

PRODUCTION OF MONOAMMONIUM PHOSPHATE AT YARA AB

Final report

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Abstract

Yara AB is a worldwide manufacturer of fertilizers and inorganic feed phosphates that considers the opportunity to produce monoammonium phosphate (MAP) at their site in Helsingborg. The production is planned to be 10 000 metric tons of food grade MAP per annum split into 10 campaigns. The existing factory is a multipurpose facility which means that part of the process equipment is used in production of other products.

A literature study was made where the theoretical background and properties of the compounds and process was investigated thoroughly. Based on this study three basic process designs were developed and the most promising alternative was chosen for a further, more detailed, investigation. Unit operations such as the reactor and condenser were designed in detail based on basic mass and energy balances, the two film theory of mass transfer and empirical relations for process parameters and dimensioning. A HazOp risk assessment over the process was performed where the most crucial risk for every analysis point was determined. A feasibility study was made according to the Ulrich and the annuity methods and the most relevant cost parameter was analyzed in a sensitivity study.

The recommended process design includes a bubble reactor operating at 2 bar pressure consisting of four zones. The reactor is filled with phosphoric acid in excess. Basically, the product, MAP, gravitates to the bottom of the reactor due to density differences and the evaporated water is taken out from the top. Ammonia is introduced through a sparger slightly above the melt zone and the bubbles travel upwards through the phosphoric acid in the reaction zone. There is headspace at the top of the reactor. After the reactor, the product is granulated, dried and screened.

The bubble reactor production of MAP is considered to have a low risk of incidents but the biggest concern is release of ammonia. The operating cost was found to be large compared to the investment cost. The biggest contribution to the operating cost is the cost of raw material, especially phosphoric acid. This is due to the large consumption of phosphoric acid along with its high market price. It has been shown that the process is not profitable at the current price situation. However, both a small decrease of the market price of phosphoric acid and a small increase of the selling price of MAP will give positive annual net revenue.

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1 Introduction

1.1 Presentation of Yara AB and the project

Yara AB is a Norwegian company originating from Norsk Hydro and is world leading in the manufacturing of fertilizers. Besides fertilizers, they produce several different inorganic phosphate feeds and industrial process solutions. This project is done in cooperation with Yara AB in Helsingborg, situated in the Industry Park of Sweden, and focuses on animal feed additives including calcium phosphates, magnesium compounds and feed acidifiers. Currently, there is a multipurpose facility at the site which produces various feed minerals in campaigns. The company now considers producing monoammonium phosphate (MAP). This study seeks to determine the feasibility associated with expanding the production at the site so that it also includes monoammonium phosphate. Thereby, a detailed process design was developed and is presented in the study. This product fulfills a specific demand for a feed mineral with a high content of phosphorous compared to many other existing additives like the ones already produced at the site or polyammonium phosphates. High phosphorous levels is especially desired in the fish and shellfish industry, where phosphorous is often the limiting nutrient. In the planned production of monoammonium phosphate, the on-site already available phosphoric acid is reacted with ammonia. Anhydrous ammonia is delivered to the site by railway. The reaction with ammonia and phosphoric acid is exothermic and since ammonia is both flammable and toxic safety precautions are necessary. Thus, a risk assessment is requested by Yara and included in this study. The planned annual production of monoammonium phosphate is 10 000 metric tons split over ten campaigns. The designed process should be sustainable in the sense of profitability and safety.

1.2 Phosphorous

Intake of phosphorous is essential for all life forms. Thus, phosphoric compounds are widely used in agriculture as fertilizers and in animal feed additives. The majority of the industrial phosphorous originates from mineral ores, so called phosphate rock [1]. Considering that the resource is limited, products containing phosphorous should be handled as efficiently as possible. Furthermore, both phosphorous and ammonia contributes to eutrophication in aquatic ecosystems and emissions must therefore be minimized.

Yara's phosphorous source is Apatite mined in Siilinjärvi in Finland and has volcanic origin which makes the phosphoric acid relatively free from impurities such as heavy metals [2]. Another phosphorous source is sedimentary bedrock, mainly mined in Africa which contains much more impurities. Any impurities in the phosphoric acid end up in the product and since the product is intended for animal feed, a pure acid is of great importance. However, these levels are easily monitored since the impurities are directly transferable in to the product.

Wet process phosphoric acid is delivered to the Helsingborg site with a slightly varying concentration depending on the season - around 60 % P_2O_5 in the summer and 57 % P_2O_5 in the winter [2]. It is mixed on the site to desired concentration for each production campaign. As a standard the phosphorous content of phosphoric acid is often referred to as a percentage of P_2O_5 even though there is no actual P_2O_5 . For example, 50 % P_2O_5 means that half the weight of the acid is P_2O_5 .

Phosphoric acid is highly corrosive and exposure to it may cause serious injuries. The corrosiveness is a concern when choosing suitable materials in the process, none the less at high temperatures. [3]

1.3 Ammonia

Ammonia is a colorless gas at room temperature with a very distinct smell. It is highly soluble in water and is therefore likely to cause severe damage to the respiratory system and to aquatic animals. Apart from this, ammonia is flammable which adds to the risks associated with the compound. Therefore, Yara has set a maximum amount of ammonia that they feel comfortable holding at the site. This limit is 50 metric tons i.e. one railway car.

Ammonia causes irritation in concentrations as low as 20 ppm. The flammability region for ammonia is in the range of 16-25%. Maximum daily doses and other thresholds are presented in Table 1 below.

Table 1. Threshold values for ammonia exposure.

TLV-C Threshold Limit Value-Ceiling	50 ppm
TWA the eight-hour time weighted average	25 ppm
Perception limit	10 ppm [4]
Odor threshold	5 ppm [5]
Concentration when irritation occurs	20-25ppm [6]
Severe damage or death	5000 ppm (3600 mg/m ³)

The P-T phase diagram is presented in Figure 1.

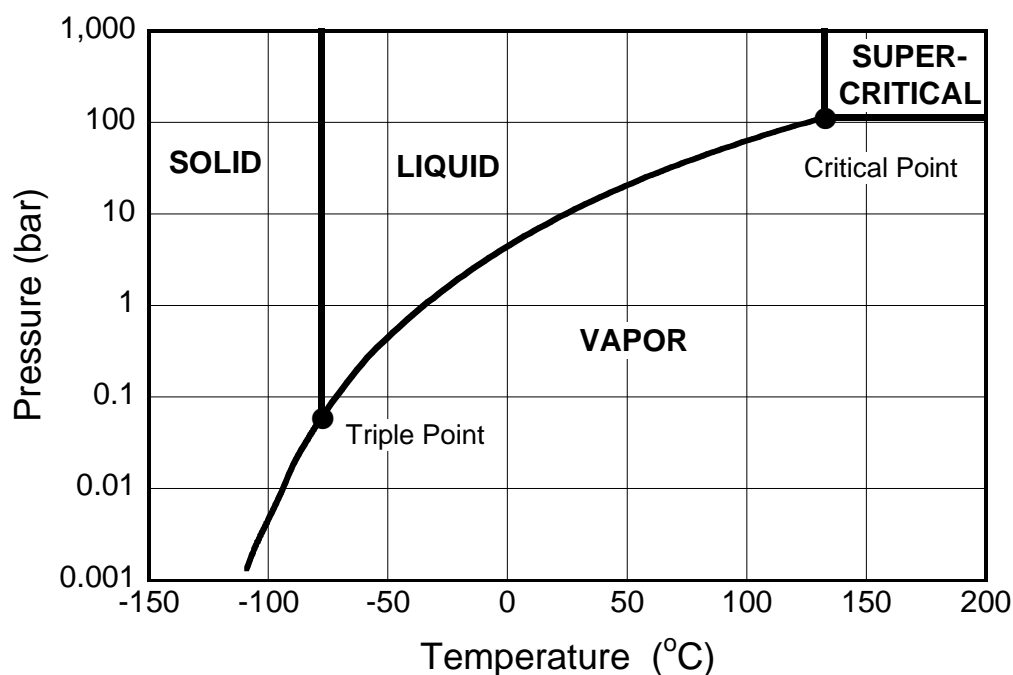


Figure 1. Phase diagram of ammonia. [7]

1.4 Monoammonium phosphate

Monoammonium phosphate, MAP, is formed from ammonia and phosphoric acid in an exothermic reaction.



ΔH_R was calculated from the enthalpy of formation of the substances, see Appendix A.

MAP is a salt with a tetragonal crystal structure. The molecular structure is shown below in Figure 2.

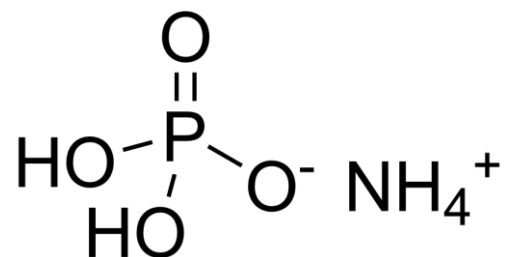


Figure 2. Molecular structure of monoammonium phosphate.

The product is distributed as solid granules in size range 0.063-0.71 mm [2], which is optimal for an even distribution in the animal feed. Typically, the content of nitrogen, phosphorous and potassium (NPK) of MAP is in the range (11-13)-(48-61)-0 [8]. This can be compared to the theoretical value of pure MAP which is 12-62-0.

MAP is soluble in water. However, the solubility varies with the N to P ratio in the solution, see Figure 3. This will be further discussed in section 3.3.

