one of (DOW 1994). The general process hazard factor only comprises the base factor as none of the other penalties (exothermic reaction, endothermic reaction, etc) apply to the refrigeration cycle.

For the special process hazards the toxicity of the material gives a small penalty of 0.2. Since part of the cycle, the evaporator, operates at a pressure of 0.032 MPa, a 0.5 penalty is applied for vacuum operation. The process also has a high pressure of 1.308 MPa which gives another 0.49 penalty. Since propylene is combustible and quite a lot of the material is needed for the refrigeration cycle, this results in a penalty of 0.91. Also, the process is partly operated at low pressures which can potentially cause leakages. Lastly, the compressor used requires more than 500kW (in this case approximately 880kW)power. which gives a penalty of 0.5. This results in a total special process hazard factor of 3.9.

Then the fire and explosion index for the refrigeration cycle is 81.9, which means the degree of hazard is moderate.

Hazard and Operability Study

A Hazard and Operability Study (HAZOP) is a qualitative method that can identify the possible hazard in a plant that is still under design. This means that a HAZOP can lead to modifications in the P&ID diagram and in this way can be used to prevent accidents. In each HAZOP four questions are addressed to each piping section (Kletz 1999; Crawley 2008):

1. What can go wrong?
   Here a systematic procedure is used where all the relevant variables of the process (flow, pressure, temperature, etc.) are studied using guide words (such as no, more, less, etc.).
2. What will be the consequences of each incident that can occur?
   A qualitative assessment is made of the severity of the hazard that could occur where severity is ranked.
3. How often is each incident likely to occur?
   Again a qualitative assessment, this time of the degree of likelihood that a hazard can occur.
4. How can each incident be prevented?
   What changes need to be made in the piping section so that this incident does not occur?

Due to time constraints this project will contain only a limited HAZOP over the most important process section. The section that has been defined here as most important is the reactor section. The HAZOP will therefore focus on the reactor and the piping sections around it. Each piping section (or 'node') is studied along the four questions as defined above.

The reactor section has five associated piping sections that will be studied using HAZOP:

1. The in-stream containing H_2SO_4, HNO_3 and water
2. The in-stream containing ammonium sulfamate
3. The in-stream containing the inert sweep-gas
4. The out-stream containing N_2O and the sweep-gas
5. The out-stream containing the remaining reactants and products
6. The refrigerant stream

As a template the HAZOP tables as used in the Product and Process Design course will be used. The full tables can be found in the Appendix P: HAZOP tables.

Conclusion

The results from the HAZOP can be summarized as follows: valves need to be placed at every reactant stream so that if something goes wrong with one of the streams, all the other streams can be adjusted so that no dangerous situations occur. Also, it is decided that a redundant compressor should be added to the refrigeration cycle, as problems with the compressor could quickly lead to reactor shutdown which is detrimental for the production process.

Hazard prevention and risk reduction

To prevent the change of accident on the plant, there are a couple of safety precautions that can be used to reduce the risk, and prevent hazardous situations. The factory will produce the ADN, which is an oxidizer, which will mean that extra care should be taken with materials that can serve as a fuel. So, the refrigeration cycle should be sealed properly, to prevent leakage of the propylene to the ADN. Also no open fire should be allowed to reduce the risk of explosion or fire in the case of leaking propylene.

Waste

The further design of waste treatment is out of scope for this design, however it can be noted that if process options can be found for the neutralization and separation steps, it might be possible to recycle the acids and minimize the waste streams.

If the acid salts cannot be recycled, they might be used as fertilizers, which is a common application for these salts. This might be an opportunity to use the waste streams, and sell the waste, reducing the impact on the environment.

Life cycle analysis

As an addition to this project, a life cycle analysis was performed by a former member of this design project. This life cycle analysis was completed earlier than this project, so some values are based on estimates that can differ from the values obtained in this project.

This life cycle analysis compared the production of ADN with the production of the current oxidizer, ammonium perchlorate (AP). The conclusion of this life cycle assessment was that even though ADN production emits more NO_x, the use of ADN is still better than the use of AP because fewer acidification gasses are emitted in the atmosphere, due to the lack of HCL emission in the ADN process. However ADN gives increased NO_x emissions.

According to the life cycle analysis for the production of ADN, the main contributor to the emissions is the production of the raw material ammonia. This causes more pollution than the production of the ADN itself (Tzanetis 2011).

Conclusion

In this chapter, two ways to determine the safety of the process were used. First the Dow Fire and Explosion index is used.

The F&EI for the two most important process units is determined using the method as outlined in the F&EI manual. The first unit is the reactor which has a high penalty for the exothermic reaction leading to a high base factor. The special process factor is also quite high mainly due to a combination of corrosive reactants and moving parts. Together with the material factor for the reaction mixture, this leads to a F&EI of 153 which corresponds to a heavy degree of hazard. The second unit is the refrigeration cycle, which for general process hazards has only the base penalty. However, because propylene is flammable, the pressures in the system are quite high and the system contains rotating equipment, the compressor, the special hazards factor is quite high. The total combined with the material factor leads to a F&EI of 82 which corresponds with a moderate degree of Hazard. Concluding the F&EI study: the degree of hazard for the reactor is especially high and therefore special attention should be given to the operation of this unit.

A HAZOP of the reactor was also performed. This means that all the streams entering and exiting the reactor were studied to see if unforeseen changes to the system would have hazardous consequences. The conclusion that can be drawn from the HAZOP is that valves for controlling all the flows separately are essential and that a back-up compressor for the refrigeration unit is recommended due to the importance of cooling in the reactor system.

The treatment of the waste from the process is out of scope for this process; however the salts that are produced as waste now might be sold as fertilizer.

In addition, a LCA was done for the process which concluded that the production of raw ammonia would be the main contributor to the emissions as that causes more pollution than the production of ADN itself.

Chapter 9: Economic analysis

A very important part of any new project is the economic analysis, mainly because at the bottom line the installation should (with a high degree of certainty) be able to pay back its investment and generate some profit. For this project it is therefore decided to do an economic evaluation based on the competitiveness of the project, so the following criteria will be studied. To start the investment costs are estimated using the so-called 'Lang Method'. Then, the operating costs are determined using the criteria as defined in "Plant design and Economics for Chemical Engineers" (Peters and Timmerhaus 1991), leading to an estimated income and cash flow. These values can be used to determine certain economic criteria, here payback time (PBT), return on investment (ROI) and internal rate of return (IRR) are used. Finally, an economic sensitivity analysis is performed on the feedstock prices to examine the effect of price fluctuations.

Investment costs

In order to determine the total capital investment (TCI) the 'Lang Method' is used. This method consists of three steps (Seider, Seader et al. 2010):

1. Identifying all (relevant) equipment units in the project
2. Estimate cost per item (and transfer to actual costs, keeping in account inflation, size, etc)
3. Use the appropriate Lang factor to determine the TCI (with and without working capital)

Relevant equipment units

As can be seen in Chapter 7: Equipment and unit design, this project focuses on design of the reactor and refrigeration cycle. Since only these units are designed, the neutralization step and separation step have not been taken into account in the relevant unit list. Of course this means that a large part of the total equipment cost in the end will not be accounted for. However in order to find out the influence of these extra costs on the economic criteria, a sensitivity analysis has been performed (see section Sensitivity Analysis). When these assumptions are made, the unit list is comprised of the units found in Table 15.

Table 15: Relevant Equipment Units

Unit Name	Equipment Unit
R01	Reactor
E01	Heat exchanger
E02	Heat exchanger
E03	Heat exchanger
E04	Heat exchanger
E05	Heat exchanger
E06	Heat exchanger
P01	Compressor

Estimated item costs

The next step is estimating the relevant item costs. The unit costs for the compressor and heat exchangers have been estimated(Matches). Prices from this source are in $ from 2007, so inflation correction (CoinNews 2011) has been added and they have been converted to euro's using 1 $ = 0.71

€ (XE 2011). The reactor prices are derived from (Ramshaw 2004) and are converted from pound to euro's using 1 £ = 1.41 € (XE 2011). These estimations lead to the prices seen in Table 16.

Table 16: Prices for equipment units

Unit Name	Type	Amount	Actual Price	Total
R01	Spinning disc	14	€ 319,890	€ 4,478,456
E01	Shell and Tube	1	€ 25,449	€ 25,449
E02	Shell and Tube	1	€ 2,817	€ 2,817
E03	Shell and Tube (GL)	1	€ 21,838	€ 21,838
E04	Double Pipe (CS)	1	€ 929	€ 929
E05	Double Pipe	1	€ 2,213	€ 2,213
E06	Shell and Tube (CS)	1	€ 104,110	€ 104,110
P01	Screw	2	€ 362,974	€ 725,948
Total equipment costs				**€ 4,506,722**

For the spinning disc reactor, the price of a unit has been adjusted with a material factor of 1.5 for stainless steel that can resist the acid and a temperature factor of 1.3 for the operation at -50 °C (Peters and Timmerhaus 1991). Heat exchangers E01, E02 and E05 have been designed using stainless steel (and are therefore more expensive) to withstand the cold temperatures. These unit prices also include the 1.3 temperature factor. The E03 heat exchanger has been designed with glass lined stainless steel. The price for glass lined stainless steel. has been estimated by using the difference factor between normal carbon steel and glass lined carbon steel and applying that factor (1.3) to the stainless steel price. The heat exchangers E04 and E06 do not handle acids or extremely cold temperatures and can therefore be made from carbon steel with no temperature factor applied. More detail on these calculations can be found in Appendix Q: Cost estimates for equipment units. These unit prices lead to a total equipment cost of M€ 4.5.

Calculating the total capital investment

One method of calculating the total capital investment cost is using the 'Lang factor method'. With this method, a factor is applied to the total equipment cost to account for building, piping, service, utilities, etc., so that the total capital investment can be determined. The Lang factor differs for different kinds of processes; in this case it has been decided to use the factor for a "Solid-fluid-processing plant" (Seider, Seader et al. 2010). This Lang factor can be found in Table 17.

Table 17: Lang factors for a solid-fluid process

	Lang factor	TCI
Excluding working capital	4.28	€ 22,948,331
Including working capital	5.03	€ 26,969,651

The table shows that using respective Lang factors, the total capital investment (including working capital) for the reactor section of this project will be M€ 27.

Operating costs

The operating costs or manufacturing costs for a process are defined by Timmerhaus as being built up of:

1. Direct Production Costs
    a. Raw Materials
    b. Utilities
    c. Operating Labor
    d. Supervisory Labor
    e. Maintenance and Repairs
2. Fixed Charges
    a. Depreciation
    b. Plant Overhead Costs
3. General Expenses
    a. Financing Costs (interest)

Several more factors are mentioned by Timmerhaus, but it is specified in the CPD Manual that local factors (such as taxes, rent and insurance) are not to be taken into account, so these are not included here. Also, it is assumed that neither patent and laboratory charges, nor administrative charges need to be taken into account in this stage of the project.

Direct Production costs

The direct production costs of the project consist mainly of raw material costs. The cost per year (and thus per 2075 ton ADN produced) can be seen in Table 18. Please note that this table is for raw materials used in the entire process, including the neutralization and separation steps.

Table 18: Raw material cost for ADN per year

	ton/year	Cost/ton	Cost/year
Water	24440.20	€ 1	€ 31,283
H2SO4	6907.90	€ 70	€ 480,652
HNO3	26634.18	€ 156	€ 4,160,259
AS	4019.92	€ 420	€ 1,688,367
NH3	28382.40	€ 301	€ 7,356,499
Nitrogen	5266.51	€ 53	€ 280,442
Propylene	25	€ 1,070	€ 26,750
Total Raw Materials Cost			**€ 14,024,252**

The prices for raw materials have been derived from multiple sources. The price for H_2SO_4 , HNO_3 , NH_3 and propylene are from the ICIS pricing site (ICIS 2011). For the amount of propylene it has been assumed that the refrigeration cycle contains approximately 5 tons of propylene and is completely refilled 5 times per year, leading to a total of 25 tons of propylene needed per year. The price of AS is scaled from lab scale prices. The price for water is based on the price for drinking water. The price for nitrogen is based on the price for liquid nitrogen from (Fan 2007).The total raw material costs then amount to M€ 14 per year.

The utility costs have been determined by using the utilities requirements given in Appendix R: Utilities. The price for electricity is based on that of the low price of consumer electricity from (Nuon 2011). The price for cooling water and low pressure steam have been estimated using the correlations as defined in Timmerhaus, corrected for inflation and converted to euros. This results in the values as can be found in Table 19.The total utility cost are M€ 0.7 per year.

Table 19: Yearly utility cost for the production of ADN

Cooling Water	Consumption/year	Unit	Cost/ unit	cost/year
Electricity	11852280	kWh	€ 0.054	€ 644,764
Cooling Water	1471680	tons	€ 0.021	€ 31,347
Low Pressure Steam	1138.8	tons	€ 12.120	€ 13,802
			Total	**€ 689,913**

The hours of labor needed for the process have been estimated using the correlation in Timmerhaus, where it is decided that this process will be treated as a production process of average. The amount of supervisory labor needed is defined as 10% of the operating labor. The cost of labor has been estimated by using the values presented in the chapter Cost estimation of Timmerhaus, corrected and converted from dollars to euros . The result can be found in Table 20. The total labor costs for a year of production are M€ 0.84.

Table 20: Yearly labor cost for the production of ADN.

	Employee hours	$ per hour	€ per hour	€ per year
Operator	75	$38.27	€ 27.17	€ 743,825
Supervisor (10%)	7.5	$51.02	€ 36.22	€ 99,164
Total				**€ 842,989**

The costs for maintenance and repair of the plant are estimated (according to Timmerhaus) to be approximately 5% of the TCI, which corresponds to M€ 1.15.The total operating cost for a year of ADN production, as given in Table 21 is M€ 16.7

Table 21: Total yearly manufacturing costs for ADN

Type	Cost
Raw materials	€ 14,024,252
Utilities	€ 689,913
Labor costs	€ 842,989
Maintenance	€ 1,147,417
Total:	**€ 16,704,570**

Fixed charges

The fixed charges in this project are defined to be the depreciation and the plant overhead. The depreciation is determined as straight line depreciation of 10%. This means that 10% of the TCI. The

plant overhead is determined as 50% of the cost for labor and maintenance. The total for fixed charges can then be seen in Table 22.

Table 22: Fixed charges on a yearly basis for ADN production

Charge	Amount	Cost
Plant overhead	50% of labor, maintenance	€ 995,203
Depreciation	10% of TCI	€ 2,294,833
Total fixed charges costs		**€ 3,290,036**

General Expenses

The only factor that has been taken into account for the general expenses is the interest. It has been assumed to be 10% of the TCI, which means that interest costs are M€ 2.3.

Conclusion

The total yearly operating costs can be found in Table 23. It can be seen that the manufacturing costs are the most important. Of the manufacturing costs, the raw material costs are by far the largest. For this reason, the raw materials have been selected for a sensitivity analysis that can be found in the section on Sensitivity Analysis.

Table 23: Total yearly operating cost for the ADN plant

Manufacturing costs	**€ 16,704,570**
Fixed charges	€ 3,290,036
General Expenses	€ 2,294,833
Total operating costs	**€ 22,289,439**

Income and Cash flow

In the Basis of Design report, the selling price for ADN has been estimated at €21 per kg, for more information see Appendix S: Selling price for ADN. This, together with the operating costs and depreciation leads to a total annual cash flow:

$$CF = €43{,}575{,}000 - €22.289{,}439 = €25{,}875{,}227 \qquad \text{Eq. (9.1)}$$

Economic Criteria

In order to determine the potential of a project, economic criteria are often used. In this project it is decided to use payback time, return on investment and the internal rate of return as criteria. The time value of money is taken into account only for the internal rate of return calculations. The payback time outlines the time it takes for the TCI to be paid back with the estimated cash flows. The IRR is the interest rate that, in order to make more profit, a bank should offer for 10 years (lifespan of the project) so that putting the money in the bank is more profitable than investing in the project. For more information about the calculation methods behind these criteria and the exact values used see Appendix T: Economic Criteria.

These values are for a project with a 10 year lifespan (which is a safe guess given the market conditions) and can be found in Table 24.