Prolonged skin contact with MAP may cause irritation and ingestion of large quantities may cause gastro-intestinal disorder. [9]

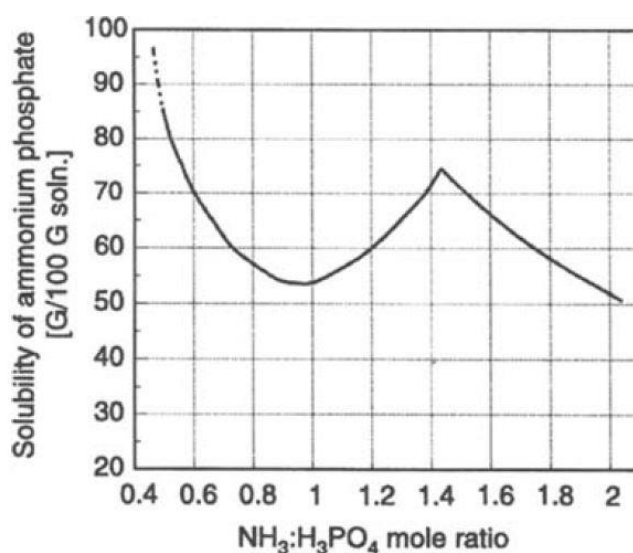


Figure 3. Effect of NH₃ - H₃PO₄ molar ratio on solubility of monoammonium phosphate at 75°C [10].

2 Method

Through a literature study the most important parts of the process were studied in detail. Based on this study three basic process designs were developed and the most promising alternative was chosen for a further, more detailed, investigation. Unit operations such as the reactor and condenser were designed in detail based on basic mass and energy balances, the two film theory of mass transfer and empirical relations for process parameters and dimensioning. A HazOp risk assessment over the process was performed where the most crucial risk for every analysis point was determined. A feasibility study was made according to the Ulrich and the annuity methods and the most relevant cost parameter was analyzed in a sensitivity study.

3 Literature study

3.1 Basic description of the process

Ammonia can be used in an aqueous solution, pressurized liquid or as a gas depending on what suits the specific process. The reaction with phosphoric acid is instant resulting in a slurry which is treated in the granulator. Depending on process parameters such as temperature, pressure and water content the slurry has different properties with regards to the amount of solids, salts in ionized forms (solution) and melted salt. In the granulator the MAP particle nuclei are formed and grow in size. Excess water is removed from the MAP in the dryer and the product is screened and delivered if the size is correct, otherwise it is recycled back to the granulator.

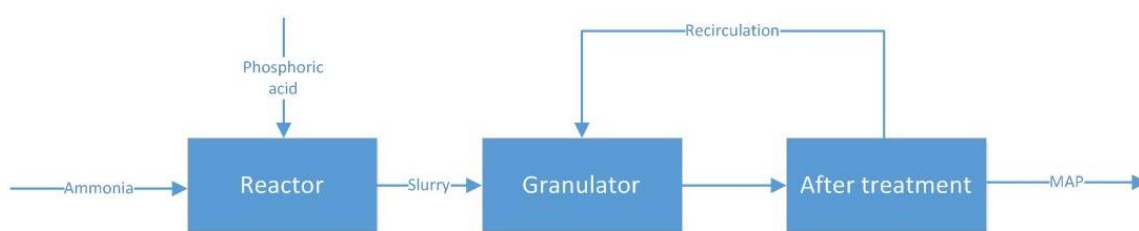


Figure 4. Essential unit operations of the process.

3.2 Raw material

Ammonia is delivered to Yara as liquid anhydrous ammonia in pressurized rail tank cars at 7 bar and 14 °C. Since ammonia is hazardous it is important to handle it with proper care. In the beginning of the process, a filling station provides the benefit of more stable running conditions since the temperature, and thereby also pressure, can be controlled throughout the year. If ammonia is stored in railway cars outdoors the temperature affects the pressure of the ingoing stream of ammonia. The physical state of ammonia in the reaction depends on the process of choice. For example, in a bubble column reactor or a draft tube reactor the ammonia needs to be in gas phase. If liquid ammonia is desired in the process, which is the case in for example the pipe reactor, it is required to further pressurize the ammonia in order to maintain it in liquid phase since the temperature is increased in the reaction.

3.3 The reaction

The reaction of ammonia and phosphoric acid to monoammonium phosphate is exothermic with a heat of reaction of -120 kJ/mol. Even though some of the heat is used to evaporate water,

cooling is required to keep the temperature at a constant level. Since the reaction can be regarded as instantaneous and complete, the pressure and temperature does not affect the formation of product. However, depending on temperature and pressure the physical state of the product from the reactor varies. Apart from water, the slurry consists of a mixture of solid crystals, MAP dissolved in a solution and melted MAP.

There are examples of processes where the reaction is carried out at sub atmospheric pressures, e.g. 60 °C and 0.16 bar. In this case a special draft tube and baffle crystallizer, a DTB crystallizer, was used [11]. No external granulation step is needed together with a DTB crystallizer since recirculation enables formation and growth of granules inside the reactor and the desired granular size can be retrieved directly. At sub atmospheric pressures, water is more easily removed from the slurry and dissociation of ammonia is prevented. Thereby loss of ammonia is diminished.

Another approach is performing the reaction in two steps and taking advantage of the solubility of MAP at different N to P ratios. When the slurry has to be pumped from the reaction vessel to the granulator, a low content of solids is beneficial. This can be achieved by partially preforming the reaction at N to P ratio 0.6 to 1 where MAP has a high solubility, see Figure 3. In the granulator, additional ammonia is added to reach the N to P ratio of 1 to 1. This design is referred to as the TVA process since the design is patented by the Tennessee Valley Authority. [12]

The pressure in the reactor determines the boiling point of water which in turn decides the temperature in the reactor. Consequentially, at higher pressures more of the MAP can be in the melted state in the product stream out from the reactor. The reaction can be performed with ammonia in either liquid or gaseous phase [12]. In case of the former, a pipe reactor or a cross pipe reactor can be used, and in the case of the latter a bubble reactor is convenient.

The solid MAP particles that may occur in the slurry out from the reactor are primarily crystals in contrast to the solids formed in the granulator. Crystals are smaller than granules since granules are formed by agglomeration of crystals. In the following section the principles of crystallization of MAP is described.

3.4 Crystallization

The N to P ratio has a significant effect on size distribution of the monoammonium phosphate crystals. It has been found that the mean crystal size increases in the range 250 μm to 450 μm when the N to P ratio increases up until 1. Further increase of N to P ratio reduces crystal size. For small N to P ratios such as 0.79, more time is required for formation of crystals which results in finer crystals and smaller quantities of crystals compared to the N to P ratio of 1 [13]. This is consistent with the fact that MAP has the lowest solubility at the N to P ratio of 1. This can be seen in Figure 3.

A seeded system has been preloaded with a certain amount of crushed product solids in order to enhance crystal formation. It has been found that in non-seeded systems the time needed for nucleation is significant compared to the total growth time. Another benefit of seeded systems is that it narrows the crystal size distribution. [13]

However, triammonium phosphate (TAP) is formed at pH values above 8 [13]. Production of MAP is carried out at approximately pH 5.2 and production of DAP is carried out at pH 6.2 [10]. The pH value can be used as a control parameter since it is directly related to the consumption of phosphoric acid, see section 4.1.1.3.

It has been shown that cold spots in the process, for example in pipes, heat exchangers and pumps, can trigger crystallization leading to scaling and clogging. This is important to take into consideration when designing processes, especially in colder climates.

3.5 Granulation

The goal of a granulation step is to allow the monoammonium phosphate slurry to form crystals and to aggregate smaller crystals into larger particulates. The granulation is carried out in a rotating drum which the monoammonium phosphate slurry is sprayed into. A downstream sieving step separates granules outside the acceptable size range. Granules that are too big are crushed and can either be screened again and/or mixed with granules that are too small [14]. The mixture is subsequently returned to the granulation drum as a recycle stream. Recycle ratios of 6:1 to 5:1 are common [15].

Important parameters of granulation are the amount of available solute and the viscosity of the binding solution [15]. For the granulation of monoammonium phosphate, the median diameter increases with increasing moisture content, see Figure 5. Below 5 % moisture content, the median diameter is constant at approximately 2 mm and above 5 % the median diameter increases significantly. Furthermore, the size distribution equilibrium is reached after five minutes for a moisture content of 5 % but for higher values equilibrium is not reached even after 25 minutes. The size distribution is widened as the moisture content increases [15]. Thus, it can be concluded that it is desirable to reach moisture contents below 5 % in the design proposition for Yara.