Table 24: Economic criteria for ADN production

Criteria	Value	Unit
PBT	0.886884	years
ROI	87.95767	%
IRR	270.71643	%

It can be concluded from this numbers (low payback time, high ROI and high IRR) that the economic future of this project seems favorable. It should be noted that the IRR is very high, which is slightly unrealistic. It is believed this is caused by the fact that the TCI is very low compared to the cash flow generated. However, these criteria do not account for the downstream processing part that has not been designed yet. In order to see what the effect of extra equipment cost is a short analysis has been performed. Each of the criteria has been recalculated for added equipment costs of M€ 5, M€ 10, and M€ 15 to see if the viability still holds. These values were chosen because a doubling of the equipment costs (M€ 5) seems possible and while M€ 15 extra for equipment cost will not happen very likely it is a good way to estimate viability for an extreme case. (Higgins 2007)

Table 25: Economic criteria for extra equipment cost due to downstream processing

	Current	**M€ 5 extra**	**M€ 10 extra**	**M€ 15 extra**
PBT [year]	0.89	1.827	2.9	4.138
ROI [%]	87.96	38.286	21	12.126
IRR (10) [%]	270.72	87.83	39.81	24.9

It can be seen that the economic predictions for the process are still favorable even if the downstream processing costs are added. This means that even with M€ 15 extra costs the IRR is still 25%, which is good for a project of this size. Also the payback time will be 4,1 years which is still well under the 10 years production is expected to continue for.

Therefore, it is concluded that this project seems economically viable with the costs and selling prices as defined in this report even with equipment costs for downstream processing equipment added.

Sensitivity Analysis

Because the raw materials are such a large factor in the costs for the production of ADN, it has been decided to run a sensitivity analysis to see the change in cash flow and economic criteria if raw material prices rise or fall by 10%.the.

Table 26: Sensitivity analysis for the cost of raw materials.

Raw material cost	**Cashflow**	**PBT**	**ROI**	**IRR**
-10%	€ 27,277,652	0.84129	93.19	356.5
normal	€ 25,875,227	0.88688	87.95	270.7
+10%	€ 24,472,802	0.93771	82.73	104.3

Table 26 shows that even though the raw materials are the largest cost factor, a 10% increase in their costs have small effects on the economic parameters. Cashflow, payback time and return on investment stay roughly the same. Although the IRR decreases to 100%, it should be noted a 10% rise in raw material costs does not danger the viability of the project.

Conclusion

This chapter has shown that with a TCI of € 26,808,798, obtained with a Lang factor of 5.03 for solid-fluid processing plants and operating costs of € 22,289,439, of which the majority is raw material cost, the economic criteria used to test the viability of the project seem favorable. This means that a short payback period of approximately one year is realized, with a return on investment of 87.96% and an IRR of 270.72%.

Since these criteria are determined with a TCI that does not include equipment costs for the neutralization and separation steps, an analysis was done to test the criteria for higher TCI factors. It can be seen that even in an extreme case where equipment costs would rise by M€ 15, the economic criteria are still within levels that predict profitability, so it is expected that the entire process is economically viable.

Lastly, since the cost of raw materials plays a very important part in the operating costs, a sensitivity analysis is done where the effect of the raw material prices rising or falling by 10% is studied. It was found that this produced only slight variations in cash flow and the economic criteria. This means that fluctuations in raw material cost should not affect the profitability in a significant manner.

Chapter 10: Creativity and group process tools

In this chapter there will be a brief discussion of the creativity methods used and the group process as it has happened.

Creativity methods

Every design needs creative thinking to solve problems that are encountered along the way. In the case of this project the main issue that was encountered when developing the process was what reactor to use. The reaction is highly exothermic and needs to be operated at low temperatures, so normal reactors would be very unpractical. In order to solve this problem a creativity session was held using post-it notes for different reactor ideas. After little consideration the spinning disc reactor turned out to be the only viable option so it was decided to use this reactor in further designs.

Another method used for design was heuristics. These are rules of thumb that have been developed over the years. (Seider, Seader et al. 2010) has a very extensive list of heuristics that can be used in process design. Another good source of heuristics was our technical supervisor, Ir. drs. G. Bierman, who was often consulted. His knowledge was especially useful when trying to determine whether or not new ideas were practical and when trying to quantify a new design.

Group Process

Every project group has its problems, so did this one. As the reader can see, two of the group members that started have not been involved in the final design.

There are two reasons for this. One of the group members became seriously ill and unfortunately had to withdraw from the project.

The reason for the withdrawal of the second team member is a bit more complicated. When this project was started it was agreed that each team member would commit themselves fully to the project. However, not long after the project started it turned out this would not be possible for one of the team members. Being unable to commit causes the group member to quickly fall behind in knowledge about the project and the associated skills. In order to remedy this situation, the project group decided to call in the help of the group's creativity and group coach. After a group evaluation session the team member promised to fully commit and for a while this worked out. However, after some time it turned out that due to personal reasons the commitment seems unrealistic and by this time of 28 workdays this team member had missed about 11. During a follow-up session with the group coach, the team made clear there was little confidence that this team member would be able to make these days up and that the work that would be delivered would be of sufficient quality.

As a solution it was proposed that the team member is given a week to prepare a preliminary study of the process in batch form to make up time and regain trust of the team, so that the project could be finished with the original team composition. However, after missing multiple deadlines, it was decided by the supervisors and the team that the team member would not continue the project with the rest of the team and will continue with a separate project related to batch production of ADN.

Conclusions

The goal of this design project is to design a factory able to produce 2000 tons ADN annually, with the focus on the first step of the process. First a synthesis route is chosen. The choice of the synthesis route is made towards ammonium sulfamate as a raw material, which undergoes a double nitration, by a mixture of sulfuric acid and nitric acid as the nitrating agent. The choice for this synthesis route is made because of the relatively high yield, and the availability of the raw materials in bulk quantities, giving lower prices.

For this reaction no kinetic data, heat of reaction, conversion or selectivity was available. The only known fact is its a maximum yield at 50%. By using bond energies, the heat of reaction is estimated to be -1206 kJ/mol, and the heat of reaction for the decomposition reaction was estimated at 275 kJ/mol. Due to the high exothermicity of the overall reaction, it was decided that the heat removal should be the limiting factor in the reactor design. For this reason a product distribution of 100% conversion and 50% decomposition was chosen, giving the 50% yield, and the highest heat of reaction with this 50% yield.

Furthermore, the high yield was obtained in literature at a temperature of -50°C, and a mixture that contains the molar ratios of 1 mol AS : 1.8 mol water : 2 moles sulfuric acid : 12 moles nitric acid. The mixture at given composition is a viscous liquid.

The choice is made to operate at a fully continuous mode, because costs are lower and less investment is needed in reactors. Also, operating in a fully continuous mode decreases the flows, which is favorable from a safety point of view.

Next, the reactor is designed as 12 spinning disc reactors in parallel. These reactors are very capable of handling viscous liquids and have a high heat transfer coefficient. The 12 reactors are able to remove the heat formed by the reaction, operating at 3500 rpm. These reactors need in total a cooling of 1188 kW.

For the cooling load of the reactors, at the temperature of -50°C, a refrigerant cycle needs to be designed. For this cycle, the choice is made to use propylene, which gives the best coefficient of performance for our process. In this cycle a total of 5.43 kg/s propylene is needed to cool all the streams for the process. Excluded is the cooling of the neutralization step, because the design of this step was out of scope of the project. The refrigerant cycle operates at 0.32 bar, where the propylene is -70°C. The choice is made to not use a colder refrigerant because the reaction mixture can then achieve temperatures that are too low for reaction.

The downstream processing is designed globally, but not in detail. This downstream processing results in a neutralization column, in which the acids are neutralized, and the dinitramidic acid is converted to ammonium dinitramide. After this step an adsorption-desorption column system is added, in which the ADN is adsorbed, and the other salts are flushed through. Next the ADN is desorbed by the use of water at 80°C. The last step is a crystallizer in which by the use of evaporative crystallization the ADN crystals are formed.

Looking at the economics, this project looks favorable, even considering that the downstream processing is not included. The total capital investment is M€ 26.8, excluding downstream processing. An analysis is performed, which showed that even if the downstream processing costs

would be in the order of M€ 15, the process would still meet the criteria that predict profitability. The criteria used for analysis are the payback time, IRR and ROI. Also the economic feasibility is not very sensitive to increasing cost price of raw material, even though this is the main part of the costs.

Assessing the health safety and environment aspect of the process, it is found that according to the Dow Fire and Explosion index the reactors and the refrigeration cycle need extra attention, as they are identified to have a heavy and moderate degree of hazard. For the reactor this is due to the exothermicity of the reaction, and for the refrigeration cycle this is due to the use of propylene, which is flammable. Also a HAZOP of the reactors has been done, concluding that the valves controlling the flows to the reactors are essential.

Combining the process flow data with the economic analysis, it can be seen that the process looks promising for further design. Even if the downstream processing will be about 3 times as expensive as the reactor part, the process is still economically viable.

Recommendations

The following recommendations for further research into the production of ADN on industrial scale can be made:

- Perform study on the reaction kinetics. These are now unknown and if a process is to be designed further it is essential to know the kinetics.
- It should be attempted to get enough data about the reaction so that the process can be modeled in a software suite like ASPEN.
- A verification of the heat of reaction estimates should be done
- The neutralization step should be designed in more detail, keeping in mind that there will be a lot of heat released in this reaction.
- The separation step is now seen as an adsorber/desorber followed by an evaporator. These units should be designed in more detail and alternatives should be considered.
- If the adsorber/desorber is designed further a cycle diagram for this unit should be set up so that continuous operation will be disturbed as little as possible.
- At this point, cooling of the SDR is only done by propylene. Gas cooling is also possible, and further investigation on this possibility can optimize cooling in the SDR.

List of symbols

A	m^2	area
c_p	kJ/mol K	heat capacity
d	m	disc diameter
D	m	sphere diameter
$\mathbb{D}$	m^2/s	diffusion coefficient
E	kWh/h	electricity
h	W/m^2K	heat transfer coefficient
H	W/m^2K	overall heat transfer coefficient
H	kJ/kg	enthalpy
ΔH_r	kJ/mol	heat of reaction
ΔH_{evap}	kJ/mol	heat of evaporation
k	m/s	mass transfer coefficient
m	kg	mass
M	g/mol	molecular weight
M€	–	million Euros
Nh	–	National Fire Protection Association health rating
Nf	–	National Fire Protection Association flammability rating
Ni	–	National Fire Protection Association index
P	bar	pressure
Q	kJ/s	heat duty or refrigeration capacity
r	m	radial distance on disc
s	m	film thickness
t	s	time
t/h	–	ton/hour
t/a	–	ton/year
T	°C K	temperature
U	m/s	film velocity
v	m/s	velocity
V	m^3	volume
W	kJ/s	work rate
y	m	height in film
λ	W/mK	conductivity
μ	Ns/m^2 $Pa\ s$	viscosity
ρ	m^3/kg	density
ω	rad/s	angular velocity
$LMTD$	K	log mean temperature difference
ϕ_n	mol/s	mole flow
ϕ_e	kJ/s kW	energy flow
ϕ_m	kg/s	mass flow
	t/h	ton/hour
	t/a	ton/year
Re	–	Reynolds number
Nu	–	Nusselt number

List of abbreviations

ADN	ammonium dinitramide
AP	ammonium perchlorate
AS	ammonium sulfamate
CF	cash flow
CFCs	chlorofluorocarbons
CoP	coefficient of performance
CSTR	continuous stirred tank reactor
DCFROR	discounted cash flow rate of return
DNA	dinitramidic acid
F&EI	fire & explosion index
HAZOP	hazard and operability study
HCFCs	hydrofluorochlorocarbons
IRR	internal rate of return
LCA	life cycle analysis
MF	material factor
P&ID	process & instruments diagram
PBT	payback time
PFR	plug flow reactor
PFS	process flow scheme
ROI	return on investment
SDR	solid disc reactor
SHE	safety, health & environment
SRM	solid rocket motor
TCI	total capital investment

Literature

Arianespace, -. S. S. (2008). Ariane 5 User's Manual, Arianespace.

Arianespace. (2011, 2011). "Arianespace website - Ariane 5." Retrieved 27-05-2011, 2011, from http://www.arianespace.com/launch-services-ariane5/performance.asp.

ASHRAE (2009). 2009 ASHRAE Handbook - Fundamentals (SI Edition), American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

ASHRAE (2010). 2010 ASHRAE Handbook - Refrigeration (I-P Edition), American Society of Heating, Refrigerating and Air-Conditioning Engineers, Inc.

Bottaro, J. C., R. J. Schmitt, et al. (1993). Dinitramide salts and method of making same. United States, SRI International.

Chemwatch. (2010). "Chemwatch." Retrieved 27-05-2011, 2011, from http://max.chemwatch.net/integ/.

CoinNews. (2011). "US Inflation Calculator." Retrieved 15-07-2011, 2011.

Couper, J. R., W. R. Penney, et al. (2010). Chemical Process Equipment - Selection and Design, Elsevier.

Couper, J. R., W. R. Penney, et al. (2010). Heat Transfer and Heat Exchangers. Chemical Process Equipment - Selection and Design, Elsevier**:** 856.

Crawley, F. (2008). HAZOP: Guide to best practice, Institution of Chemical Engineers.

Dincer, I. (2003). Refrigeration Systems and Applications.

DOW (1994). Fire and Explosion Index Hazard Classification Guide.

EPA, U. S. E. P. A. (2011). "Ozone Layer Protection Glossary." Retrieved 06-07, 2011, from http://www.epa.gov/Ozone/defns.html#odp.

Fan, K. (2007). "Price of Liquid Nitrogen." The Physics Handbook Retrieved 14-07-2011, 2011, from http://hypertextbook.com/facts/2007/KarenFan.shtml.

Felder, R. M. and R. W. Rousseau (2000). Elementary principles of chemical processes, John Wiley & Sons.

Higgins, R. C. (2007). Analysis for financial management.

ICIS. (2011). "ICIS.com." from http://www.icis.com/StaticPages/a-e.htm#A.

Janssen, L. P. B. M. and M. M. C. G. Warmoeskerken (2006). Transport Phenomena Data Companion, VSSD.

Kletz, T. (1999). Hazop and Hazan: Identifying and assessing process industry hazards, Institution of Chemical Engineers.

Koelet, P. C. (1992). Industrial Refrigeration: Principles, Design and Applications. New York, Marcel Dekker, Inc**:** 429.

Langlet, A., H. Östmark, et al. (1999). Method of preparing dinitramidic acid and salts thereof.

Larsson, A. and N. Wingborg (2011). "Green Propellants Based on Ammonium Dinitramide." Advances in Spacecraft Technologies: 139-156.

Matches. (15-10-2003). Retrieved 14-07-2011, 2011, from http://matche.com/.

Nuon. (2011). "Prijzen Standaard Stroom." Retrieved 14-07-2011, 2011, from http://www.nuon.nl/stroom/standaard-stroom/variabele-energieprijzen.jsp.

Ostmark, H., U. Bemm, et al. (2000). "The properties of ammonium dinitramide (ADN): Part 1, Basic Properties and spectroscopic data." Journal of Energetic Materials **18**.

Peters, M. S. and K. D. Timmerhaus (1991). Plant Design and Economics for Chemical Engineers, McGraw-Hill inc.

Ramshaw, C. (2004). The Spinning Disc Reactor. Re-engineering the chemical processing plant: process intensification. A. Stankiewicz and J. Moulijn. Delft, Marcel Dekker**:** 81-131.

Rase, H. F. (1977). Chemical Reactor Design for Process Plants, Wiley and Sons.

Rhodes, F. H. (1928). "Viscosity Relationshis in the system sulfuric acid-nitric acid-water." Industrial and engineering chemistry **21**(2).

ROYMECH (2011). Fluid Viscosities.

Santhosh, G. (2005). Synthesis and Evaluation of Energetic Materials. Polymers and Special Chemicals Group, Vikram Sarabhai Space Centre. Thiruvananthapuram, Mahatma Gandhi University. **Doctor of Philosophy in chemistry:** 246.

Schmitt, R. J., J. C. Bottaro, et al. (1994). Process for forming ammonium dinitramide salt by reaction between ammonia and a nitronium-containing compound. United States, SRI International.

Seider, W. D., J. D. Seader, et al. (2010). Product and process design principles - Synthesis, Analysis, and Evaluation, Wiley.

Stern, A. G., W. M. Koppes, et al. (1998). Process for preparing Ammonium dinitramide, The United States of America as represented by the secretary of the Navy.

Stoecker, W. F. (1988). Industrial Refrigeration.

Tzanetis, K. (2011). Life Cycle Assessment: New oxidiser for advanced propellants. Delft, TU Delft**:** 19.

Venkatachalam, S., G. Santhosh, et al. (2004). "An Overview on the Synthetic Routes and Properties of Ammonium Dinitramide (ADN) and other Dinitramide Salts." Propellants, Explosives, Pyrotechnics **29**(3): 178-187.

XE. (2011). "XE - Universal Currency Converter." Retrieved 14-07-2011, 2011, from www.xe.com/ucc/.

Zevenbergen, J. (2011). Project Brief: New oxidiser for advanced propellants. Delft, TNO**:** 1.