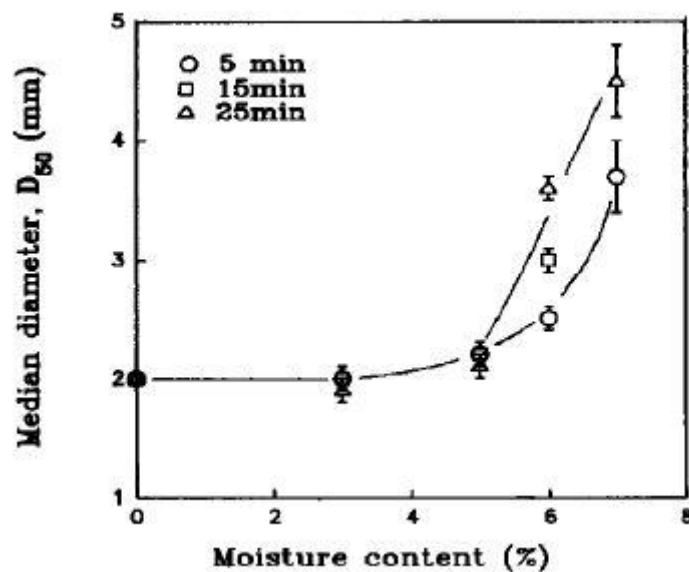


Figure 5. The relation between moisture content and median diameter of MAP. [2]

If the reaction of ammonia with phosphoric acid is carried out at a lower molar ration than 1:1 $\text{NH}_3:\text{H}_3\text{PO}_4$ in the reactor, ammonia must be added in the granulation step. This is done because the solubility of monoammonium phosphate is higher at lower molar ratios. This is described later in section 4.3. When ammonia is added in the granulator the solubility decreases, thereby making granulation easier [14].

In the process described in [11], no explicit granulation step is used; the monoammonium is formed in a draft tube baffle crystallizer and the crystal slurry is centrifuged and washed in water. The slurry is then dried in a rotary drier at around 150°C to take the moisture content from approximately 5% to 0.1% [11]. This is because the crystal size and size range can be directly controlled in a draft tube baffle crystallizer.

3.6 Scrubbing

The purpose of a wet scrubber is to clean a dirty gas from pollutants using a liquid, commonly water. The pollutants can either be particles, gas or both. The pollutants are captured in the scrubbing liquid. In order to achieve a high efficiency a good contact between gas and liquid is required. There are numerous ways to accomplish this, e.g. by spraying the gas stream and using a packed tower. The scrubber liquid is chosen depending on which pollutant is present in the process. [16]

An important part of scrubbing a gas stream is also to saturate and cool it. This is done partially to lower the volume of the gas stream in order to decrease equipment cost and to minimize water vaporization downstream, which can lead to scaling. [16]

3.7 Drying, screening and crushing

In any industry, removal of water is often a costly but necessary operation. In the production of MAP, water needs to be removed from the formed granules. Drying is an energy intensive operation due to the high heat of evaporation of water. Removal of water from a solid can be performed using a drying drum. For this purpose, the dryer could be constituted of a rotating cylinder which is heated by combustion gases. See Figure 6 for an example of what such a dryer could look like.

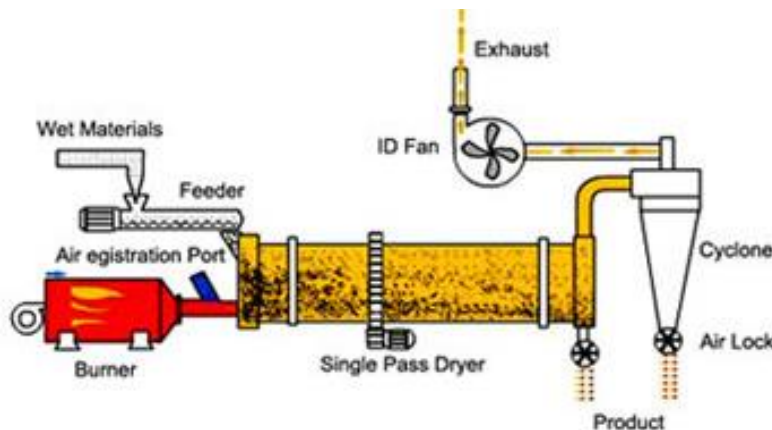


Figure 6. An example of a rotary drying drum [17].

Wet materials of moisture content less than 5% is delivered from the granulation step to the dryer where the moisture content is decreased to less than 0.1%. A cyclone separates particulates from the combustion gases and water vapor before it is vented to the atmosphere.

The dry granules are screened and particles smaller than a certain size are recirculated to the granulator where they serve as seeding material. Particles larger than a certain size are crushed and screened again. The particles within the right size range are filled into bags and delivered to the costumers.

4 Proposed designs

The proposed designs are based on the equipment that is already available on the site in Helsingborg. Here follows a description of the existing unit operations:

- Granulator
- Scrubber
- Dryer
- Screener and crusher

The granulation drum operates at a slight sub atmospheric pressure, which is obtained by the use of a fan. The result of the sub atmospheric pressure is one directional transport of air from the surroundings into the granulator. When the production is not running, the fan also stops which means that the granulator is no longer closed in relation to the atmosphere. Therefore, transport is then possible in both directions, to and from the granulator. A cylindrical rotary dryer with a burner fueled by natural gas is present at Yara's site in Helsingborg and can be used for drying of the MAP granules. Furthermore, equipment for screening and crushing is also available. To conclude, basically only the reaction step is missing for a complete production chain.

4.1 Bubble reactor process

Ammonia and phosphoric acid form monoammonium phosphate in the reactor, see Figure 7 for the complete process schematics. Due to the high heat of reaction water is evaporated along with trace amounts of ammonia and small amounts of inert gases originating from the phosphoric acid. The flue gases are condensed in a heat exchanger using cooling water and inert gases are purged. The reason for the condensation is to achieve hydrous ammonia which can be treated and cleaned as opposed to emitting gaseous ammonia to the atmosphere directly. The solution/slurry/melt from the reactor is introduced to the granulator with a moisture content of 3-4 %. Compared to the TVA process, see section 4.3, the design is similar with the exception that no additional ammonia is added in the granulator. After the granulation the product is dried and screened before it is packaged.

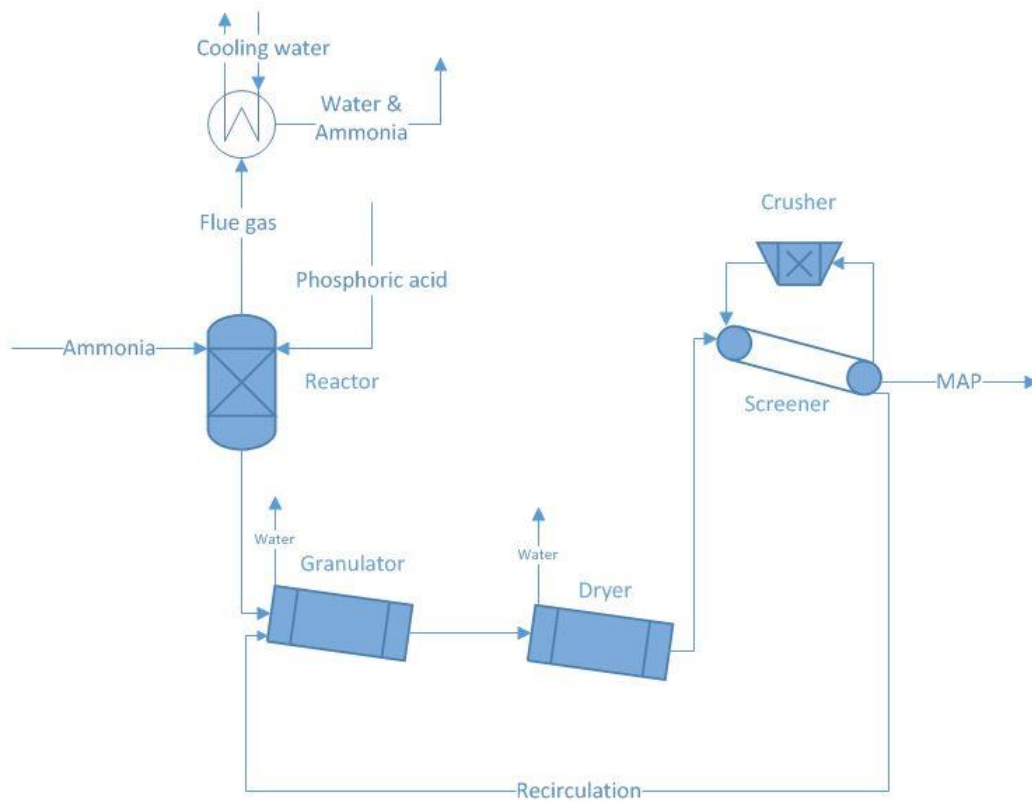


Figure 7. Process flow sheet for the bubble reactor design.

4.1.1 Calculations

A preliminary investigation showed that the bubble reactor design was promising. Therefore, it is further investigated in this section.

4.1.1.1 Mass balances

The general expression for the mass balance is:

$$IN - OUT + PRODUCTION = ACCUMULATION$$

With a “black box” perspective, the overall mass balance for the reactor, assuming no accumulation, is:

$$IN - OUT = 0$$

which can be expressed as the following, where notations are explained in Figure 8:

$$m_{in} - m_{out} - m_{g,out} = 0$$

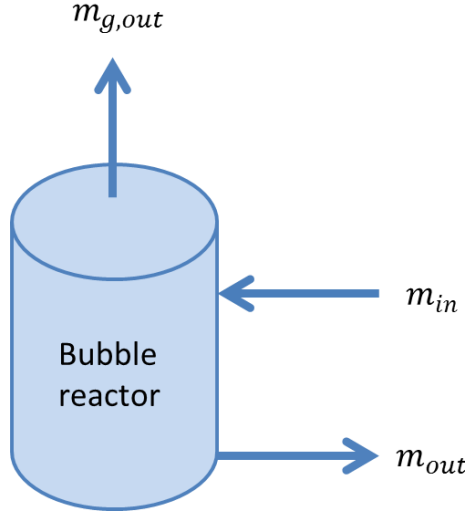


Figure 8. Simplified schematic model of the bubble reactor.

Thus m_{in} consists of phosphoric acid, ammonia and water. The amount of ammonia is calculated from the information given in the project description, the planned annual production is 10 000 tonnes of MAP and spread over 10 campaigns. This corresponds to a consumption of ammonia of 150 tonnes per week. One week corresponds to one campaign. Knowing the amount of ammonia coming in and the stoichiometric relations according to the reaction formula, the amount of phosphoric acid required and MAP produced can be calculated. Since the phosphoric acid is 60 % P_2O_5 the amount of water in the acid is 17 wt%.

m_{out} consists of MAP and water and $m_{g,out}$ is assumed to be pure steam in these calculations. In reality $m_{g,out}$ does contain trace amounts of inert gases and ammonia which will be discussed later. These amounts are assumed to be so small that they do not affect the mass and energy balances.

$$m_{in} = m_{NH_3} + m_{H_3PO_4} + m_{H_2O,in}$$

$$m_{out} = m_{MAP} + m_{H_2O,out}$$

The moisture content of the melt, x , is for the design calculations assumed to be 4 % which gives the following expression.

$$m_{H_2O,out} = x \cdot m_{out} \rightarrow$$

$$m_{H_2O,out} = \frac{x}{1 - x} \cdot m_{MAP}$$

Since the reaction is complete and all the stoichiometric coefficients of the reaction are 1 it can be assumed that all ammonia is converted into MAP. Thereby the amount of phosphoric acid, containing a known percentage of water, enables the mass balance of water to be formulated.

$$m_{H_2O,in} = m_g + m_{H_2O,out}$$

Thereby m_g can be calculated and the results of the calculations above can be seen in Table 2 below.

Table 2. Summary of calculation results from the mass balances.

Parameter	Description	Value
m_{NH_3}	Mass flow ammonia	0.3472 kg/s
$m_{H_3PO_4}$	Mass flow phosphoric acid	1.9975 kg/s
$m_{H_2O,in}$	Mass flow water in	0.3596 kg/s
m_g	Mass flow steam	0.2619 kg/s
m_{MAP}	Mass flow monoammonium phosphate	2.3447 kg/s
$m_{H_2O,out}$	Mass flow water out	0.0977 kg/s

4.1.1.2 Energy balance

An energy balance was formulated over the reactor in order to calculate the cooling requirement of the reactor, Q .

$$IN - OUT + REAC = Q$$

The energy of one stream can generally be formulated as E:

$$E = \sum_{i=1}^n m_i c_{p,i} T_i$$

where i is one component and $c_{p,i} T_i = H_i$. For the ingoing streams, the energy expression can be seen below.

$$IN = (m_{NH_3} \cdot T_{NH_3} \cdot c_{p,NH_3}) + (m_{H_2O,in} \cdot T_{H_2O,in} \cdot c_{p,H_2O,in}) + (m_{H_3PO_4} \cdot T_{H_3PO_4} \cdot c_{p,H_3PO_4})$$

In the same way the energy of the stream leaving the reactor is described by:

$$OUT = (m_g \cdot T_g \cdot c_{p,g}) + (m_{MAP} \cdot T_{MAP} \cdot c_{p,MAP}) + (m_{H_2O,out} \cdot T_{H_2O,out} \cdot c_{p,H_2O,out})$$

Using a group contribution technique, an estimation of an expression for the specific heat capacity of MAP was derived. [18]

$$c_{p,MAP} = 65.903 + 284.75 \cdot 10^{-3} \cdot T - 0.674 \cdot 10^6 \frac{1}{T^2} + 5.333 \cdot 10^{-6} \cdot T^2 \text{ J/(K mol)}$$

The $REAC$ term includes both the heat of reaction, heat of dissolution and energy required for evaporation of water:

$$REAC = \Delta H_R \cdot m_{NH_3} - \Delta H_{dil} \cdot m_{MAP} - \Delta H_{vap,H_2O} \cdot m_g$$

Thus, the energy balance can be solved for the cooling requirement, see Table 3 for results. In the calculations all streams going into the reactor has been assumed to have the same temperature and all the streams leaving the reactor were also assumed to have the same temperature.

$$T_{in} = T_{NH_3} = T_{H_2O,in} = T_{H_3PO_4}$$

$$T_{out} = T_g = T_{MAP} = T_{H_2O,out}$$

Note that the temperature inside the reactor, and thereby also T_{out} , depends on the boiling point of water at the given pressure.

Table 3. Summary of parameters and calculation results associated with the energy balance.

Parameter	Description	Value
$c_{p,NH_3}(20\text{ }^{\circ}C)$	Specific heat capacity ammonia	$35.65\text{ J}/(K\text{ mol})$
$c_{p,H_2O}(20\text{ }^{\circ}C)$	Specific heat capacity water	$4181\text{ J}/(K\text{ kg})$
$c_{p,H_3PO_4}(20\text{ }^{\circ}C)$	Specific heat capacity phosphoric acid	$143.5\text{ J}/(K\text{ kg})$
$c_{p,MAP}(165\text{ }^{\circ}C)$	Specific heat capacity monoammonium phosphate	$188\text{ J}/(K\text{ mol})$
T_{in}	Temperature of the inflow	$20\text{ }^{\circ}C$
T_g	Temperature of the steam	$165\text{ }^{\circ}C$
T_{out}	Temperature of the outflow	$165\text{ }^{\circ}C$
ΔH_R	Reaction enthalpy (MAP)	$-120.13\text{ kJ}/mol$ ¹
ΔH_{dil}	Dissolution enthalpy (MAP)	$11.2\text{ kJ}/mol$
$\Delta H_{vap,H_2O}$	Vaporization enthalpy of water (1 atm)	$2066\text{ kJ}/kg$
Q	Cooling requirement	586.5 kW

4.1.1.3 Detailed reactor design

In this section the dimensions of the reactor equipment is determined including spargers, heating and cooling coils, condenser and reaction vessel. The heating coils are necessary during the startup of the process in order to melt any residual MAP.

The reactor can be designed as a cylinder divided into four sections; a melt in the bottom, a reaction zone where ammonia is introduced through a sparger in the lower part of the middle of the reactor, a zone with a solution of excess phosphoric acid in the upper middle part and steam headspace at the top that provides a margin for splashing due to boiling. The headspace is assumed to be 1 m. Steam is taken out from the top and phosphoric acid is introduced in the excess phosphoric acid zone. The reaction takes place on the surface of the bubbles and the near proximity of the bubbles of ammonia traveling through the phosphoric acid. Due to differences in density, MAP gravitates through the liquid to the bottom of the reactor where the product is taken out. See Figure 9 for the detailed design of the bubble reactor.

¹ See Appendix A for calculation of ΔH_R .

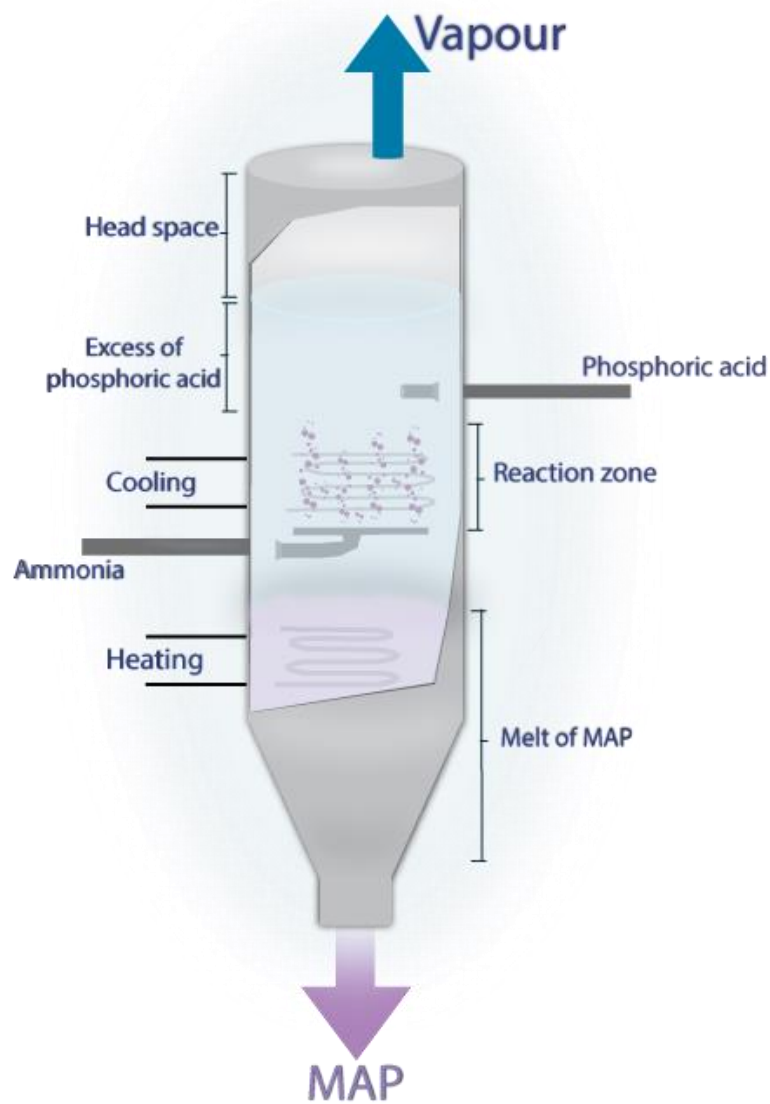
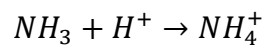
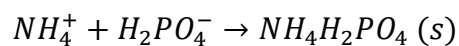


Figure 9. Detailed design of bubble reactor.