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Appendix A: Project brief

CONCEPTUAL DESIGN PROJECT (CH3843)
~ PROJECT DESCRIPTION FOR TEAM CDP-3381 ~

Title: New oxidiser for advanced propellants.

Date of issue: 18/04/2011

Part 1: PROJECT SUPERVISION & CONTACT DETAILS

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Part 2: PROJECT OBJECTIVES & DESCRIPTION

Title: New oxidiser for advanced propellants.

Background

Currently the European Ariane 5 launcher and the soon to be phased out Space Shuttle use ammonium perchlorate as oxidiser in the solid rocket motors (SRMs) to generate sufficient thrust to escape Earth's gravity well. In these SRMs roughly 70 wt% of the propellant mass is ammonium perchlorate. Ammonium perchlorate has two major disadvantages. Firstly, upon combustion a substantial part of the ammonium perchlorate is converted to hydrochloric acid, which is particularly harmful on the ground. In the air, studies have shown that the influence of the exhaust gases of solid rocket motors is negligible. Secondly, the power generated by these SRMs could be improved if ammonium perchlorate would be replaced by more energetic oxidisers, which will significantly reduce launch costs. When ammonium perchlorate would be replaced by ammonium dinitramide, the result would be an increase in thrust of roughly 6 - 7 %, which equates to a reduction in launch costs by 50%.

Ammonium dinitramide, originally synthesized in Russia, has received a lot of attention in Europe as a possible replacement for ammonium perchlorate. The substance has now reached a so-called Technology Readiness Level sufficiently high enough to encourage the investigation of large scale production plants needed for supplying rockets the size of Ariane 5.

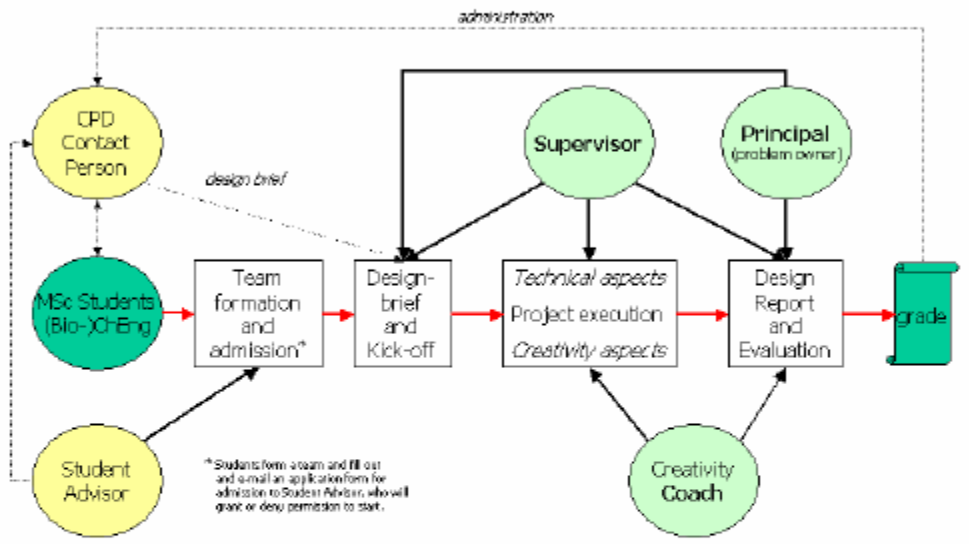
Objectives

- Design goals (process and/or product): the current accepted production process for ammonium dinitramide consists of 3 major steps. The task for the team is to start with the first major step, design the plant and identify the bottlenecks that need to be solved in order to optimise the process. Upon completion of this phase, the second major step is designed, bottlenecks identified and integrated with the first major step. The same applies for the third major step. The outcome of the project would be at least a CPD of the first major step.
- Design Basis/Specifications (e.g. scale, capacity, purity, feed & product composition, conditions, ...): the design team should consider the current launch rate of the Ariane 5 rocket and derive from that the required scale and capacity. The other specifications will be supplied during the kick-off meeting and are available.
- Constraints (e.g. environment, regulatory, ATEX, GMP, ...). the design team should recognize that an energetic oxidiser will be produced and hence that safety is of utmost importance.

References/Topic Specific Data

The design team is challenged to find the appropriate literature needed for completing the task described above. During the kick-off any relevant but missing data will be supplied by the principal.

Part 3: ORGANISATION AND SCHEDULE OF PROJECT



The team is responsible for communication between the team members and the principal, supervisor and coach, i.e. appointments for meetings, writing of minutes, distribution of the report, inviting representatives for the assessment meeting, organising presentation facilities, etc.

Note that the technical supervisor and the principal may not live in the vicinity of Delft and may not travel to Delft frequently. Therefore, plan ahead for meetings, propose several dates and don't expect others to agree on the first date you propose. The team should convince the principal and supervisor that the project is in good hands by keeping them up-to-date on the progress by telephone and/or e-mail. Please make the necessary arrangements during the kick-off meeting.

Prior to the multiplication and distribution of the final report, a draft should be sent to the technical supervisor. Upon his approval, the report can be multiplied in black & white (!) and bound; arrange this with the student contact person. Then the team can distribute the report, and the arrangements for the assessment meeting can be finalised. Please make sure all people involved in the assessment meeting own a hard-copy of the final report two weeks before the meeting, unless agreed otherwise. Please note that two PDEng trainees may take part in the milestone meetings; if so, they also require a hard-copy of the report. The student contact person will inform you in time.

The Conceptual Design Project is a **12 credits** course. This equals **336 hours** of nominal effort, roughly equal to 8½ forty-hour working weeks, usually spread out over 10 to 11 weeks. Please note that, like with

every other course, the effort you may have to put in could exceed the nominal effort. It is highly recommended that all team members don't plan too many other activities (including attending other courses) or holidays during or right after the scheduled project. Tell the other team members and the student contact person about your plans during this period during the "issue of project" meeting.

Below is an example of what could be your CDP project schedule. Keep in mind that this schedule is tentative. The team will present its plan (project approach) and planning during the kick-off meeting. During this meeting, the team and staff will make clear arrangements and set deadlines.

Milestone	Date or week	Duration	Action
Issue of project description	**April 19** week 16	1 hr.	To be arranged with student contact person.
Submit articles on creativity	week 16		E-mail to coach.
Discuss creativity articles	week 16/17		To be arranged with coach.
Prepare presentation for kick-off	Week 16/17		Done by team.
Kick-off Meeting (With principal, supervisor and coach, incl. presentation by team)	**week 17** (1 week after briefing)	2 hrs.	To be arranged by team.
Submission of the Basis of Design (BOD) Report	week 19 (3 weeks after briefing)		Post or e-mail to supervisor, principal and coach.
Prepare presentation for BOD review			
Review of the Basis of Design (With principal and Supervisor, incl. presentation by team)	**week 20** (4 weeks after briefing)	2 hrs.	To be arranged by team.
Submission of draft report	week 24 (8 weeks after briefing)		Post or e-mail to supervisor.
Submission of the final report	week 26 (10 weeks after briefing)		Post and e-mail to supervisor, principal and coach.
Prepare presentation for assessment meeting			
Assessment Meeting (With principal, supervisor, coach, incl. presentation by team)	**week 27** **July 3 – July 9** (11 weeks after briefing)	3 hrs.	To be arranged by team.

Facilities

Group page on Blackboard

To share information within the team and with supervisors, the team will be given access to the Group's facilities on the TUD Blackboard system (CH3843/Groups/CDP-xxxx).

Shared network space

The team will also get a dedicated filing directory on the TUD network: I:\Courses\CH3843\CDPxxxx.

Meeting room (informal)

If available, the team can have a meeting room in the basement of the ChemE building (rooms K.425, K.426, K.427, and K.432). These rooms are meant for having private meetings and storage of books and paperwork.

The rooms may be equipped with one or two PC's connected to the network and internet, a whiteboard and some tables and chairs. Additional PC's will not be provided, so you'll need to go upstairs to one of the computer rooms. Alternatively, you can bring your own laptop to connect to the wireless network.

Please contact Mr. Ruud de Ruiter (room 1.027) to acquire a key to the office in exchange for a €20 cash deposit, which will be refunded when you've cleaned up the room and returned the key. Use of a meeting room is not guaranteed due to limited availability.

Use of household appliances (e.g. water boilers, coffee makers, toasters, refrigerators) is prohibited. Staff members will remove these appliances upon discovery. Please make sure that all windows are closed properly when you leave the room to prevent water from flooding the room during heavy rainfall (not uncommon in basements in Delft!) and prevent thieves from entering the building. When a window doesn't shut properly, inform Mr. Ruud de Ruiter immediately.

Meeting room (formal)

The PPE conference room (room 1.404) is at your disposal for milestone meetings. Please contact the PPE secretary Mrs. Caroline Monna (room 0.418) for reservations of the room, beamer and laptop.

Final arrangements upon project completion

After the assessment meeting, the supervisor will submit the grade(s) to the student contact person for his administration. The student contact person will only send the grades to the grades administration at Educational & Student Affairs when the students have complied with the following rules:

1) Submit a hard-copy of the report and a CD/DVD to the student contact person for the education's archive. The disc should contain all your report and presentation files and all other files generated during the project.
2) Clean up your room. Don't forget to take all your belongings.
3) Return the keys of the room to Mr. Ruud de Ruiter and collect your cash deposit.

Thanks in advance.

Appendix B: Pure component properties

PURE COMPONENT PROPERTIES

Component Name	Technological Data									Health &Safety data							
Design	Formula	Mol. Weight g/mol	Phase	Boiling Point [1] °C	Melting Point [1] °C	Flash Point [1] °C	Liquid Density [2] kg/m^3	Vapour Density [3] kg/m^3	Heat Capacity [a], [b], [c] kJ/kg/K	Auto-ignition Temp. [1] °C	Flammable Limits % by vol in air	Lower Explosion Limit (LEL) %	Upper Explosion Limit (UEL) %	LC $_{50}$ In air/ water Mg/m^3	MAC Value Mg/m^3	LD$_{50}$ Oral [4] g	Chemical Reactivity
Ammonia	NH_3	17.04	V	-33.4	-77.7	N.A	0.9 [7]	0.60	2.06	669.0	0.5967	16.0	25	2000 ppm/4H (rat)		10.5	Toxic gas, corrosive
Ammonium hydrogen sulfate	NH_4HSO_4	115.109	S	350 decompose	145.0	N.A	1.79 [7]	N.A.	not know	N.A.	N.A.	N.A	N.A.			149.8 (rat)	
Ammonium Dinitramide	$H_4N_4O_4$	124.06	S	93.2	< 150	N.A	1.82 [7]	N.A.	1.80	N.A.	N.A.	N.A	N.A.			< 70 (rat)	
Ammonium Nitrate	NH_4NO_3	80.04	S	210	169.6	N.A	1.72 [7]	N.A.	1.74	N.A.	N.A	N.A	N.A			155.19 (rat)	Soluble in water
Ammonium sulfamate	$NH_4SO_3NH_2$	114.14	S	160 decompose	130	N.A	0.95 [7]	N.A	1.30	N.A.	N.A	N.A	N.A.			217 (mouse) - 140 (rat)	Weak oxidising agent
Ammonium sulfate	$(NH_4)_2SO_4$	132.14	S	N.A.	235-280 (decompose)	N.A	1.77 [7]	N.A.	1.42	N.A	N.A	N.A	N.A			105	Very soluble in water
Dinitramidic acid	HN_3O_4	107.026	not known	-16 decompose	-16 decompose	not know	not know	not know	not know	not know	not know	not know	not know	not know	not know	not know	
Nitric Acid	HNO_3	63.02	L	86(122@68%)	-42	N.A	1.3-1.42 [7]	1.5 [8]	1.70	N.A		N.A	N.A			30.1	Highly corrosive
Nitrogen	N_2	28.02	V	-195.8	-209.9	N.A.	N.A.	0.97 [8]	1.04	N.A.	N.A.	N.A.	N.A.				
Nitrous oxide	N_2O	44.013	V	-88.5	-90.8	N.A.	1.23 [9]	1.53 [8]	0.88			None	None	160 mg/m^3/6H (rat)			
Propylene	C_3H_6	42.0797	V	-47.4	-185.2	-108	0.5193 [7]	1.49 [8]	1.87	499		2	11.1	8.4-9.6 mg/L (fish)			extremely flamable
Sulfuric Acid	H_2SO_4	98.7	L	315-338	3-10	N.A	1.6-1.84 [7]	3.40 [8]	1.00	N.A		N.A	N.A	510 mg/m^3/2H (rat)		149.8 (rat)	Highly corrosive, very soluble in water
Water	H_2O	18.02	L	100	0	N.A	0.99987	>1 [8]	4.18	N.A	N.A.	N.A	N.A	N.A.	N.A.	N.A.	Polar liquid

Notes:

[1] At 101.3 kPa

[2] Density at 25 °C, unless specified otherwise

[3] At 0 °C

[4] Oral ingestion in (g) for a male of 70kg weight (Value*70)

[5] Density at -47 °C from H_2O at 4 °C

[6] Density at -45 °C from H_2O at 4 °C

[7] Specific gravity, water =1

[8] relative vapor density, air =1

[9] specific gravity @ -89

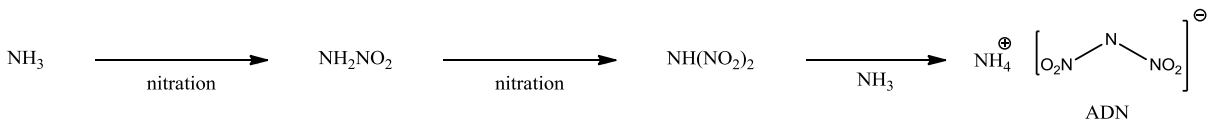
*Converting mg/m3 -->ppm & vice versa: mg/m3 to ppm calculator

Appendix C: Description of chemical reactions

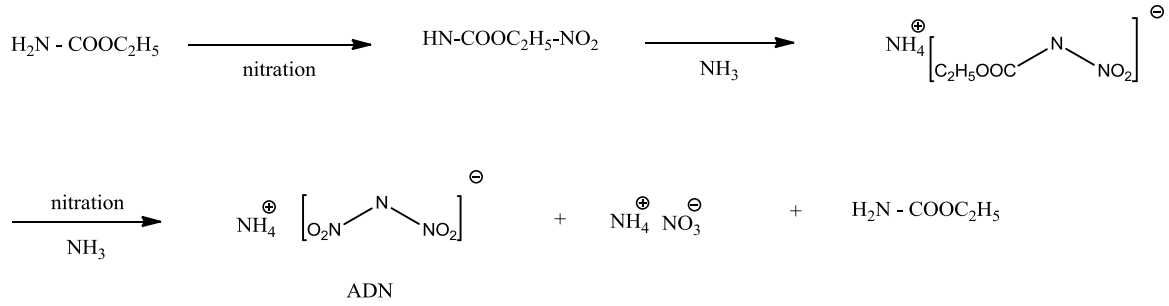
Synthesis options by (Bottaro, Schmitt et al. 1993; Stern, Koppes et al. 1998; Langlet, Östmark et al. 1999).

For more information the reader is referred to the Basis of Design report.