The reaction takes place in two steps. First, ammonia reacts with free hydrogen ions in the near proximity of the bubble, see Figure 10. This reaction is shifted to the right and is irreversible.



The reaction above is the rate determining step of formation of MAP. In the next step, NH_4^+ reacts with the deprotonated phosphoric acid, H_2PO_4^- , to form MAP, $\text{NH}_4\text{H}_2\text{PO}_4$.



Applying the two film theory, the concentration gradient can be illustrated, see Figure 10. It is assumed that the concentration of ammonia is constant within the gas bubbles.

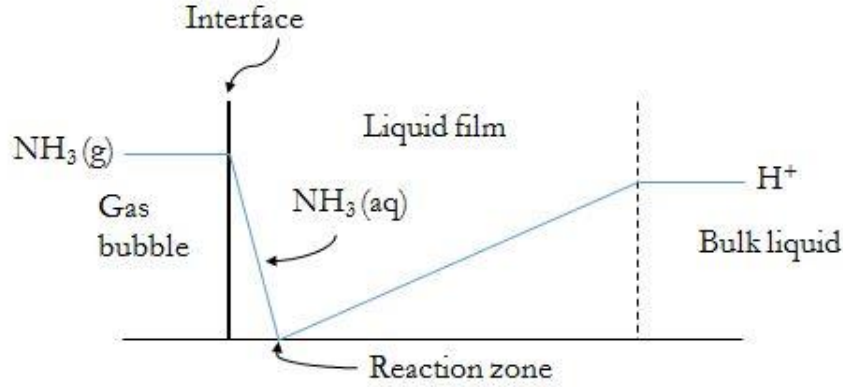


Figure 10. Concentration gradient according to the two film theory. It is assumed that the concentration of ammonia is constant within the gas bubbles.

The mass transfer of ammonia, N_A , can be described by the following expression:

$$N_A = k \cdot C_{NH_3} \cdot E$$

Where C_{NH_3} is the liquid concentration of ammonia at the interface and E is an enhancement factor used in order to account for the amount of hydrogen ions, C_{H^+} , in the solution. The reaction is instantaneous, hence:

$$E = 1 + \sqrt{3} \cdot \frac{C_{H^+}}{C_{NH_3}}$$

The concentration of hydrogen ions is related to the surplus of phosphoric acid in the reaction zone. The surplus of phosphoric acid is defined as $(1 - x)$ where x is the fraction of phosphoric acid that is converted into MAP in the reaction zone.

$$C_{H^+} \approx 2 \cdot 10^4 \cdot (1 - x)$$

To calculate the amount of ammonia dissolved in the phosphoric acid Henrys constant, H_{NH_3} , is used together with the partial pressure of ammonia, P_{NH_3} , as shown below. Henrys constant is calculated by using the reactor temperature, T_{reac} :

$$C_{NH_3} = P_{NH_3} / H_{NH_3}$$

$$H_{NH_3} = 6.0 \cdot e^{\left(-2100 \cdot \left(\frac{1}{T_{reac}} - \frac{1}{298}\right)\right)}$$

There is no mass transport resistance in the gas bubbles since the gas bubbles contains pure ammonia. The only mass transport resistance occurs on the liquid side.

The reaction constant, k , can be calculated by using the ammonia bubble diameter, d_b , the bubble rise velocity, μ , and the diffusion constants for the surface of the bubble as well as the solution, D_A .

$$k = 113 \cdot \sqrt{\frac{d_b \cdot \mu}{D_A}} \cdot \left(\frac{d_b}{0.45 + 20d_b}\right) \cdot \frac{D_A}{d_b}$$

The bubble rise velocity can be assumed to be between 0.22 and 0.26 m/s if the bubble diameter is larger than 2 mm. If the diameter is smaller, the bubble rise velocity can be calculated using Stokes law where $\Delta\rho$ is the difference in density of the bubble and the liquid. As the bubbles rise through the reactor the bubble diameter decreases.

$$u = \frac{d_b^2 \cdot \Delta\rho}{18\mu} \text{ m/s}$$

The reactor height is decided by the height of each section. 1 meter is designated to the melt zone. In order to decide the height of the reaction zone, h , which is the middle sector in the reactor, the bubble rise velocity is needed. The following equation is used to calculate the total height of the reaction zone depending on the bubble diameter, where R is the gas constant. The optimal reactor design can be made by varying the following parameters; pressure, P_A , bubble temperature, T , and initial bubble diameter.

$$\frac{dd_b}{dh} = -N_A \cdot \frac{2RT}{P_A \cdot u}$$

The volume of the reaction zone can be calculated from its height, the gas flow of ammonia, Q_g , the bubble diameter, the bubble rise velocity and the gas void, ε . The gas void represents the fraction of the reaction zone which at any given time is occupied by gas. As a rule of thumb the gas void should not exceed 0.2 and therefore the reactor is designed to have a gas void of 0.1 as a safety precaution.

$$\frac{dV}{dh} = \frac{Q_g}{\varepsilon \cdot u} \cdot \left(\frac{d_b}{(d_b)_0} \right)^3$$

When dimensioning the ammonia sparger the bubble rise velocity needs to be higher than the gas velocity of ammonia. Assuming that the bubble diameter is larger than 2 mm means that the bubble rise velocity is approximately 0.24 m/s. The sparger area, A_S , is given by the following equation.

$$A_S = \frac{Q_g}{u}$$

The sparger hole diameter must be at least 3 times as big as the diameter of the bubbles. The desired bubble is 0.01 m, which means that the sparger hole diameter can be calculated to 0.03 m assuming the surface tension 0.10 N/m [19]. The amount of sparger holes, n , can then be calculated from the total sparger area and the area for one sparger hole with the following equation. d_s is the diameter of one sparger hole.

$$n = \frac{A_S}{\left(\frac{\pi \cdot (d_s)^2}{4} \right)}$$

As a safety margin approximately 30 % more holes are added. The set values for the parameters used to calculate the reactor dimensions can be found in Table 4.

Table 4. Chosen values of some parameters used in the reactor dimensioning.

Parameter	Description	Value
D_A	Diffusion constant for ammonia in water adjusted for temperature and viscosity	$1 \cdot 10^{-9} \text{ m}^2/\text{s}$
d_b	Bubble diameter	0.01 m
$1 - x$	The surplus of hydrogen ions	0.1
ρ	Density of phosphoric acid [20]	1300 kg/m^3
μ	Dynamic viscosity [20]	$10^{-2} \text{ Pa} \cdot \text{s}$
ε	Gas void	0.1

Using the aforementioned equations, the reactor dimensions were calculated in MATLAB by varying pressure, bubble temperature and the initial bubble diameter.

In order to make a final design a simulation is done where the pressure varies from 2 to 7 bar to see the effect on the diameter and height of the reaction zone. The temperature in the reactor is decided by the boiling point of water which increases with pressure. Results for the two cases can be found in Table 5.

To calculate the area of the cooling coil approximately 100 kW was added to the cooling requirement in order to assure an efficient cooling. The method used for calculating the heat exchanger area is described in detail in section 4.1.1.4 below. The heat transfer coefficient is $580 \text{ W/m}^2\text{K}$ [21].

The heating requirement is set to be the same as the cooling requirement. To calculate the area of the heating coil approximately 100 kW was added to the heating requirement in order to assure an efficient heating. The heat transfer coefficient is $355 \text{ W/m}^2\text{K}$ [21].

Table 5. Results for the two reactor cases.

Parameter	2 bar	7 bar
Reactor cooling	250 kW	350 kW
Area cooling coil	4 m ²	5 m ²
Area heating coil (6 bar steam)	11 m ²	164 m ²
Area heating coil (19 bar steam)	5 m ²	22 m ²
Temperature	120 °C	165 °C
Cross-sectional area of reactor	2.71 m ²	0.82 m ²
Radius	0.93 m	0.51 m
Reaction zone height	0.04 m	0.08 m
Condenser cooling	761 kW	816 kW
Heat exchanger area	11.9 m ²	8.7 m ²
Mass flow cooling water	3.0 kg/s	3.2 kg/s
Total area of all sparger holes	1 m ²	0.3 m ²
Amount of sparger holes	2000	600

For simplicity and for safety the height designated for the reaction zone is set to 1 meter. This gives plenty of room for fluctuations and changes of the actual reaction zone.

4.1.1.4 Design of shell and tube condenser

The water vapour is condensed and stored and is later used for dilution of phosphoric acid in production of other products. The proposed condenser is a counter flow shell and tube heat exchanger with cooling water, CW , inside the tubes operating at a pressure slightly below the pressure inside the reactor. A picture of the condenser can be seen in Figure 11. The cooling water has a temperature of 20 °C and to ensure an efficient heat transfer, it is assumed that the hot stream is condensed and cooled to 80 °C. By choosing this temperature of the cooling water and assuming a heat transfer coefficient of 1300 W/(m² K) [21], the area of the heat exchanger is estimated.

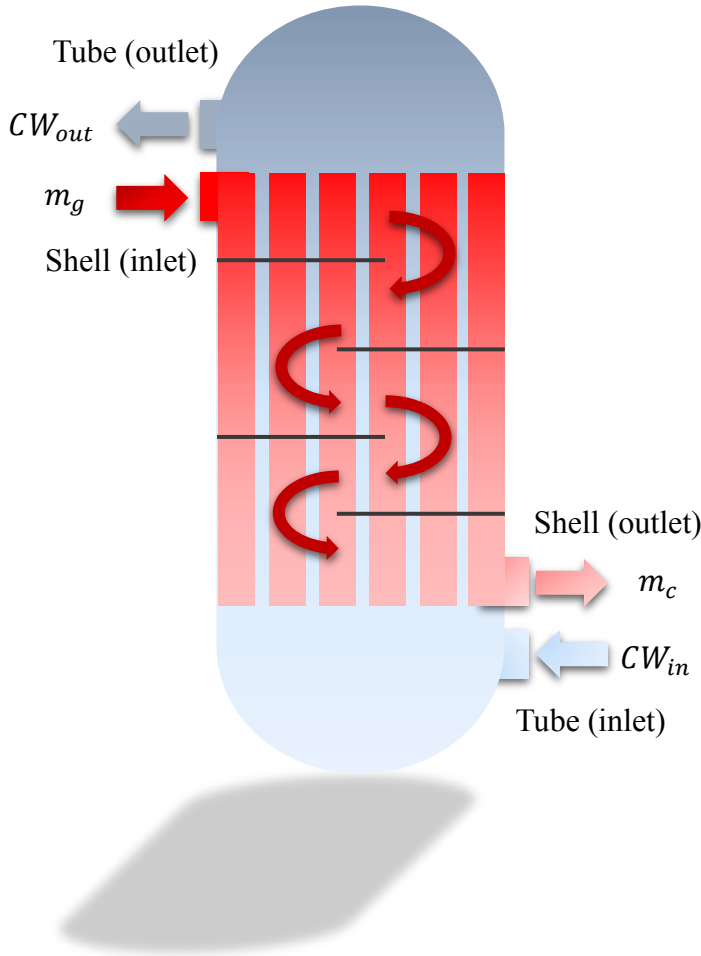


Figure 11. Shell and tube heat exchanger where the richer color of the gradient represents the higher temperature.

The heat transfer inside the heat exchanger, Q_{HEX} , can be calculated from the expression below which describes the hot side (tube side).

$$Q_{HEX} = m_g c_{p,g} (T_g - T_{H_2O,dp}) + m_g \Delta H_{vap,HEX} + m_l c_{p,c} (T_{H_2O,dp} - T_c)$$

In the expression above, the first term represents the energy required to lower the temperature of the steam to its dew point, the second term represents the energy required for condensation and the last term represents the energy required to lower the temperature of the condensed water stream. If no heat loss is assumed, the heat transfer is the same on the cold side as on the hot side which is described by the following expression from which the mass flow of cooling water, m_{CW} , can be determined.

$$Q_{HEX} = m_{CW} (c_{p,CW,out} T_{CW,out} - c_{p,CW,in} T_{CW,in})$$

The heat exchanger area can be calculated from the relation below.

$$Q_{HEX} = k \Delta T_L A$$

The mean logarithmic temperature, ΔT_L , is calculated according to:

$$\Delta T_L = \frac{\Delta T_1 - \Delta T_2}{\ln \left(\frac{\Delta T_1}{\Delta T_2} \right)}$$

where ΔT_1 and ΔT_2 is:

$$\Delta T_1 = T_g - T_{CW,out}$$

$$\Delta T_2 = T_c - T_{CW,in}$$

The temperature profile is illustrated in Figure 12.

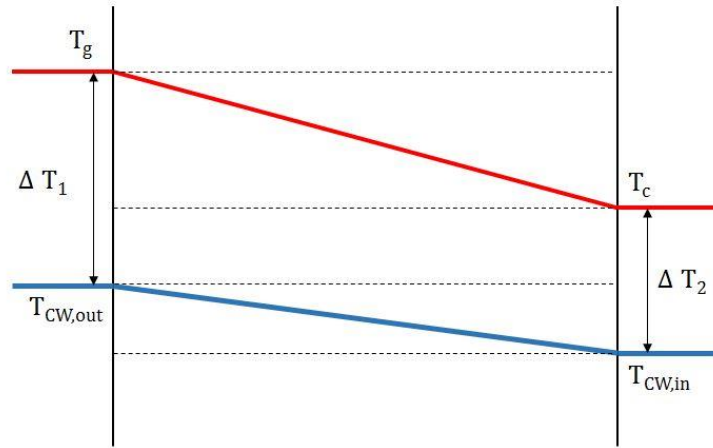


Figure 12. Temperature profile of the streams in the condenser.

The parameter used and calculation results regarding the condenser are displayed in Table 6 and Table 7 respectively.

Table 6. Parameters used in calculations associated with the condenser.

Parameter	Description	Value
m_g	Mass flow steam	0.2619 kg/s
m_c	Mass flow of condensate	0.2619 kg/s
$c_{p,g}$	Specific heat capacity of steam	1.9 kJ/(kg K)
$c_{p,c}$	Specific heat capacity of condensate ²	4.25 kJ/(kg K)
$\Delta H_{vap,HEX}$	Heat of evaporation	2760 kJ/kg
T_g	Temperature in	165 °C
$T_{H_2O,dp}$	Temperature at dew point	162 °C
T_c	Temperature out	80 °C
$T_{CW,out}$	Temperature cooling water out	80 °C
$T_{CW,in}$	Temperature cooling water in	20 °C
k	Heat transfer coefficient	1.3 kW/(m ² K) [21]

Table 7. Summary of calculation results of the condenser.

Parameter	Description	Value
Q_{HEX}	Cooling requirement	815.6090 kW
ΔT_L	Logarithmic mean temperature	71.7758 °C
A	Heat exchanger area	8.7410 m ²
m_{CW}	Mass flow cooling water	3.1985 kg/s

Purging of inert gases

Since there are small amounts of air dissolved in the phosphoric acid, this will end up in the steam, m_g , see Figure 11. Thus, it is necessary to purge gas from the condenser in order to prevent accumulation of inert gases. Assuming that phosphoric acid has the same air solubility as water, the amount of air that needs to be vented can be calculated.

The solubility of air in water is 0.023 g/kg at atmospheric pressure and the mass flow of the phosphoric acid is 2.4 kg/s. The mass flow of air in and out of the system can be calculated as follows.

$$m_{air} = m_{H_2O+H_3PO_4} \cdot sol_{air}$$

To put the size of the purge gas stream in perspective, it can be compared to the total stream of steam reaching the condenser, m_g , by creating the purge ratio, pr .

$$pr = \frac{m_{air}}{m_g}$$

² The specific heat capacity of the condensate is assumed to be that of water even though trace amounts of ammonia are present.

Table 8. Parameters used in calculations of purge gas stream and results.

Parameter	Description	Value
$m_{H_2O+H_3PO_4}$	Mass flow of phosphoric acid (60 % P_2O_5)	2.3571 kg/s
sol_{air}	Solubility of air in water (1 atm, 25 °C)	0.023 g/kg [22]
m_g	Mass flow of stream from reactor	0.2619 kg/s
m_{air}	Mass flow of air in and out of the system	$5.42 \cdot 10^{-5}$ kg/s
pr	Purge ratio	0.02 %

4.2 Pipe reactor process

By using liquid ammonia under high pressure, the size of the equipment can be drastically decreased compared to the bubble reactor described above and the TVA process described in section 4.3. Ammonia and phosphoric acid is introduced to a pipe reactor shaped like the letter T or Y.

In order to remove water from the product stream a flash unit is necessary. Once the moisture content of the product stream is below 5 % after the flashing step, the process is identical to the bubble reactor process described in section 4.1.

It can be noted that in order to keep ammonia as a liquid at high temperatures, incredibly high pressures are required, see Figure 1 in section 1.3. Ammonia reaches its critical point at around 130 °C and 100 bar. Therefore, this process is not further investigated in this study.

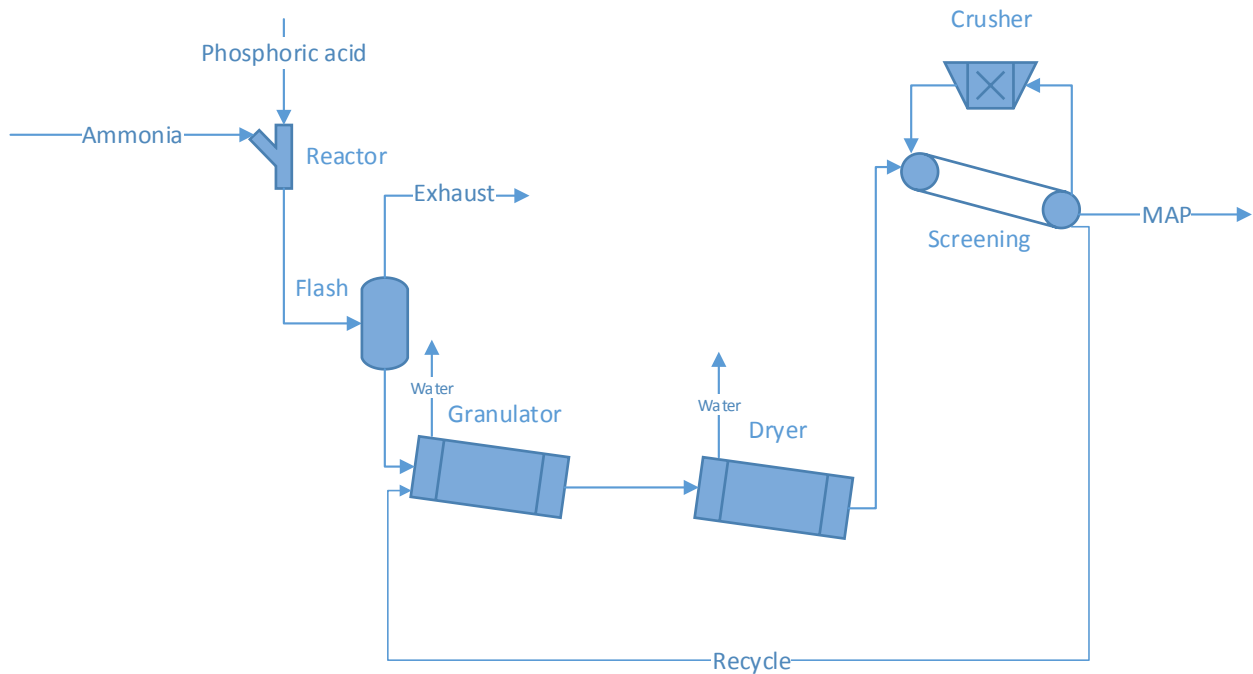


Figure 13. Process flow sheet for the pipe reactor design.