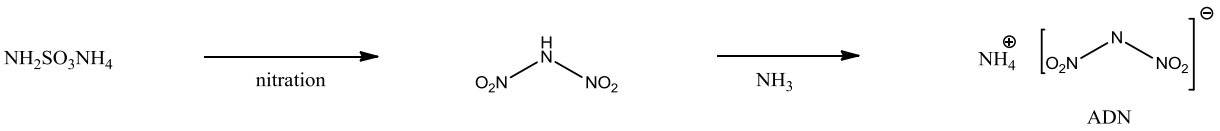
(1)



(2)



(3)



Appendix D: Bond energy calculations

Table 27: Bond energy calculations for Ammonium sulfamate

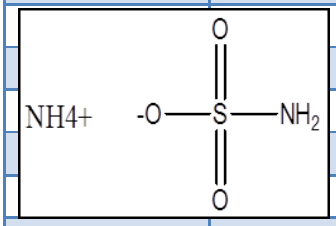
Ammonium Sulfamate		# of bonds	Type	Energy	total
		1	NH4+		0
		2	S=O	522	1044
		1	S-O	452	452
		1	S-N	335	335
		2	N-H	386	772
				Bond E	**2603**

Table 28: Bond energy calculations for Nitronium Ion

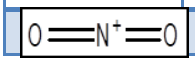
Nitronium Ion		# of bonds	Type	Energy	total
		2	N=O	607	**1214**

Table 29: Bond energy calculations for DNA

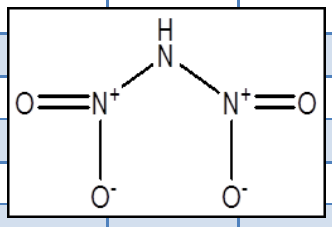
DNA			# of bonds	Type	Energy	total
			2	N=O	607	1214
			2	N-O	201	402
			2	N-N	167	334
			1	N-H	386	386
					Bond E	**2336**

Table 30: Bond energy calculations for NH4HSO4

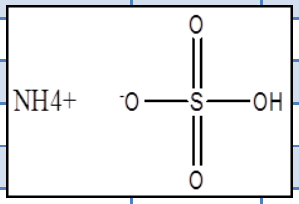
NH4HSO4			# of bonds	Type	Energy	total
			1	NH4+		
			2	S=O	522	1044
			2	S-O	452	904
			1	O-H	459	459
					Bond E	**2407**

Table 31: Bond energy calculations for N2O

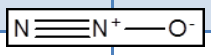
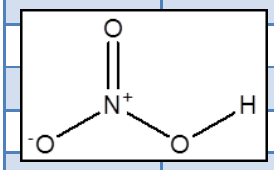
N2O			# of bonds	Type	Energy	total
			1	N≡N	942	942
			1	N-O	201	201
					Bond E	**1143**

Table 32: Bond energy calculations for HNO3

HNO3			# of bonds	Type	Energy	total
			1	N=O	607	607
			2	N-O	201	402
			1	O-H	459	459
					Bond E	**1468**

Appendix E: Viscosity estimates

Due to the fact that viscosity is a property highly dependent on temperature, the following method was used to estimate the viscosity of the reaction mixture.

The following data on viscosity of sulfuric and nitric acid could be found (ROYMECH 2011) ,see Table 33.

Table 33: Values for the viscosity of sulfuric and nitric acid

Temperature (K)	Viscosity (cP)	
	H_2SO_4	HNO_3
248	90	2.1
273	36	1.5
293	25	1.2
323	10.5	0.85
373	3.4	0.5

With these values, and the fact that viscosity depends exponential on temperature, a plot can be made to extrapolate viscosity at a function of temperature (Rhodes 1928; Couper, Penney et al. 2010) .

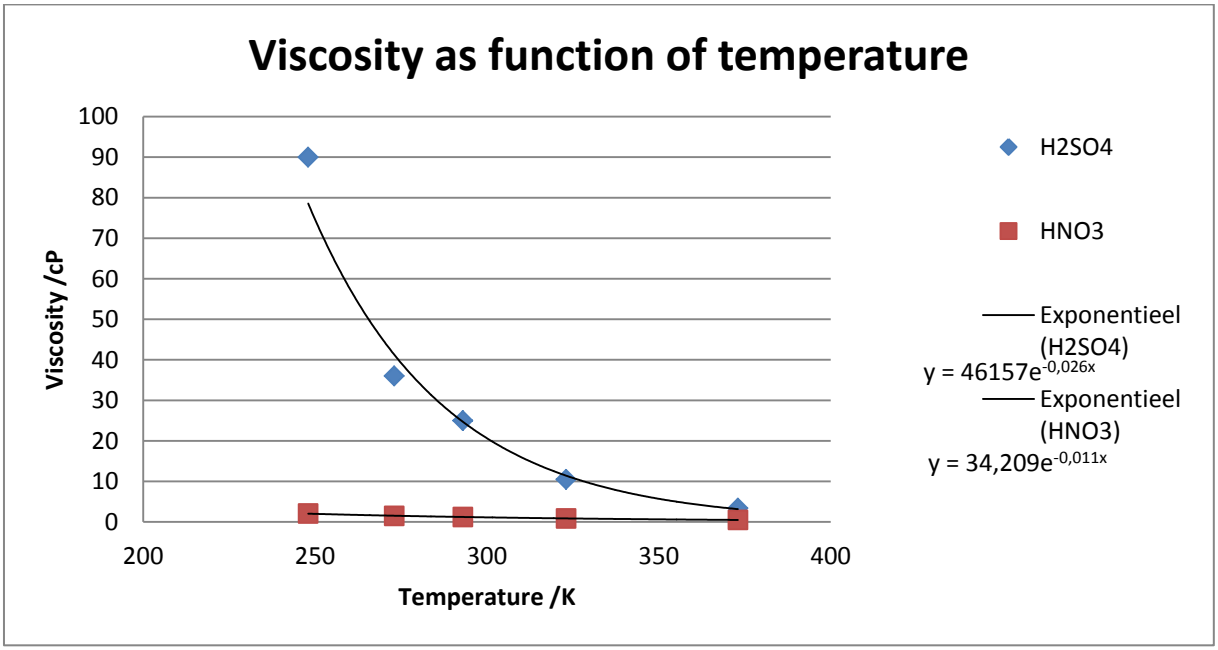


Figure 11: Viscosity of sulfuric and nitric acid as function of temperature

Using the equations of the fitting of the data, and the mass fractions of nitric and sulfuric acid in the mixture, the viscosity can be estimated, yielding 32 cP which equals 0.032 Ns/m^2.

Appendix F: Solving the particle

To estimate the solving rate of the AS as it enters into the reactor a mass balance was set up over a single particle of AS.

Here it is assumed that the fluid along the particle is moving so there is forced convection alongside the particle. Also assumed is the fact that the particles are spherical. Since there is a small concentration of AS in the reactor, the bulk concentration is taken to be zero.

Starting with the general mass balance we get:

$$\frac{dM}{dt} = \phi_{m,in} - \phi_{m,out}$$

Filling this in using a constant density:

$$\rho \frac{dV}{dt} = k * A * \Delta c$$

Then using

$$A_{sphere} = \pi * D^2$$
$$V_{sphere} = \frac{1}{6} * \pi * D^3$$

The mass balance then becomes:

$$\rho \frac{d\ \frac{1}{6} * \pi * D^3}{dt} = -\pi * D^2 * k * (C^* - C_b)$$

Rewriting and differentiating, still assuming $C_b = 0$

$$\rho * \frac{\pi}{2} * D^2 * \frac{dD}{dt} = -\pi * D^2 * k * C^*$$

With $C^* = \rho$ and further simplification, the equation becomes

$$\frac{dD}{dt} = -2k$$

Here:

$$k = Sh * \frac{\mathbb{D}}{D}$$

With $Sh = 2.0 + 0.66 * Re^{1/2} Sc^{1/3}$ and Re = 200 in a spinning disc reactor.

Substitution gives:

$$k = 2.0 + 0.66 * Re^{1/2} Sc^{1/3} * \frac{\mathbb{D}}{D}$$

Boundary conditions:

$$D(0) = D_0$$

Solving the differential equation:

$$\frac{2}{3} * \left(D^{3/2} - D_0^{3/2}\right) = -1.32 * \frac{M}{\rho} * \frac{P^*}{RT} * \mathbb{D}^{2/3} * \nu^{1/2}$$

Appendix G: Economic evaluation using DCFROR

The paragraph below gives the method and results of a preliminary economic study using the DCFROR method. They were taken from the BoD report.

Calculation of DCFROR

The Discount Cash Flow Rate of Return or DCFROR (also called the internal rate of return) can be used to estimate the value of an investment. The rate of return calculated by this method is the maximum interest rate at which money can be borrowed for the current project so that the net cash flow generated by the project is precisely enough to pay back the loan and any interest generated. When a DCFROR of 10% is assumed, it is possible to calculate the maximum amount that can be borrowed so that the net cash flow over the project life is precisely enough to repay the loan and interest generated. The present value of an investment is calculated using a discount factor, using 10%. The discount factor is generated using the following formula.

$$Discount\ Factor = \frac{1}{(1+r)^{year}}\ , \qquad r = 0.10$$

Because at this stage almost nothing is known about the process that will be designed it was decided to use the financial margin as a first estimate for the average cash flow. If the margin as described above is used, the maximum investment (for different project life spans) can be calculated as seen in

(Peters and Timmerhaus 1991).

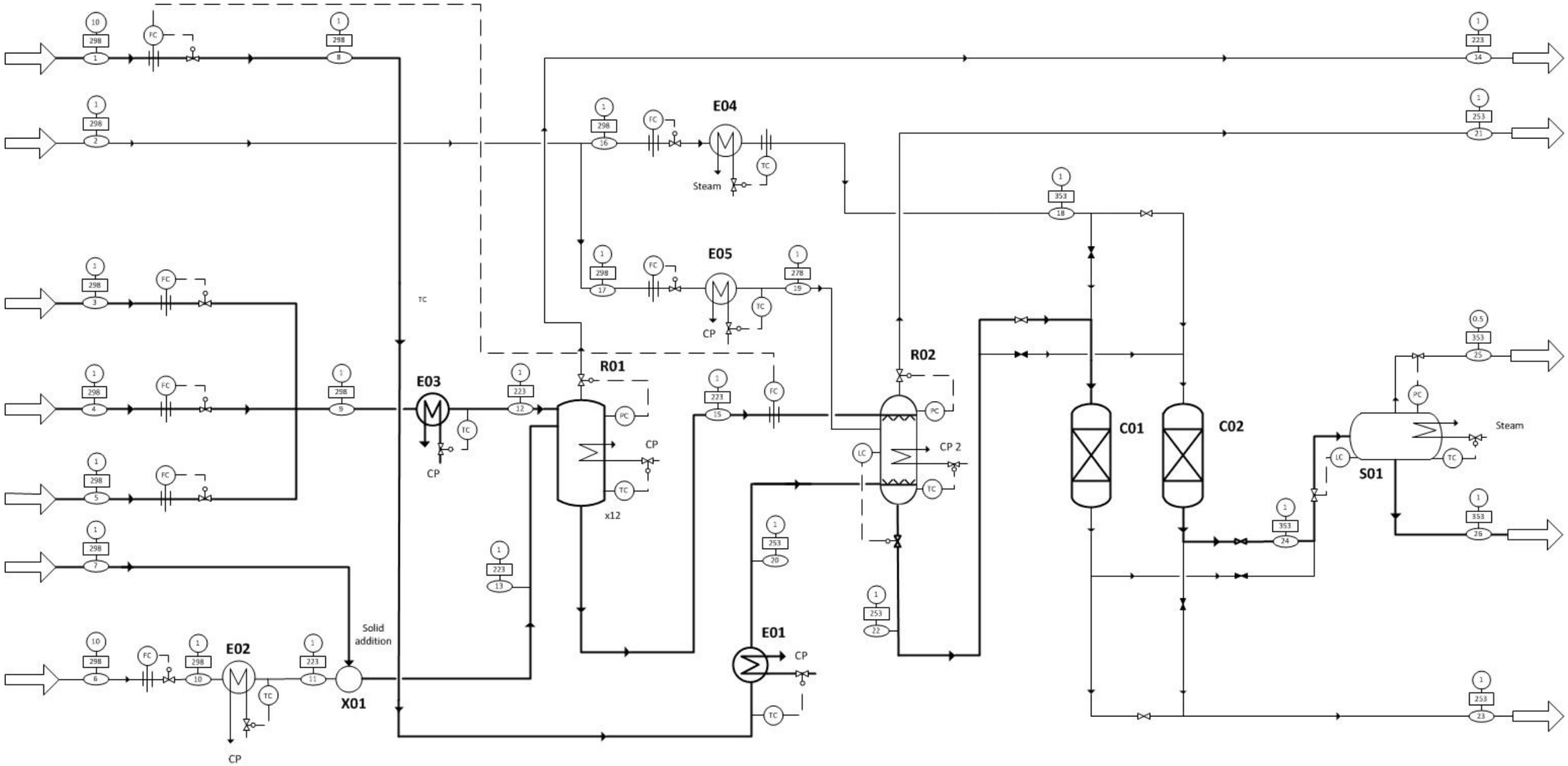
Table 34: Calculation of maximum initial investment using DCFROR

Year	Estimated Cash Flow (Here Financial Margin as estimate) in €	Discount Factor (1/((1+r)^year)) and r = 0.10	Present Value
1	€ 34,000,000	0.9091	€ 30,909,091
2	€ 34,000,000	0.8264	€ 28,099,174
3	€ 34,000,000	0.7513	€ 25,544,703
4	€ 34,000,000	0.6830	€ 23,222,457
5	€ 34,000,000	0.6209	€ 21,111,325
		Total for 5 years	€ 128,886,750
6	€ 34,000,000	0.5645	€ 19,192,114
7	€ 34,000,000	0.5132	€ 17,447,376
8	€ 34,000,000	0.4665	€ 15,861,251
9	€ 34,000,000	0.4241	€ 14,419,319
10	€ 34,000,000	0.3855	€ 13,108,472
		Total for 10 years	€ 208,915,282
11	€ 34,000,000	0.3505	€ 11,916,793
12	€ 34,000,000	0.3186	€ 10,833,448
13	€ 34,000,000	0.2897	€ 9,848,589
14	€ 34,000,000	0.2633	€ 8,953,263
15	€ 34,000,000	0.2394	€ 8,139,330
		Total for 15 years	€ 258,606,703

It can be seen from Table 34 that when the project lifespan is 15 years the maximum allowed investment at a DCFROR of 10% is about €260 million. However, as discussed in the financial margin, this excludes any utility costs, taxes, regulatory costs, etc. Only the cost of raw materials have been used to determine the financial margin and therefore the actual maximum investment cost will be much lower. Nevertheless, in this case it might give clear maximum for all costs that can be used in a later stage of the report.

Appendix H: Process flow schemes

Process flow scheme



Process Equipment Summary					
C01	Adsorption column	E05	Water cooler	○	Pressure (bar)
C02	Desorption column	R01	Spinning disc reactors		
E01	Neutralization feed cooler	R02	Bubble column reactor	⬭	Stream number
E02	Inert cooler	S01	Evaporation crystallizer		
E03	Acid cooler	X01	Solid addition	▭	Temperature (K)
E04	Water heater				

Designers
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Jerry Chen

Process Flow Scheme	
Project:	New Oxidizer for Advanced Propellants
Project ID Number:	CDP Group 3381
Completion Date:	July 15th 2011

Stream summary

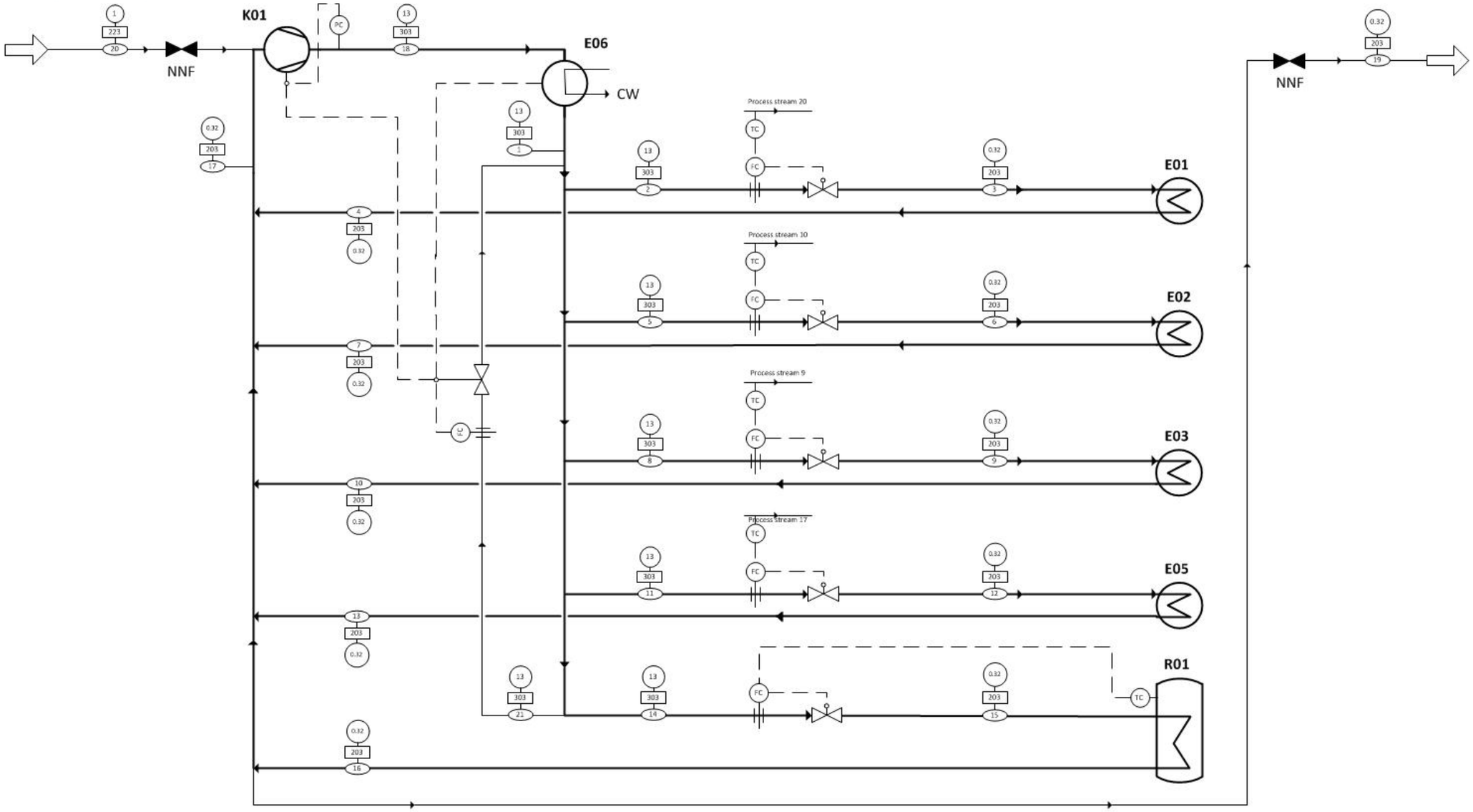
STREAM Nr. :		1	IN	2	IN	3	IN	4	IN	5	IN	6	IN	7	IN
Name :		Ammonia feed		Water feed		Sulfuric acid 80% feed		Sulfuric acid 98% feed		Nitric acid feed		Nitrogen feed		Ammonium sulfamate feed	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Water	18.00			0.7388094	0.0410	0.016	0.0009	0.003	0.0002	0.02	0.0010				
H_2SO_4	98.07					0.06	0.0006	0.1560	0.0016						
HNO_3	63.02									0.84	0.0134				
Ammonium Sulfamate	114.14													0.127471	0.0011
DNA	107.03														
N2O	44.00														
NH4HSO4	115.10														
NH3	17.03	0.90	0.0528												
ADN	124.06														
(NH4)2SO4	132.14														
NH4NO3	80.04														
Nitrogen	28.02											0.1674318	0.0060		
Propylene	42.08														
Total		0.900	0.053	0.739	0.041	0.079	0.002	0.159	0.002	0.862	0.014	0.167	0.006	0.127	0.001
Enthalpy	kW														
Phase		L		L		L		L		L		G		S	
Press.	Bara	10.0		1.0		1.0		1.0		1.0		10.0		1.0	
Temp	oC	25.0		25.0		25.0		25.0		25.0		25.0		25.0	