4.3 TVA process

As described in section 3.3 the Tennessee Valley Authority (TVA) process utilizes the difference in solubility of monomammmonium phosphate at different N to P ratios. The design is illustrated in Figure 14. Ammonia in deficit is reacted with phosphoric acid at molar ratios of 0.6 to 1 (N to P) in the preneutralizer in order to maintain high solubility of MAP. Gaseous ammonia is introduced through a sparger and the preneutralizer operates at atmospheric pressure. Due to the heat of reaction water is evaporated. The product from the preneutralizer, now in the form of a solution, is delivered to the granulator where additional ammonia is added in order to reach the N to P ratio of 1:1 and thereby complete the formation of MAP. At this N to P ratio the solubility of MAP is low and thus granulation is facilitated. Just like in the preneutralizer water is evaporated due to the high heat of reaction. Since ammonia is not in deficit in the granulator, some gaseous ammonia escapes together with the water vapor. In order to minimize emissions of ammonia, the exhaust gas stream is cleaned through scrubbing using the phosphoric acid that is fed to the process. In this way ammonia is recycled and more MAP can be produced. After the granulation the product is dried and screened before it is packaged. [12]

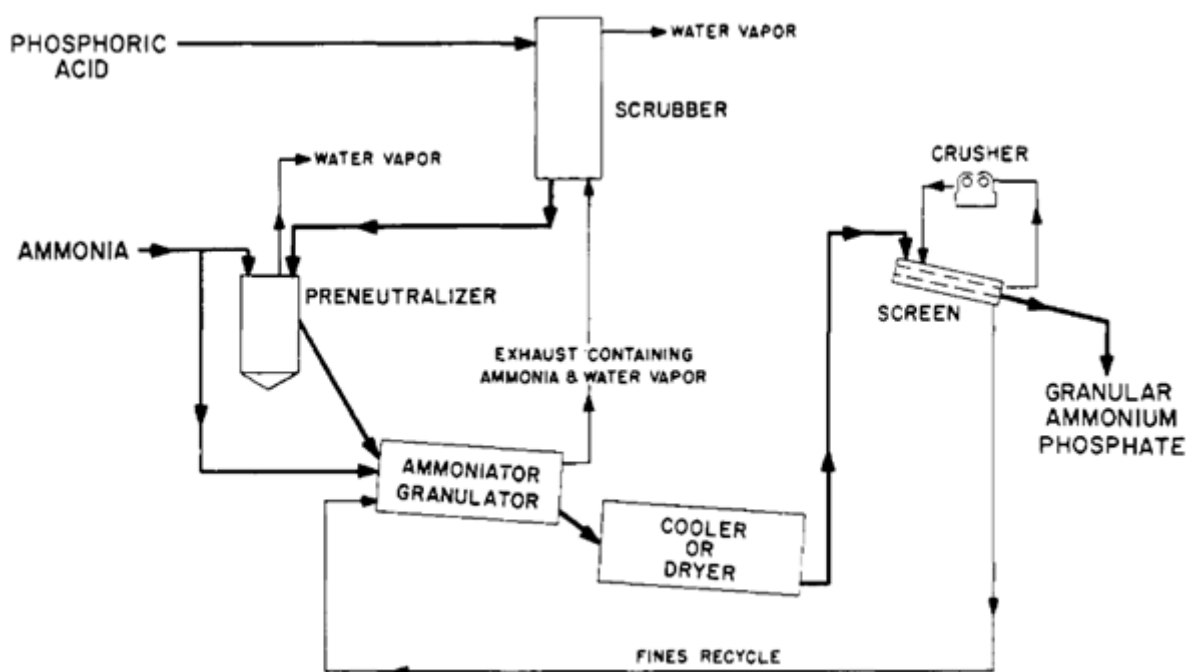


Figure 14. Process flow sheet of the TVA process design. [12]

It can be noted that the TVA process also can be used for production of diammonium phosphate but at different N to P ratios and pH values.

Although an interesting alternative for production of MAP, this design will not be investigated further because of the limitations of the granulator available at Yara. Since unforeseen disruptions of the process causes severe leakage of ammonia this design is considered unsustainable. Therefore it will not be further investigated.

4.4 Removal of ammonia

This section describes one of several possible ways of preventing emissions of ammonia. However, the proposed design of this design does not require additional removal techniques. If the amount of ammonia in the gas stream from the reactor, m_g , is low it may be beneficial to use a catalyst to decompose ammonia into nitrogen gas and water instead of condensing the gas stream and treat the hydrous ammonia separately. One proposition is to implement a technology where the gas is heated to 350 °C, first by utilizing the heat of the treated stream and then by heating with external energy. The heated gas stream is run through a reactor with a catalyst bed with high selectivity for ammonia. The selectivity is high at low concentrations of ammonia, up to 1000 ppm. If concentrations exceed this level, the gas stream can be diluted with air. The exothermic decomposition of ammonia generates heat and the optimum condition for the catalyst is 350-450 °C. It is estimated that the catalyst must be changed every 3 or 4 years. [23] A schematic flow sheet of the decomposition of ammonia can be seen in Figure 15.

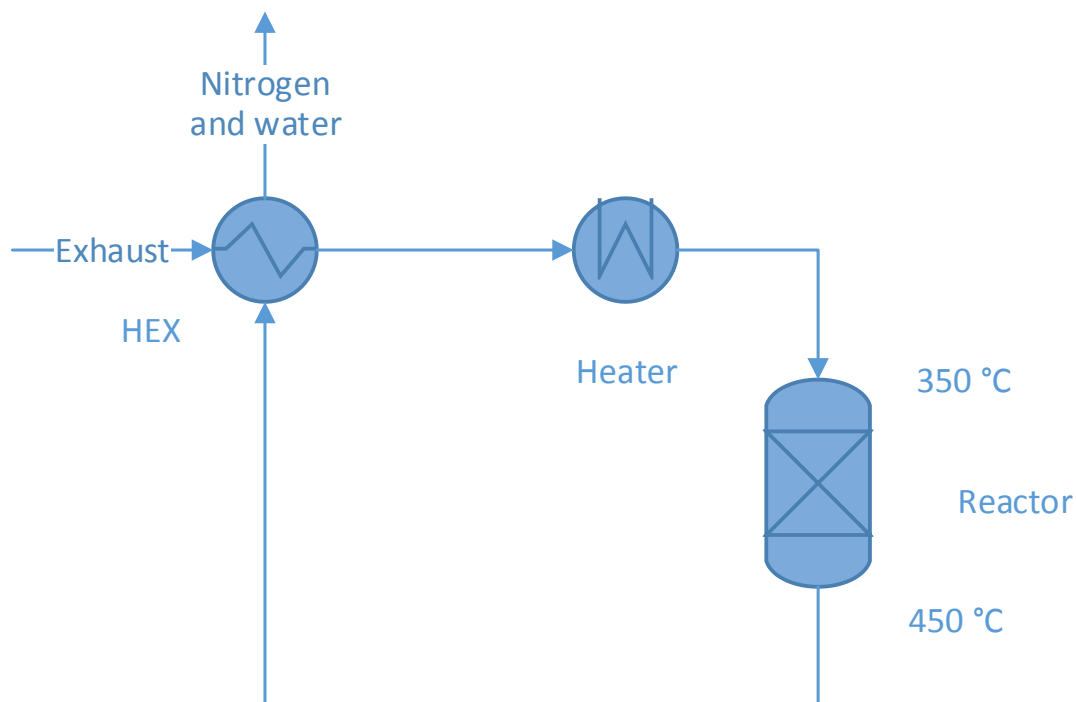


Figure 15. Schematic flow sheet of decomposition of trace amounts of ammonia using a solution from Hulteberg chemistry and engineering. [23]

5 Risk assessment

A risk assessment is done in order to identify possible risks and hazards in the process. In the bubble reactor process five analysis points are estimated to be particularly vulnerable and are evaluated. These are the reactor, the ammonia stream, the phosphoric acid stream, the condenser, and the granulator. These five points are analyzed using the HazOp method.

5.1 HazOp – hazards and operability study

HazOP is a method to systematically explain the hazards and deviations that may occur in a process, and give a solution to avoid them. The method is based on process parameters and given keywords in specific analysis points. If a risk is identified, causes and appropriate measures are proposed.