STREAM Nr. :		8		9	=3+4+5	10		11		12		13	=11+7	14	OUT
Name :		Ammonia vapor		Mixed acids		Nitrogen pressure adjusted		Nitrogen cooled		Cooled reactor feed		AS + nitrogen reactor feed		Gas reactor out	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Water	18.00			0.0361841	0.0020					0.04	0.0020				
H_2SO_4	98.07			0.219048	0.0022					0.22	0.0022				
HNO_3	63.02			0.8445644	0.0134					0.84	0.0134				
Ammonium Sulfamate	114.14											0.1274709	0.0011		
DNA	107.03														
N2O	44.00													0.02	0.0006
NH4HSO4	115.10														
NH3	17.03	0.90	0.0528												
ADN	124.06														
(NH4)2SO4	132.14														
NH4NO3	80.04														
Nitrogen	28.02					0.17	0.0060	0.17	0.0060			0.1674318	0.0060	0.17	0.0060
Propylene	42.08														
Total		0.900	0.053	1.100	0.018	0.167	0.006	0.167	0.006	1.100	0.018	0.295	0.007	0.192	0.007
Enthalpy	kW														
Phase		V		L		V		V		L		V+S		V	
Press.	Bara	1.0		1.0		1.0		1.0		1.0		1.0		1.0	
Temp	oC	25.0		25.0		25.0		-50.0		-50.0		-50.0		-50.0	

STREAM Nr. :		15		16		17	=2-16	18		19		20		21	
Name :		Reactor out		Water to E04		Water to E05		Heated up water		Cooled water		Ammonia neutralizer in		Ammonia neutralizer out	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Water	18.00	0.056	0.0031	0.0388094	0.0022	0.700	0.0389	0.039	0.0022	0.70	0.0389				
H_2SO_4	98.07	0.22	0.0022												
HNO_3	63.02	0.74	0.0117												
Ammonium Sulfamate	114.14														
DNA	107.03	0.06	0.0006												
N2O	44.00														
NH4HSO4	115.10	0.13	0.0011												
NH3	17.03											0.90	0.0528	0.60	0.0350
ADN	124.06														
(NH4)2SO4	132.14														
NH4NO3	80.04														
Nitrogen	28.02														
Propylene	42.08														
Total		1.203	0.019	0.039	0.002	0.700	0.039	0.039	0.002	0.700	0.039	0.900	0.053	0.596	0.035
Enthalpy	kW														
Phase		L		L		L		L		L		V		V	
Press.	Bara	1.0		1.0		1.0		1.0		1.0		1.0		1.0	
Temp	oC	-50.0		25.0		25.0		80.0		5.0		-20.0		-20.0	

STREAM Nr. :		22		23	OUT	24		25	OUT	26	OUT	1+2+3+4+5+6+7		14+21+23+25+26	
Name :		Liquid neutralizer out		Waste		To crystallizer		Water crystallizer out		ADN produced		Overall in		Overall out	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Water	18.00	0.756	0.0420	0.7562864	0.0420	0.039	0.0022	0.039	0.0022			0.775	0.0431	0.7950958	0.0442
H_2SO_4	98.07											0.219	0.0022		
HNO_3	63.02											0.845	0.0134		
Ammonium Sulfamate	114.14											0.13	0.0011		
DNA	107.03														
N2O	44.00													0.0245695	0.0006
NH4HSO4	115.10														
NH3	17.03											0.90	0.0528	0.5956959	0.0350
ADN	124.06	0.07	0.0006	0.0034637	0.0000	0.07	0.0005			0.07	0.0005			0.0692747	0.0006
(NH4)2SO4	132.14	0.44	0.0034	0.4427195	0.0034									0.4427195	0.0034
NH4NO3	80.04	0.94	0.0117	0.9385761	0.0117									0.9385761	0.0117
Nitrogen	28.02											0.17	0.0060	0.1674318	0.0060
Propylene	42.08														
Total		2.207	0.058	2.141	0.057	0.105	0.003	0.039	0.002	0.066	0.001	3.034	0.119	3.033	0.101
Enthalpy	kW														
Phase		L		L		L		V		S					
Press.	Bara	1.0		1.0		1.0		0.5		1.0					
Temp	oC	-20.0		-20.0		80.0		80.0		80.0					

Refrigeration cycle process flow scheme



Process Equipment Summary			
K01	Compressor		
R01	Spinning Disc Reactors		
E01	Neutralization feed cooler	○	Pressure (bar)
E02	Inert cooler	⬭	Stream number
E03	Acid cooler	▭	Temperature (K)
E05	Water cooler		
E06	Condenser		

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Process Flow Scheme	
Project:	New Oxidizer for Advanced Propellants
Project ID Number:	CDP Group 3381
Completion Date:	July 15th 2011

Refrigeration cycle stream summary

STREAM Nr. :		1	IN	2	IN	3	IN	4	IN	5	IN	6	IN	7	IN
Name :		Condenser Out		Expansion Valve 1 feed		E01 In		E01 Out		Expansion Valve 2 feed		E02 In		E02 Out	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Propylene	42.08	5.84	0.1388	0.33	0.0078	0.33	0.0078	0.33	0.0078	0.05	0.0012	0.05	0.0012	0.05	0.0012
Total		5.840	0.139	0.330	0.008	0.330	0.008	0.330	0.008	0.050	0.001	0.050	0.001	0.050	0.001
Enthalpy	kW					82.50		166.58				12.50		25.24	
Phase		L		L		L		G		L		L		G	
Press.	Bara	13.0		13.0		0.3		0.3		13.0		0.3		0.3	
Temp	oC	30.0		30.0		-70.0		-70.0		30.0		-70.0		-70.0	

STREAM Nr. :		8	IN	9	IN	10	IN	11	IN	12	IN	13	IN	14	IN
Name :		Expansion Valve 3 feed		E03 In		E03 Out		Expansion Valve 4 feed		E04 In		E04 Out		Expansion Valve 5 feed	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Propylene	42.08	0.57	0.0135	0.57	0.0135	0.57	0.0135	0.23	0.0055	0.23	0.0055	0.23	0.0055	4.66	0.1107
Total		0.570	0.014	0.570	0.014	0.570	0.014	0.230	0.005	0.230	0.005	0.230	0.005	4.660	0.111
Enthalpy	kW			142.50		287.73				57.50		116.10			
Phase		L		L		G		L		L		G		L	
Press.	Bara	13.0		0.3		0.3		13.0		0.3		0.3		13.0	
Temp	oC	30.0		-70.0		-70.0		30.0		-70.0		-70.0		30.0	

STREAM Nr. :		15	IN	16	IN	17	IN	18	IN	19	IN	20	IN
Name :		Reactor In		Reactor Out		Compressor In		Compressor Out		Propylene Out		Propylene In	
COMP	MW	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s	kg/s	kmol/s
Propylene	42.08	4.66	0.1107	4.66	0.1107	5.84	0.1388	5.84	0.1388	normally no flow		normally no flow	
Total		4.660	0.111	4.660	0.111	5.840	0.139	5.840	0.139	0.000	0.000	0.000	0.000
Enthalpy	kW	1165.00		2352.32									
Phase		L		G		G		G		G		G	
Press.	Bara	0.3		0.3		0.3		13.0		0.3		1.0	
Temp	oC	-70.0		-70.0		-70.0		30.0		-70.0		25.0	

Appendix I: CSTR calculations

Jacketed cooled CSTR

For the CSTR a model was found in (Rase 1977) , which can model the heat transfer inside an agitated reactor. This is an agitated reactor with a 6 blade flat turbine as agitator.

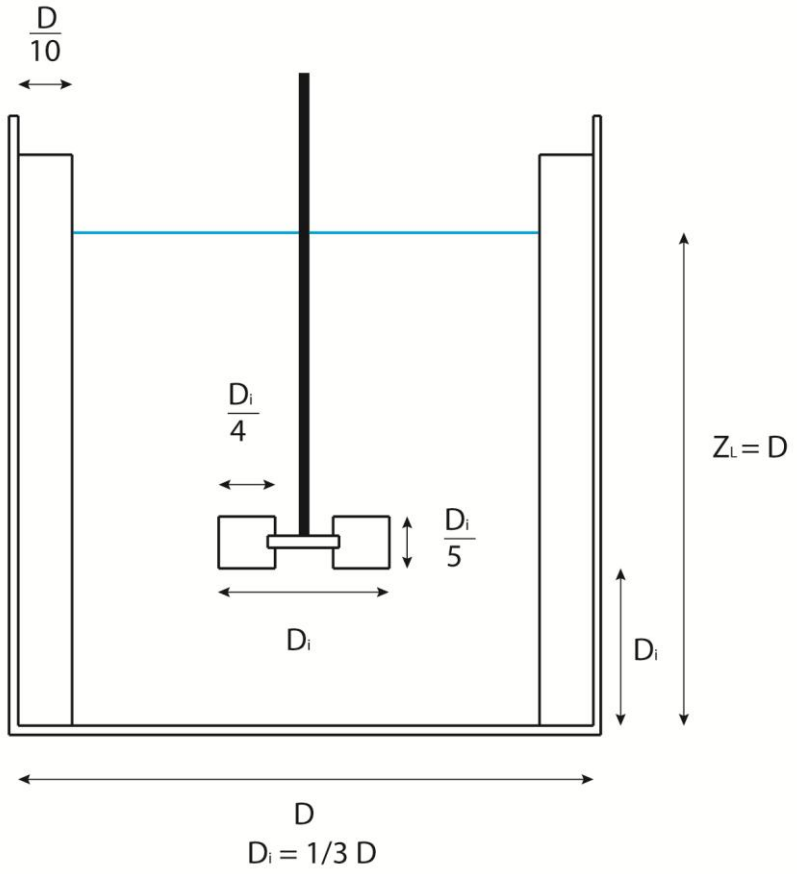

Figure 12: CSTR with jacketed cooling

Corresponding to this model, the following formula could be used to find the heat transfer.

$$\frac{hD}{\lambda_f} = 0.73\left(\frac{\rho N D_I^2}{\mu}\right)^{0.65}\left(\frac{c_p\mu}{\lambda_f}\right)^{0.33}\left(\frac{\mu_b}{\mu_w}\right)^{0.24}$$

With entering typical values, as found in Table 35, the area can be calculated that is needed for the heat transfer.

Table 35: Values for the calculations of the CSTR heat transfer

Parameter	Symbol	Values	Units	Details
Stirrer rotation	N	1	/s	Estimate
Diameter stirrer	D_I	0.5	m	1/3 * Diameter tank
Viscosity	μ	0.032	kg/m/s	Bulk viscosity
Heat capacity liquid	C_p	1600	J/kg/K	Estimate
Heat transfer coefficient	λ_f	0.2853	W/m/K	Estimate
Viscosity bulk	μ_b	0.032	kg/m/s	Bulk viscosity
Viscosity wall	μ_w	0.041	kg/m/s	Conservative assumption that the wall is 213 K
Diameter reactor	D	1.5	m	Estimate
Density liquid	ρ	1600	kg/m^3	Estimate

Using the following formula, the area needed for the desired heat transfer can be estimated.

$$\phi_q = h * A * \Delta T$$

Here ΔT is 20 K, h is calculated with the formula on the previous page, and ϕ_q is the 2181 kW for weekend shut down, and 1188 kW for fully continuous.

This resulted in the following areas for a CSTR with a diameter of 1.5m:

Table 36: Areas the heat transfor of a CSTR with a diamter of 1.5 m

	Fully continuous	weekend shutdown
Area	326.68	177.94

Cooling coil inside CSTR

With the same procedure it is also possible to calculate the area of cooling coil needed to obtain the desired cooling. For this the following formula is used (Rase 1977):

$$\frac{hD}{\lambda_f} = 0.17\left(\frac{\rho N D_I^2}{\mu}\right)^{0.67}\left(\frac{c_p\mu}{\lambda_f}\right)^{0.37}\left(\frac{\mu_b}{\mu_w}\right)^{e^{-0.202\ln(\mu-0.357)}}\left(\frac{D_I}{D}\right)^{0.1}\left(\frac{d_{ct}}{D}\right)^{0.5}$$

Here the μ in the power is in cP.

Using this formula and a diameter of the coil of 0.3 m, the length of the coil that is needed is in the order of 500 m.

Appendix J: PFR calculations

To check the heat transfer of a PRF a turbulent flow through a tube was used. For this the following formula was used(Janssen and Warmoeskerken 2006):

$$Nu = 0.027\ Re^{0.8} Pr^{0.33}\ with\ Re > 10^4\ and\ Pr \geq 0.7$$

Using the same values as in Appendix I: CSTR calculations, and the same method of calculating the area from the Nusselt relation, an estimate can be obtained for the area needed.

For a PFR with a diameter of 0.15 m, and a velocity of 1 m/s, the area needed from this is around the 300m^2, which is also quite high. For this a Reynolds number of 7500 is achieved.

Appendix K: Cooling neutralization

Table 37: Calculations for the heat balance of the neutralization step

Streams in:	**15+19+20**							
COMP	**MW**	**kg/s**	**kmol/s**	**T (K)**	**dHf (kJ/mol)**	**Cp (J/mol/K)**	**flows 253 K (kJ)**	**Enthalpy (kJ/s)**
Water	18	0.7	0.0389	278	-285.8	75.3	-73.22925	-11249.43
Water	18	0.056	0.0031	223	-285.8	75.3	7.0029	-896.4844
H2SO4	98.07	0.22	0.0022	223	-814	138.9	9.1674	-1804.551
HNO3	63.02	0.74	0.0117	223	-174.1	109.9	38.5749	-2094.832
DNA	107.03	0.06	0.0006	223	-112.3	188.16	3.386844	-72.46027
NH4HSO4	115.1	0.13	0.0011	223	-768.6	180.75	5.96475	-854.4071
NH3	17.03	0.9	0.0528	223	-46.19	35.15	55.6776	-2522.348
							46.545144	-19494.52
Streams out:	21+22							
COMP	**MW**	**kg/s**	**kmol/s**	**T (K)**	**dHf (kJ/mol)**	**Cp (J/mol/K)**		**Enthalpy (kJ/s)**
Water	18	0.756	0.042	253	-285.8	75.3		-12145.92
NH3	17.03	0.6	0.035	253	-46.19	35.15		-1672.011
ADN	124.06	0.07	0.0006	253	-148	223.31		-94.82932
(NH4)2SO4	132.14	0.44	0.0034	253	-1173.1	215.9		-4021.573
NH4NO3	80.04	0.94	0.0117	253	-399.36	139.3		-4745.853
								-22680.18
difference in enthalpy + energy for heating up / cooling down to 223 K:								**-3139.122**

The following assumptions have been made to get the heat of formations:

$$\Delta H_{f298}{}^{0}(DNA) = \Delta H_{f298}{}^{0}(DNA) + heat\ of\ solution\ (ADN)$$

$$C_p\ (DNA) = \ C_p\ (ADN) - C_p\ (NH_3)$$

$$C_p\ (NH_4HSO_4) = \ C_p\ ((NH_4)_2SO_4) - C_p\ (NH_3)$$

These estimated are crude, but the best values that could be obtained, the other values are obtained from ((Ostmark, Bemm et al. 2000) (Felder and Rousseau 2000) (Larsson and Wingborg 2011))

Appendix L: Equipment summary and specification sheets

REACTORS, COLUMNS & VESSELS – SUMMARY

EQUIPMENT NR. :	C01 Adsorption column	C02 Desorption column	R01 Spinning disc reactors	R02 Bubble column reactor	S01 Evaporative crystallizer
Pressure [bara] :	1.0	1.0	1.0	1.0	0.47
Temp. [°C] :	-20.0	80.0	-50.0	-20.0	80.0
Volume [m^3] :	-	-	-(1)	-	-
Diameter [m] :	-	-	0.7	-	-
L or H [m] :	-	-	-	-	-
Internals					
- Tray Type :	n.a.	n.a.	n.a.	n.a.	n.a.
- Tray Number:	n.a.	n.a.	n.a.	n.a.	n.a.
- Fixed Packing					
Type :	activated carbon	activated carbon	n.a.	n.a.	n.a.
Shape :	n.a.	n.a.	n.a.	n.a.	n.a.
- Catalyst					
Type :	n.a.	n.a.	n.a.	n.a.	n.a.
Shape :	n.a.	n.a.	n.a.	n.a.	n.a.
- Speed [rpm]			3500		
-					
-					
Number					
- Series :	1	1	-	1	1
- Parallel :	-	-	12	-	-
Materials of Construction :	SS	SS	GSS	SS	CS
Other :					

Remarks:

(1) = The reactors are designed for the ability of the heat transfer. The residence time is 0.28 seconds

CS = Carbon steel
SS = Stainless steel
GSS = Glass lines stainless steel (to resist acidity)

Designers :	Thiemo Pronk Jerry Chen	Anne van de Wouw	Project ID-Number : **CDP3381** Date : July 15th 2011

HEAT EXCHANGERS & FURNACES – SUMMARY

EQUIPMENT NR. : **NAME :**	E01 Neutralization deed cooler	E02 Inert cooler	E03 Acid cooler	E04 Water heater	E05 Water cooler
	Shell- and-tube	Shell- and-tube	Shell- and-tube	Double-pipe	Double-pipe
Substance **- Tubes :** **– Shell :**	NH_3 Propylene	N_2 Propylene	HNO_3 H_2SO_4 Propylene	H_2O Steam	H_2O Propylene
Duty [kW] :	-83.59	-13.05	-144.81	9.12	-58.66
Heat Exchange area [m^2] :	19.87	4.52	15.04	2.38	2.31
Number **- Series :** **– Parallel :**	1 -	1 -	1 -	1 -	1 -
Pressure [bara] **- Tubes :** **- Shell :**	1 0.32	1 0.32	1 0.32	1 3	1 0.32
Temperature In / Out [°C] **- Tubes :** **- Shell :**	25/-20 -70/-70	25/-50 -70/-70	25/-50 -70/-70	25/80 190/140	25/5 -70/-70
Special Materials of Construction *(1)* **:**	Tubes : SS Shell : SS	Tubes : SS Shell : SS	Tubes : GSS Shell : SS	Tubes : CS Shell : CS	Tubes : SS Shell : SS
Other :					

Remarks:

(1):
GSS = Glass lined stainless steel - needed for the very acidic flow
SS = Stainless steel
CS = Carbon steel

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number :	**CDP3381**
	Jerry Chen		Date :	July 15th 2011

HEAT EXCHANGERS & FURNACES – SUMMARY

EQUIPMENT NR. :	E06				
NAME :	Condenser				
	Shell- and-tube				
Substance					
- Tubes :	Propylene				
– Shell :	Water				
Duty [kW] :	-2410.73				
Heat Exchange area [m^2] :	391				
Number					
- Series :	1				
– Parallel :	-				
Pressure [bara]					
- Tubes :	13				
- Shell :	1				
Temperature In / Out [°C]					
- Tubes :	30/30				
- Shell :	20/25				
Special Materials of Construction *(1)* :	Tubes : CS Shell : CS				
Other :					

Remarks:

(1):
GSS = Glass lined stainless steel - needed for the very acidic flow
SS = Stainless steel
CS = Carbon steel

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number :	**CDP3381**
	Jerry Chen		Date :	July 15th 2011

PUMPS, BLOWERS & COMPRESSORS – SUMMARY

EQUIPMENT NR. :	K01				
NAME :	Compressor				
Type :	Screw compressor				
Number :	2				
Medium transferred :	Propylene				
Capacity					
[kg/s] :	5.84				
[m^3/s] :					
Density [kg/m^3] :	0.818 / 27.76 (1)				
Pressure [bara]					
Suct. / Disch. :	0.32/13				
Temperature					
In / Out [°C] :	-70.0/30.0				
Power [kW]					
- Theor. :	1082				
- Actual :					
Number					
- Theor. :					
- Actual :	2 (2)				
Special Materials of Construction :					
Other :					

Remarks:
(1) Suct. / Disch.
(2) One installed spare included.

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number :	**CDP3381**	
	Jerry Chen		Date :	July 15th 2011	

HEAT EXCHANGER – SPECIFICATION SHEET

EQUIPMENT NUMBER	:	E-01	**In Series**	:	1
NAME	:	E-01 Neutralization feed cooler	**In Parallel**	:	none

General Data

Service	:	- ~~Heat Exchanger~~	- ~~Vaporizer~~
		- Cooler	- ~~Reboiler~~
		- ~~Condenser~~	
Type	:	- Fixed Tube Sheets	- ~~Plate Heat Exchanger~~
		- ~~Floating Head~~	- ~~Finned Tubes~~
		- ~~Hair Pin~~	- ~~Thermosyphon~~
		- ~~Double Tube~~	-
Position	:	- Horizontal	
		- ~~Vertical~~	

Capacity	[kW]	:	83.59	(Calc.)
Heat Exchange Area	[m^2]	:	19.87	(Calc.)
Overall Heat Transfer Coefficient	[$W/m^2.°C$]	:	60	(Approx.)
Log. Mean Temperature Diff. (LMTD)	[°C]	:	-70.1	
Passes Tube Side		:	1	
Passes Shell Side		:	n.a.	
Correction Factor LMTD (min. 0.75)		:	1	
Corrected LMTD	[°C]	:	-70.1	

Process Conditions

			Shell Side	Tube Side
Medium		:	Propylene	Ammonia
Mass Stream	[kg/s]	:	0.33	0.90
Mass Stream to				
- **Evaporize**	[kg/s]	:	0.33	n.a.
- ~~**Condense**~~	~~[kg/s]~~	:		
Average Specific Heat	[kJ/kg.°C]	:	-	2.06
Heat of Evap. / Condensation	[kJ/kg]	:	254.8	-
Temperature IN	[°C]	:	-70.0	25.0
Temperature OUT	[°C]	:	-70.0	-20.0
Pressure	[bara]	:	0.3	Atm.
Material (1)		:	SS	SS

Remarks:
(1): SS = Stainless steel
Heat transfer coefficient is an estimate for a shell-tube liquid gas heat exchanger

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number	:	**CDP3381**
	Jerry Chen		Date	:	July 15th 2011

HEAT EXCHANGER – SPECIFICATION SHEET

EQUIPMENT NUMBER	:	E-02		**In Series**	: 1
NAME	:	E-02 Inert cooler		**In Parallel**	: none

General Data

Service	:	- ~~Heat Exchanger~~	- ~~Vaporizer~~
		- Cooler	- ~~Reboiler~~
		- ~~Condenser~~	
Type	:	- Fixed Tube Sheets	- ~~Plate Heat Exchanger~~
		- ~~Floating Head~~	- ~~Finned Tubes~~
		- ~~Hair Pin~~	- ~~Thermosyphon~~
		- ~~Double Tube~~	-
Position	:	- Horizontal	
		- ~~Vertical~~	

Capacity	[kW]	:	-13.05	(Calc.)
Heat Exchange Area	[m^2]	:	4.52	(Calc.)
Overall Heat Transfer Coefficient	[$W/m^2 \cdot °C$]	:	60	(Approx.)
Log. Mean Temperature Diff. (LMTD)	[°C]	:	-48.13	
Passes Tube Side		:	1	
Passes Shell Side		:	1	
Correction Factor LMTD (min. 0.75)		:	1.0	
Corrected LMTD	[°C]	:	-48.13	

Process Conditions

			Shell Side	Tube Side
Medium		:	Propylene	Nitrogen
Mass Stream	[kg/s]	:	0.05	0.17
Mass Stream to				
- **Evaporize**	[kg/s]	:	0.05	
- ~~**Condense**~~	~~[kg/s]~~	:		
Average Specific Heat	[kJ/kg·°C]	:	-	1.03
Heat of Evap. / Condensation	[kJ/kg]	:	254.8	-
Temperature IN	[°C]	:	-70.0	25.0
Temperature OUT	[°C]	:	-70.0	-50.0
Pressure	[bara]	:	0.3	Atm.
Material *(1)*		:	SS	SS

Remarks:
(1): SS = Stainless steel

Heat transfer coefficient is an estimate for a shell-tube liquid gas heat exchanger

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number :	**CDP3381**
	Jerry Chen		Date :	July 15th 2011

HEAT EXCHANGER – SPECIFICATION SHEET

EQUIPMENT NUMBER :	**E-03**	**In Series** :	1
NAME :	**E-03 Acid Cooler**	**In Parallel** :	none

General Data

Service	:	- ~~**Heat Exchanger**~~	- ~~**Vaporizer**~~
		- **Cooler**	- ~~**Reboiler**~~
		- ~~**Condenser**~~	
Type	:	- **Fixed Tube Sheets**	- ~~**Plate Heat Exchanger**~~
		- ~~**Floating Head**~~	- ~~**Finned Tubes**~~
		- ~~**Hair Pin**~~	- ~~**Thermosyphon**~~
		- ~~**Double Tube**~~	-
Position	:	- **Horizontal**	
		- ~~**Vertical**~~	

Capacity	[kW]	:	-144.81	**(Calc.)**
Heat Exchange Area	[m^2]	:	15.04	**(Calc.)**
Overall Heat Transfer Coefficient	[$W/m^2 \cdot °C$]	:	200	**(Approx.)**
Log. Mean Temperature Diff. (LMTD)	[°C]	:	-48.13	
Passes Tube Side		:	1	
Passes Shell Side		:	1	
Correction Factor LMTD (min. 0.75)		:	1.00	
Corrected LMTD	[°C]	:	-48.13	

Process Conditions

			Shell Side	**Tube Side**
Medium		:	Propylene	Nitric-, sulphuric acid
Mass Stream	[kg/s]	:	0.57	1.10
Mass Stream to				
- **Evaporize**	[kg/s]	:	0.57	-
- ~~**Condense**~~	~~[kg/s]~~	:		-
Average Specific Heat	[kJ/kg·°C]	:	-	1.76
Heat of Evap. / Condensation	[kJ/kg]	:	254.8	-
Temperature IN	[°C]	:	-70.0	25.0
Temperature OUT	[°C]	:	-70.0	-50.0
Pressure	[bara]	:	0.3	Atm.
Material *(1)*		:	SS	GSS

Remarks:
(1) SS = Stainless steel, GSS = Glass lined stainless steel

Heat transfer coefficient is an estimate for a shell-tube liquid and vaporizing liquid heat exchanger, and a lower value is chosen due to the acid mixture, which is viscous.

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number :	**CDP3381**
	Jerry Chen		Date :	July 15th 2011

HEAT EXCHANGER – SPECIFICATION SHEET

EQUIPMENT NUMBER	: E-04	**In Series**	: 1
NAME	: E-04 Water heater	**In Parallel**	: none

General Data

Service	:	- **Heat Exchanger**	- ~~**Vaporizer**~~
		- ~~**Cooler**~~	- ~~**Reboiler**~~
		- ~~**Condenser (Air cooled)**~~	
Type	:	- ~~**Fixed Tube Sheets**~~	- ~~**Plate Heat Exchanger**~~
		- ~~**Floating Head**~~	- **Finned Tubes**
		- ~~**Hair Pin**~~	- ~~**Thermosyphon**~~
		- **Double Tube**	-
Position	:	- **Horizontal**	
		- ~~**Vertical**~~	

Capacity	[kW]	:	9.12	(Calc.)
Heat Exchange Area	[m^2]	:	2.38	(Calc.)
Overall Heat Transfer Coefficient	[$W/m^2 \cdot °C$]	:	34	(Approx.)
Log. Mean Temperature Diff. (LMTD)	[°C]	:	112.48	
Passes Tube Side		:	1	
Passes Shell Side		:	n.a.	
Correction Factor LMTD (min. 0.75)		:	1	
Corrected LMTD	[°C]	:	112.48	

Process Conditions

			Shell Side	Tube Side
Medium		:	Steam	Water
Mass Stream	[kg/s]	:	0.037	0.039
Mass Stream to				
- ~~**Evaporize**~~	~~[kg/s]~~	:		
- ~~**Condense**~~	~~[kg/s]~~	:		
Average Specific Heat	[kJ/kg·°C]	:	2.20	4.19
Heat of Evap. / Condensation	[kJ/kg]	:	-	-
Temperature IN	[°C]	:	190	25.0
Temperature OUT	[°C]	:	140	80.0
Pressure	[bara]	:	3	Atm.
Material (1)		:	CS	CS

Remarks:

(1) CS = Carbon steel
Heat transfer coefficient is an estimate for a double pipe heat exchanger

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number	:	**CDP3381**
	Jerry Chen		Date	:	July 15th 2011

HEAT EXCHANGER – SPECIFICATION SHEET

EQUIPMENT NUMBER	:	E-05	**In Series**	:	1
NAME	:	E-05 Water cooler	**In Parallel**	:	none

General Data

Service	:	- ~~Heat Exchanger~~	- ~~Vaporizer~~
		- Cooler	- ~~Reboiler~~
		- ~~Condenser (Air cooled)~~	
Type	:	- ~~Fixed Tube Sheets~~	- ~~Plate Heat Exchanger~~
		- ~~Floating Head~~	- ~~Finned Tubes~~
		- ~~Hair Pin~~	- ~~Thermosyphon~~
		- Double Tube	-
Position	:	- Horizontal	
		- ~~Vertical~~	

Capacity	[kW]	:	-58.66	(Calc.)
Heat Exchange Area	[m^2]	:	2.31	(Calc.)
Overall Heat Transfer Coefficient	[$W/m^2 \cdot °C$]	:	300	(Approx.)
Log. Mean Temperature Diff. (LMTD)	[°C]	:	-84.6	
Passes Tube Side		:	1	
Passes Shell Side		:	n.a.	
Correction Factor LMTD (min. 0.75)		:	1	
Corrected LMTD	[°C]	:	-84.6	

Process Conditions

			Shell Side	Tube Side
Medium		:	Propylene	Water
Mass Stream	[kg/s]	:	0.23	0.7
Mass Stream to				
- **Evaporize**	[kg/s]	:	0.23	
- ~~Condense~~	~~[kg/s]~~	:		
Average Specific Heat	[kJ/kg.°C]	:	-	4.19
Heat of Evap. / Condensation	[kJ/kg]	:	254.8	-
Temperature IN	[°C]	:	-70.0	25.0
Temperature OUT	[°C]	:	-70.0	5.0
Pressure	[bara]	:	0.3	Atm.
Material		:	SS	SS

Remarks:
(1) SS = Stainless steel

Heat transfer coefficient is an estimate for a double pipe heat exchanger

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number	:	**CDP3381**
	Jerry Chen		Date	:	July 15th 2011

HEAT EXCHANGER – SPECIFICATION SHEET

EQUIPMENT NUMBER	: E-06	**In Series**	: 1
NAME	: E-06 Condenser	**In Parallel**	: none

General Data

Service	:	- ~~Heat Exchanger~~	- ~~Vaporizer~~
		- Cooler	- ~~Reboiler~~
		- ~~Condenser (Air cooled)~~	
Type	:	- Fixed Tube Sheets	- ~~Plate Heat Exchanger~~
		- ~~Floating Head~~	- ~~Finned Tubes~~
		- ~~Hair Pin~~	- ~~Thermosyphon~~
		- ~~Double Tube~~	-
Position	:	- Horizontal	
		- ~~Vertical~~	

Capacity	[kW]	:	-2410.73	(Calc.)
Heat Exchange Area	[m^2]	:	391	(Calc.)
Overall Heat Transfer Coefficient	[$W/m^2 \cdot °C$]	:	500	(Approx.)
Log. Mean Temperature Diff. (LMTD)	[°C]	:	-12.33	
Passes Tube Side		:	1	
Passes Shell Side		:	n.a.	
Correction Factor LMTD (min. 0.75)		:	1	
Corrected LMTD	[°C]	:	-12.33	

Process Conditions

			Shell Side	Tube Side
Medium		:	Water	Propylene
Mass Stream	[kg/s]	:	46.67	5.84
Mass Stream to				
- ~~Evaporize~~	~~[kg/s]~~	:		
- Condense	[kg/s]	:	n.a.	5.84
Average Specific Heat	[kJ/kg·°C]	:	4.19	-
Heat of Evap. / Condensation	[kJ/kg]	:	-	412.80
Temperature IN	[°C]	:	20.0	30.0
Temperature OUT	[°C]	:	25.0	30.0
Pressure	[bara]	:	Atm.	13.0
Material (1)		:	CS	CS

Remarks:
(1) CS = Carbon steel

Heat transfer coefficient is an estimate for a shell-tube liquid and condensing vapour heat exchanger.

Designers :	Thiemo Pronk	Anne van de Wouw	Project ID-Number :	**CDP3381**
	Jerry Chen		Date :	July 15th 2011

Appendix M: SDR calculations

For the calculations of the heat transfer of the SDR the reactor was split up into multiple parts. With the values and formulas as used in Chapter 7: Equipment and unit design, the values as shown in could be calculated.

r (m)	s (m)	U (m/s)	h ($W/m^2/K$)	A (m^2)	ΔT (K)	Φ_q (J/s)
0.05	0.000122	1.66	4680			
0.075	9.3E-05	1.45	6132	0.0098	20	1204
0.1	7.68E-05	1.32	7429	0.0137	20	2042
0.125	6.62E-05	1.23	8620	0.0177	20	3047
0.15	5.86E-05	1.15	9734	0.0216	20	4205
0.175	5.29E-05	1.10	10788	0.0255	20	5507
0.2	4.84E-05	1.05	11792	0.0295	20	6946
0.225	4.47E-05	1.01	12756	0.0334	20	8515
0.25	4.17E-05	0.97	13684	0.0373	20	10210
0.275	3.91E-05	0.94	14581	0.0412	20	12025
0.3	3.69E-05	0.92	15452	0.0452	20	13957
0.325	3.5E-05	0.89	16299	0.0491	20	16002
0.35	3.33E-05	0.87	17125	0.0530	20	18157
Total Φ_q of the entire disc						**101817**

Appendix N: Pressure-Enthalpy diagrams for hydrocarbons

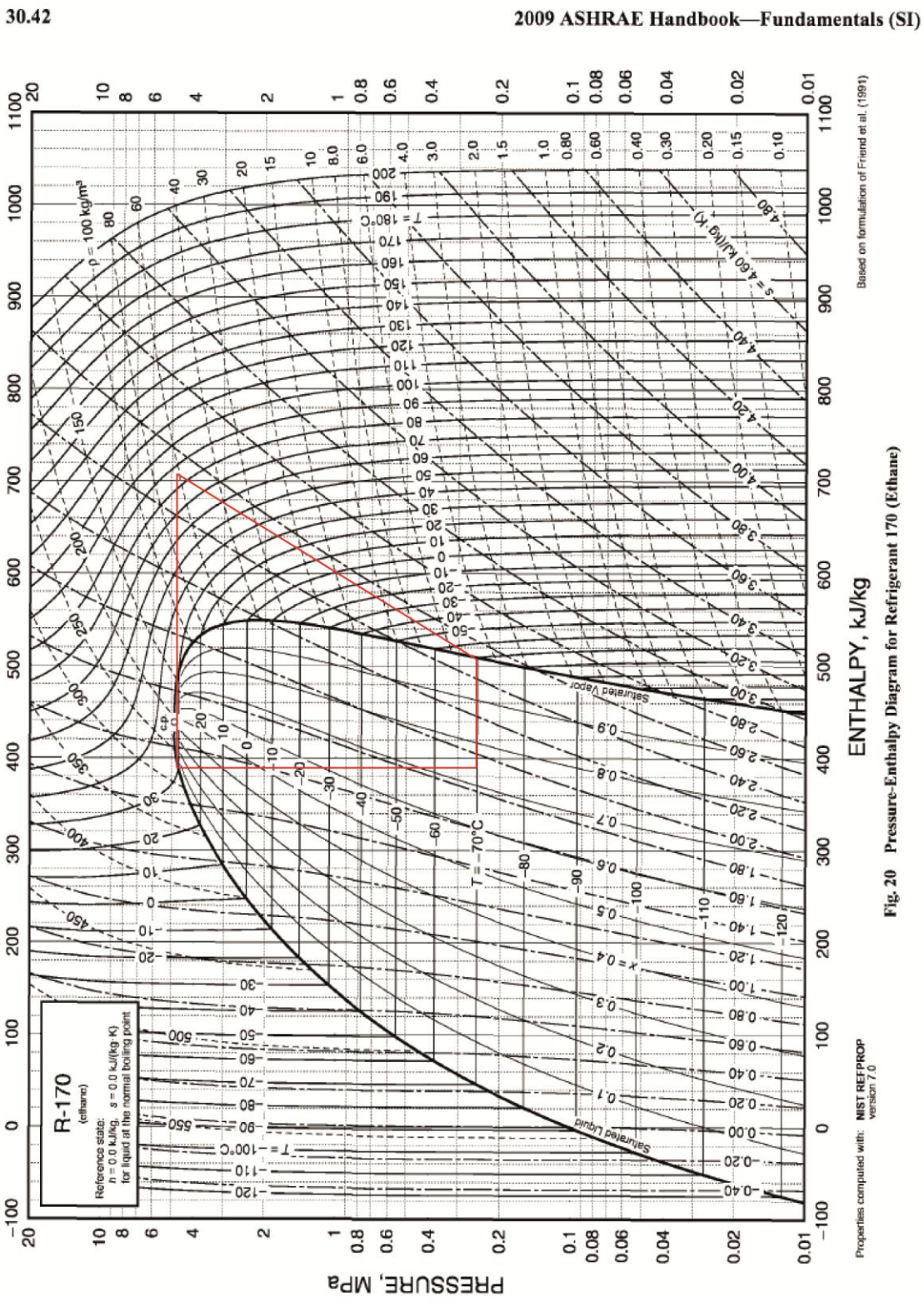

Fig. 20 Pressure-Enthalpy Diagram for Refrigerant 170 (Ethane)

Figure 13: Pressure Enthalpy Diagram with refrigeration cycle for Ethane

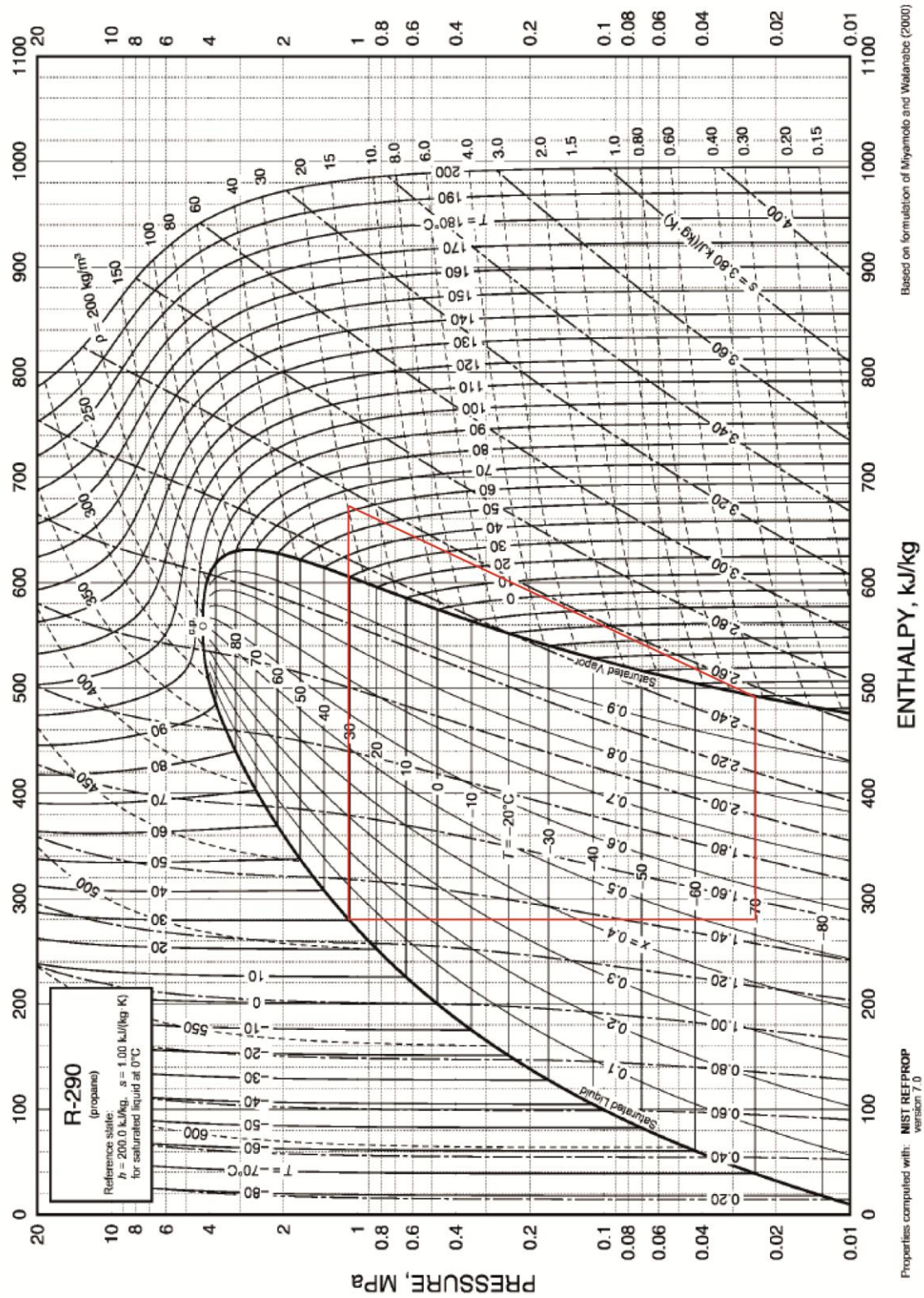

Fig. 21 Pressure-Enthalpy Diagram for Refrigerant 290 (Propane)

Figure 14: Pressure Enthalpy Diagram with refrigeration cycle for Propane

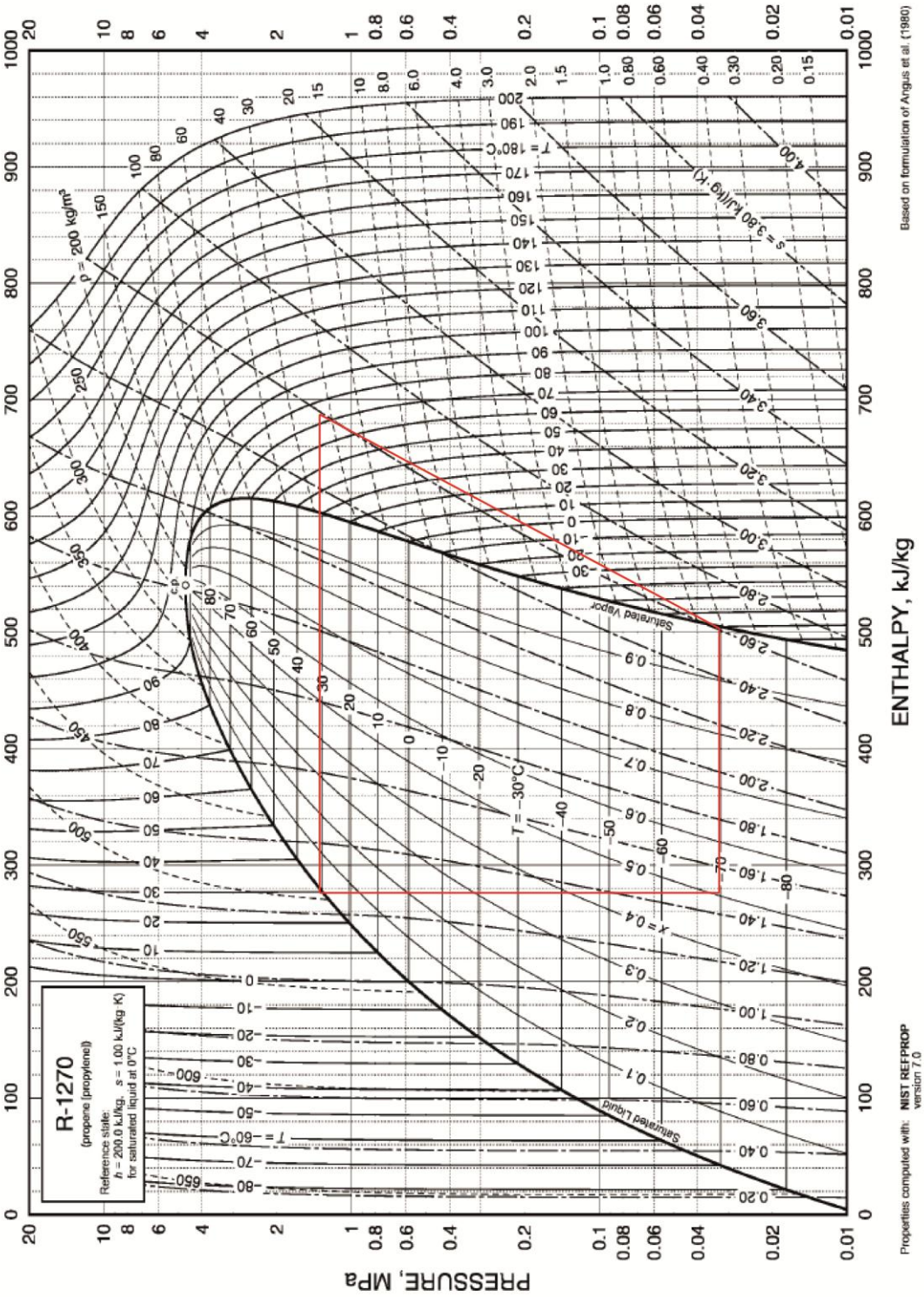

Fig. 25 Pressure-Enthalpy Diagram for Refrigerant 1270 (Propylene)

Figure 15: Pressure Enthalpy Diagram with refrigeration cycle for Propene

Appendix O: Complete Fire and Explosion Index

Table 38: Fire and Explosion Index for the reactor process unit

Fire & Explosion Index					
Area/Country: France		**Division:** -		**Location** -	**Date**
Site -	**Manufacturing Unit** ADN plant			**Process Unit** Reactor	
Materials in Process Unit					
State of Operation		**Basic Materials for Material Factor** DNA H2SO4 HNO3			
Material Factor					24
1. General Process Hazards				**Penalty Factor Range**	**Penalty Used**
Base Factor				1.00	1.00
A. Exothermic Chemical Reactions				0.30 - 1.25	1.25
B. Endothermic Processes				0.20 - 0.40	0.00
C. Material Handling and Transfer				0.25 - 1.05	0.40
D. Enclosed or Indoor Process Units				0.25 - 0.90	0.00
E. Acces				0.20 - 0.35	0.00
F. Drainage and Spill Control				0.25 - 0.50	0.00
General Process Hazards Factor (F1)					2.65
2. Special Process Hazards				**Penalty Factor Range**	**Penalty Used**
Base Factor				1.00	1.00
A. Toxic Material(s)				0.20 - 0.80	0.60
B. Sub-Atmosferic Pressure (< 500 mm Hg)				0.50	0.00
C. Operation In or Near Flammable Range					0.00
	1. Tank Farms Storage Flammable Liquids			0.50	
	2. Process Upset or Purge Failure			0.30	
	3. Always in Flammable Range			0.80	
D. Dust Explosion				0.25 - 2.00	0.00
E. Pressure	Operating Pressure:		kPa		0.00
	Relief Setting:		kPa		
F. Low Temperature				0.20 - 0.30	0.00
G. Quantity of Flammable Material:		8000	kg		0.00

Hc = 7333 kcal/kg		
1. Liquids or Gases in Process		
2. Liquids or Gases in Storage		
3. Combustible Solids in Storage, Dust in Process		
H. Corrosion and Erosion	0.10 - 0.75	0.20
I. Leakage - Joints and Packing	0.10 - 1.50	0.10
J. Use of Fired Equipment		0.00
K. Hot Oil Heat Exchange System	0.15 - 1.15	0.00
L. Rotating Equipment	0.50	0.50
Special Process Hazards Factor (F2)		2.40
Process Units Hazards Factor (F1 x F2) = F3		6.36
Fire and Explosion Index (F3 x MF = F&EI)		**153**

Table 39: Fire and Explosion Unit for the refrigeration process unit

Fire & Explosion Index

Area/Country:	**Division:**	**Location**	**Date**
France	-	-	

Site	**Manufacturing Unit**	**Process Unit**
-	ADN Plant	Refrigeration Cycle

Materials in Process Unit

State of Operation	**Basic Materials for Material Factor**
	Propylene

Material Factor		21
1. General Process Hazards	**Penalty Factor Range**	**Penalty Used**
Base Factor	1.00	1.00
A. Exothermic Chemical Reactions	0.30 - 1.25	0.00
B. Endothermic Processes	0.20 - 0.40	0.00
C. Material Handling and Transfer	0.25 - 1.05	0.00
D. Enclosed or Indoor Process Units	0.25 - 0.90	0.00
E. Acces	0.20 - 0.35	0.00
F. Drainage and Spill Control	0.25 - 0.50	0.00
General Process Hazards Factor (F1)		1.00
2. Special Process Hazards	**Penalty Factor**	**Penalty**

				Range	Used
Base Factor				1.00	1.00
A. Toxic Material(s)				0.20 - 0.80	0.20
B. Sub-Atmosferic Pressure (< 500 mm Hg)				0.50	0.50
C. Operation In or Near Flammable Range					0.00
	1. Tank Farms Storage Flammable Liquids			0.50	
	2. Process Upset or Purge Failure			0.30	
	3. Always in Flammable Range			0.80	
D. Dust Explosion				0.25 - 2.00	0.00
E. Pressure	Operating Pressure:	1030	kPa		0.49
	Relief Setting:	1200	kPa		
F. Low Temperature				0.20 - 0.30	0.00
G. Quantity of Flammable Material:		8000	kg		
	Hc =	19700	kcal/kg		0.91
	1. Liquids or Gases in Process				
	2. Liquids or Gases in Storage				
	3. Combustible Solids in Storage, Dust in Process				
H. Corrosion and Erosion				0.10 - 0.75	0.00
I. Leakage - Joints and Packing				0.10 - 1.50	0.30
J. Use of Fired Equipment					
K. Hot Oil Heat Exchange System				0.15 - 1.15	0.00
L. Rotating Equipment				0.50	0.50
Special Process Hazards Factor (F2)					3.90
Process Units Hazards Factor (F1 x F2) = F3					3.90
Fire and Explosion Index (F3 x MF = F&EI)					**82**

Appendix P: HAZOP tables

Apparatus:	Reactor Ammonium Sulfamate	Intention of Aparatus:	Producing ADN
Line Number:	IN	Intention of line:	Deliver Reactants
Parameter			

Guide Word	Deviation	Cause	Consequences	Necessary Actions
NO	No Flow	Pump Malfunction Clogged Pipe	No reaction in reactor	
LESS	Less Flow	Pump Malfunction Clogged Pipe	Less reaction in reactor	
MORE	More Flow	Pump malfunction	Higher product formation leading to T rise	Increase cooling Close other reactant valves

Apparatus:	Reactor	Intention of Aparatus:	Producing ADN
Line Number:	Acid/Water IN	Intention of line:	Deliver Reactants
Parameter			

Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
NO	No Flow	Pump Malfunction Valve Closed Clogged Pipelines	No reaction in reactor Reactor gets clogged with solid	Close AS and Inert valves
LESS	Less Flow	Pump Malfunction Clogged Pipelines Valve Malfunction	Less product formation Reactor clogs with solid	Adjust AS and Inert valves
MORE	More Flow	Valve malfunction	Flooding Rise in T	Stop pump close AS and inert
PART OF	Partly Flow	Upstream Valve closed	less product Possible Reactor clogging	Close other valves Close AS and Inert Valves
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	More PRESSURE	Pump Malfunction	Possible Reactor damage	Shutdown reactor
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	Higher TEMPERATURE	Refrigeration Cycle malfunction	Reactor T rises	Increasing cooling flow
LESS	Lower TEMPERATURE	Refrigeration Cycle malfunction	Reactor T drops Less Reaction	Decrease cooling flow

Apparatus:	Reactor	Intention of Aparatus:	Producing ADN
Line Number:	Sweep Gas In	Intention of line:	Deliver Reactants
Parameter			

Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
NO	No Flow	Compressor Malfunction	Reactor T rising slightly	none necessary
LESS	Less Flow	Compressor Malfunction	Reactor T rising slightly	none necessary
MORE	More Flow	Compressor Malfunction	no consequences	none necessary
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	More PRESSURE	Compressor Malfunction	If above 10 bar, reactor damage	shutdown compressor
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	Higher TEMPERATURE	To little refrigeration	Warm up of reactor	Adjust reactor cooling
LESS	Lower TEMPERATURE	To little refrigeration	Cooling down of reactor	Adjust reactor cooling

Apparatus:	Reactor	Intention of Aparatus:	Producing ADN
Line Number:	Products Out	Intention of line:	Deliver Reactants
Parameter			

Guide Word	Deviation	Cause	Consequences	Necessary Actions
NO	No Flow	Reactor Malfunction Clogged line	Damage to pump	Shut down downstream pump
LESS	Less Flow	Reactor Malfunction Clogged line	Damage to pump	Shut down downstream pump
MORE	More Flow	Up stream	no dangerous consequences	none necessary
PART OF	Partly Flow	no reaction	no dangerous consequences	none necessary
OTHER THAN	Different Flow	All flows besides gas stop	Damage to the pump	shut down gas flow
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	Higher TEMPERATURE	To high reactor T	no dangerous consequences	none necessary
LESS	Lower TEMPERATURE	To low reactor T	no dangerous consequences	none necessary

Apparatus:	Reactor	Intention of Aparatus:	Producing ADN
Line Number:	Refrigerant	Intention of line:	Deliver Reactants
Parameter			

Guide Word	Deviation	Cause	Consequences	Necessary Actions
NO	No Flow	Compressor Malfunction Clogged line, Clogged Valve	Reactor Heat Up	Close AS Valve
LESS	Less Flow	Compressor Malfunction	Reactor Heat Up	Close AS Valve
MORE	More Flow	Compressor Malfunction	Reactor Cool Down Little reaction and clogging	Close all reactant valves shutdown reactor
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	More PRESSURE (compressor)	Compressor Malfunction	Higher Discharge T	Increase Coolwater Flow
LESS	Less PRESSURE (compressor)	Compressor Malfunction	Lower Discharge T	Increase Coolwater Flow due to lower ΔT
MORE	More PRESSURE (Evaporator)	Evaporation Valve Malfunction	Higher Evaporator T, lower ΔT in reactor	Increase Refrigerant flow
LESS	Less PRESSURE (Evaporator)	Evaporation Valve Malfunction	Lower Evaporator T, Higher ΔT in reactor	Decrease Refrigerant flow
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	Higher TEMP (compressor)	To little flow	same as pressure	same as pressure
LESS	Lower TEMP (Compressor)	To much flow	same as pressure	same as pressure

Apparatus:	Reactor	Intention of Aparatus:	Producing ADN
Line Number:	Reactor	Intention of line:	Deliver Reactants
Parameter			

Guide Word	Deviation	Cause	Consequences	Necessary Actions
NO	No Flow	Closed Valves	Nothing happens	none necessary
LESS	Less Flow	Closed valve	Nothing happens	none necessary
MORE	More Flow	Valve Malfunction	Reactor can heat up (more reaction)	Increase cooling flow
PART OF	Partly Flow	Valve Malfunction	No reaction Clogging Cooling Flow Wrong	Close all valves
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	More PRESSURE	Gas flow to high	Above 10 bar: Reactor Desintegration	Increase gas outflow
Guide Word	**Deviation**	**Cause**	**Consequences**	**Necessary Actions**
MORE	Higher TEMPERATURE	refrigeration cycle	More Decomposition Less product	Adjust reactant flow
LESS	Lower TEMPERATURE	refrigeration cycle	Higher viscosity	Adjust reactant flow

Appendix Q: Cost estimates for equipment units

Table 40: Cost estimates for relevant equipment units

Unit Name	Equipment Unit	Type	Size	Amount	Currency	Price Estimate	Factors	Euro's	Actual Price	Total	Source
R01	Reactor	Spinning disc	0.50	14	£	319889.70	1.95	1.14	€ 319,890	€ 4,478,456	PI book, timmerhaus
E01	Heat Exchanger	Shell and Tube	213.90	1	$	27572.27	1.30	0.71	€ 25,449	€ 25,449	matche.com
E02	Heat Exchanger	Shell and Tube	48.62	1	$	3051.48	1.30	0.71	€ 2,817	€ 2,817	matche.com
E03	Heat Exchanger	Shell and Tube (GL)	161.92	1	$	23660.00	1.30	0.71	€ 21,838	€ 21,838	matche.com
E04	Heat Exchanger	Double Pipe (CS)	25.63	1	$	1307.78	1.00	0.71	€ 929	€ 929	matche.com
E05	Heat Exchanger	Double Pipe	24.88	1	$	2397.59	1.30	0.71	€ 2,213	€ 2,213	matche.com
E06	Heat Exchanger	Shell and Tube (CS)	4208.55	1	$	112795.64	1.30	0.71	€ 104,110	€ 104,110	matche.com
P01	Compressor	Screw	1082 kw	2	$	511,231	1.00	0.71	€ 362,974	€ 725,948	matche.com
R02	Neutralizer	n.a.	n.a.	n.a.		n.a.			n.a.	n.a.	n.a.
C01	adsorber/desorber	n.a.	n.a.	n.a.		n.a.			n.a.	n.a.	n.a.
C02	adsorber/desorber	n.a.	n.a.	n.a.		n.a.			n.a.	n.a.	n.a.
S01	Evaporator	n.a.	n.a.	n.a.		n.a.			n.a.	n.a.	n.a.
Total equipment costs										**€ 5,361,760**	

Appendix R: Utilities

SUMMARY OF UTILITIES														
EQUIPMENT		**UTILITIES**												**REMARKS**
		Heating					**Cooling**				**Power**			
Nr.	**Name**	Load	Consumption (t/h)				Load	Consumption (t/h)			Actual	Consumption (t/h, kWh/h)		
			Steam			Hot		Cooling	Air	Refrig.	Load	Steam (t/h)		Electr.
		kW	LP	MP	HP	Oil	kW	Water			kW	HP	MP	kWh/h	
E01	Neutralization feed cooler						84			1.2					
E02	Inert cooler						13			0.2					
E03	Acid cooler						145			2.1					
E04	Water heater	9	0.1												
E05	Water cooler						59			0.8					
E06	Condenser						2411	168							
R01	SDR's						1188			16.8				12	1 kWh/h per reactor
R02	bubble column reactor						3139								OUT OF SCOPE
S01	Evaporative Crystallizer	90													OUT OF SCOPE
K01	Compressor										1082			1353	80% eff
TOTAL			**0.13**					**168**		**21**				**1365**	

Project ID Number	:	**CPD3381**
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Appendix S: Selling price for ADN

The following text is the paragraph that outlines the way the selling price for ADN was estimated as found in the BoD report.

Selling price for ADN

As given in the project brief the current fuel for the rockets is Ammonium Perchlorate (AP). The new ADN fuel will give an increase of thrust of around 6 – 7 %, and the current selling price for the AP is around €20,- per kg(Zevenbergen 2011).To calculate an estimate of the selling price of the ADN the density difference between ADN and AP also needs to be taken into account. This is due to the fact that the boosters for the rocket will still be completely filled with the rocket fuel.

The density found for AP is 1950 kg/m^3, and the density for ADN is found to be between 1800 and 1840kg/m^3(Venkatachalam, Santhosh et al. 2004; Chemwatch 2010). Using the fact that a booster contains 240 tons of solid propellant, of which 70% is solid oxidizer, it follows that 168 tons of AP propellant can be replaced with 156.8 tons of ADN propellant. If then the fact is taken into account that a single booster delivers 7000 kN of mean thrust, and the liftoff mass of a Ariane 5 rocket is 780 tons, it is possible to calculate the thrust per kg. If 6-7% extra thrust per kg oxidizer is added, as given in the project brief, and the difference in mass between the AP and ADN is taken into account, it is possible to calculate a new thrust for the Ariane 5 rockets if ADN is used(Arianespace 2008; Arianespace 2011).

These calculations are summarized in Table 41. As can be seen, the ADN gives an increase in thrust per kg of rocket mass of 0.000152kN /kg. To give more meaning to this value, it can be recalculated to 0.85%.

Table 41: Calculations for the differences in thrust per kg for Ammonium Perchlorate, and Ammonium Dinitramide.

Ammonium Perchlorate			**Ammonium Dinitramide**		
Lift off mass	780000	kg	Lift off mass	768800	kg
AP thrust per booster	7000	kN	ADN thrust per booster	6958	kN
2 boosters	14000	kN	2 boosters	13916	kN
	0.0179	kN/kg		0.0181	kN/kg

If the price paid for the oxidizer for fueling the rocket is kept the same, it is possible to calculate a price for each kg ADN. This will be a higher price, due to the fact that less oxidizer can fit in the rocket, but it still produces enough thrust to launch the rocket. With these calculations a price can be found which is €21.43 per kg ADN. So an initial selling price for the ADN can be set at €21,- per kg.

Appendix T: Economic Criteria

This appendix shows the calculation methods used and some of the tables used to calculate the PBT, ROI and IRR.

For the PBT the formula used in this report is:

$$PBT = \frac{Total\ depreciable\ capital}{cash\ flow}$$

For ROI the following formula was used:

$$ROI = \frac{Sales\ Revenues - Production\ Cost}{TCI}$$

For IRR the following method was used, as outlined in the Product and Process Design classes:

$$Cash\ in - Cash\ Out = CF$$

$$Discounted\ Cash\ Flow = DCF = \frac{(CF)_n}{(1+r)^{(n-1)}}$$

$$Cumulated\ Discounted\ Cash\ Flow = CDCF_n = \sum (DCF)_{(n-1)}$$

$$PV = CDCF_n$$

$$IRR = r\ for\ which\ (PV)_{10} = 0$$

In Table 42 an example of an IRR calculation for this project with a 10 year lifespan can be seen. For this an initial equipment cost of € 10,361,760 was used. The value for r was then found by letting the excel solver adjust r so that PV at year 10 would become zero, as per the definition of the IRR.

Table 42: Example calculation of IRR

Principal	year	Cashflow	Cumulated Cashflow	Discounted Cashflow	Present Value
0	Investment	-€ 51,808,798	-€ 51,808,798	-€ 51,808,798	-€ 51,808,798
1	2012	€ 24,270,227	-€ 27,538,571	€ 24,270,227	-€ 27,538,571
2	2013	€ 24,270,227	-€ 3,268,344	€ 12,921,457	-€ 14,617,115
3	2014	€ 24,270,227	€ 21,001,883	€ 6,879,377	-€ 7,737,738
4	2015	€ 24,270,227	€ 45,272,110	€ 3,662,577	-€ 4,075,161
5	2016	€ 24,270,227	€ 69,542,336	€ 1,949,954	-€ 2,125,207
6	2017	€ 24,270,227	€ 93,812,563	€ 1,038,155	-€ 1,087,052
7	2018	€ 24,270,227	€ 118,082,790	€ 552,713	-€ 534,339
8	2019	€ 24,270,227	€ 142,353,017	€ 294,264	-€ 240,075
9	2020	€ 24,270,227	€ 166,623,244	€ 156,666	-€ 83,409
10	**2021**	**€ 24,270,227**	**€ 190,893,471**	**€ 83,409**	**€ 0**
11	2022	€ 24,270,227	€ 215,163,698	€ 44,407	€ 44,407
12	2023	€ 24,270,227	€ 239,433,924	€ 23,642	€ 68,049
13	2024	€ 24,270,227	€ 263,704,151	€ 12,587	€ 80,636
14	2025	€ 24,270,227	€ 287,974,378	€ 6,701	€ 87,337
15	2026	€ 24,270,227	€ 312,244,605	€ 3,568	€ 90,905