Up to four process parameters are examined in the five analysis points, namely temperature, pressure, flow, and liquid level. As described earlier in the report, the ammonia is of the greatest concern. Every point where ammonia may be released during the process is critical.

5.1.1 Analysis point – Reactor

The parameters temperature, pressure, reactant flow, and liquid level have been evaluated in the reactor. The results are presented in Table 9 to Table 13 below.

The major concern with temperature deviation in the reactor is the risk of pressure buildup, which may occur if the temperature is allowed to rise uncontrollably. This is countered by increasing the cooling. The consequence of deviating temperature is mainly a varying water content in the product stream.

The biggest risk concerning pressure changes in the reactor is if the pressure increases. This may lead to equipment damage and possibly explosion. This is unlikely since the reaction is practically already instantaneous, which means that there cannot be any increase of reaction rate. However, if the ammonia flow increases uncontrollably there is a risk of pressure buildup.

The two biggest risks concerning flow are elevated levels of ammonia in the exhaust, pressure buildup, and buildup of phosphoric acid in the reactor. Elevated levels of ammonia in the exhaust occur when the ammonia flow is too high or if the phosphoric acid flow is too low. Similarly, the buildup of phosphoric acid occurs when the ammonia flow is too low or if the phosphoric acid is too high. In case of extreme buildup of phosphoric acid there is a risk that phosphoric exits the reactor through the steam exhaust and further into the condenser. The product stream is also affected if the stoichiometric ratio is changed.

Table 9. Temperature in reactor.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low temperature	Not enough water is evaporating	Too much cooling	Install temperature sensor
		Unwanted crystalizing may occur in the reactor	Reactant flow is too low	Start steam flow in HEX
High	High temperature	More water evaporates	Insufficient cooling	Automatic shutdown of ammonia flow
		The pressure rises – risk of equipment damage	Ammonia inflow is too high	

Table 10. Pressure in reactor.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low pressure	More water evaporates	Leakage	Install ammonia sensor
			Pressure too low from ammonia supply	Shutdown and start steam HEX
High	High pressure	Risk of equipment damage	Not enough cooling in the condenser	Shutdown of ammonia flow
		Risk of explosion	Outlet flows plugged	

Table 11. Flow of ammonia into the reactor.

Keywords	Deviation	Consequence	Cause	Measure
Low	Flow too low	Phosphoric acid level rises in the reactor	Ammonia valve may not be open enough	Start steam flow in HEX
			The railway car may start to empty	
High	Flow too high	Pressure increase	Ammonia valve might be too open	Install temperature sensor
		Other substances like DAP and TAP may form		Shutdown of ammonia flow Increase cooling
		Elevated levels of ammonia in the exhaust		Install ammonia alarm/detector
No	No Flow	Phosphoric acid buildup	Ammonia valve is closed	Start heating
			Empty railway car	

Table 12. Flow of phosphoric acid into the reactor.

Keywords	Deviation	Consequence	Cause	Measure
Low	Flow too low	Elevated levels of ammonia in the exhaust	Phosphoric acid valve may not be open enough	Install ammonia flow sensor
		Other substances like DAP and TAP may form	The pump may be damaged	Shutdown of ammonia flow
				Start heating
High	Flow too high	Buildup of Phosphoric acid	Phosphoric acid valve may be open too much	Close valves
No	No Flow	Other substances like DAP and TAP may form	Phosphoric acid valve is closed	Start heating
		Elevated levels of ammonia in the exhaust	The pump may be damaged	

Table 13. Liquid level in the reactor.

Keywords	Deviation	Consequence	Cause	Measure
Low	Level too low	Elevated levels of ammonia in the exhaust	Phosphoric acid valve may not be open enough	Install ammonia sensor
		Other substances like DAP and TAP may form	The pump may be damaged	Shutdown of ammonia flow
		Cooling coil not immersed	Too high product flow	Increase phosphoric acid flow
High	Level too high	Buildup of Phosphoric acid Reactor overflow	Phosphoric acid valve may be open too much	Close valves
No	No liquid in reactor	All ammonia entering the condenser	No phosphoric acid flow	Install ammonia sensor
			Bottom valve too open	Shutdown of ammonia flow
				Increase phosphoric acid flow

5.1.2 Analysis point – Ammonia stream

The parameters temperature and pressure have been evaluated in the ammonia stream. The results are presented in Table 14 and Table 15 below.

The effect of temperature changes in the ammonia stream is that the cooling requirement varies, i.e. if the ammonia enter the reactor at a cooler temperature the cooling requirement is lowered and vice versa.

The pressure in the ammonia stream governs the pressure in the reactor. If the pressure gets too high, there is a risk of equipment damage.

Table 14. Temperature in the ammonia stream.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low temperature	Less water will evaporate	Extreme weather changes	Preheat the ammonia stream
		Lower cooling requirement		Decrease cooling in reactor
High	High temperature	More water will evaporate	Extreme weather changes	Cool the ammonia stream
		Higher cooling requirement		Increase cooling in reactor

Table 15. Pressure in the ammonia stream.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low Pressure	Pressure in the reactor is reduced	Failure in ammonia supply system	Check valves and a pressure regulating pump
High	High pressure	Pressure in the reactor is increased	Too high pressure in supply system.	Pressure margin e.g. pipes rated for higher pressures
		If too high, risk for equipment damage	Too high pump pressure	Pressure regulators upstream

5.1.3 Analysis point – Phosphoric acid stream

The parameters temperature and pressure have been evaluated in the phosphoric acid stream. The results are presented in Table 16 and Table 17 below.

The effect on temperature in the phosphoric acid stream is the same as in the ammonia stream. If the pressure is too high equipment damage might occur.

Table 16. Temperature in the phosphoric acid stream.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low temperature	Less water will evaporate	Extreme weather changes	Lower cooling in the reactor
High	High temperature	More water will evaporate	Extreme weather changes	Higher cooling in the reactor

Table 17. Pressure in the phosphoric acid stream.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low Pressure	Pressure in the reactor is reduced	Failure in supply system	Check valves and a pressure regulating pump
High	High pressure	Pressure in the reactor is increased	Too high pressure in supply system.	Pressure margin e.g. pipes rated for higher pressures
		If too high, risk for equipment damage	Too high pump pressure	Pressure regulators, upstream

5.1.4 Analysis point – Condenser

The biggest concern in the condenser is lack of cooling, i.e. cooling water flow is too low, cooling water temperature too high or steam flow from reactor too high. In that case the rate of condensation will not match the steam flow. Specific cases for each parameter can be found in Table 18 to Table 22.

Table 18. Temperature in the condenser, shell side (vapor).

Keywords	Deviation	Consequence	Cause	Measure
Low	Low Temperature	No consequence	Low temperature in reactor	Increase flow of cooling water
High	High Temperature	Not complete condensation of the vapor	Too high temperature in the reactor	Lower flow of cooling water

Table 19. Temperature in the condenser, tube side (cooling water).

Keywords	Deviation	Consequence	Cause	Measure
Low	Low Temperature	No consequence	-	-
High	High Temperature	Not complete condensation of the vapor	Deviations in cooling water supply	Increase flow of cooling water

Table 20. Pressure in the condenser, shell side (vapor).

Keywords	Deviation	Consequence	Cause	Measure
Low	Low pressure	Steam overheated	Lower pressure in the reactor	Raise pressure in the condenser
		Unwanted condensational behavior	Condenser pressure too low	Raise flow of cooling water
High	High pressure	The steam may be super cooled and condensate before the condensation zone	Higher pressure in the reactor	Lower pressure in the condenser
			Condenser pressure too high	

Table 21. Flow in the condenser, tube side (pump, cooling water).

Keywords	Deviation	Consequence	Cause	Measure
Low	Low flow	Insufficient condensation	Flow set too low	Increase flow
High	High flow	-	-	-
No	No flow	No condensation	Pump failure Problems in cooling water supply	Stop the process

Table 22. Flow in the condenser, shell side (vapor).

Keywords	Deviation	Consequence	Cause	Measure
Low	Low flow	Unnecessary cooling	Too much cooling in the reactor	Lower the cooling flow
High	High flow	Risk of low condensation	Too low cooling in the reactor	Increase the cooling flow
No	No flow	Unnecessary cooling	Probably problem in reactor	Shutdown

5.1.5 Analysis point – Granulator

Two critical issues are scaling and clogging of the granulator input pipes and nozzles. This may occur if the ingoing stream temperature is too low. Another issue may be if the pressure of the ingoing stream is too high. This may result in the stream flashing and giving off too much water. The results are presented in Table 23 to Table 25.

Table 23. Flow of the stream entering the granulator.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low flow	Undesired granulation behaviors	Low production rate in reactor	Lower the recycle stream
High	High flow	Undesired granulation behaviors	High production rate in reactor	Increase the recycle stream
No	No flow	Only recycle stream	Problem upstream	Pause production

Table 24. Temperature of stream entering the granulator.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low temperature	Scaling and clogging in pipes and nozzles	Too much cooling in reactor	Lower cooling in reactor
			Too low pressure in reactor	Raise pressure in reactor
High	High temperature	Too much water is evaporated in the granulator	Too low cooling in reactor	Increase cooling
			Too high pressure in Reactor	Reduce pressure in reactor
			Heating coil is on	Turn off the heating coil

Table 25. Pressure of the stream entering the granulator.

Keywords	Deviation	Consequence	Cause	Measure
Low	Low pressure	-	-	-
High	High pressure	Too high flashing ratio	Too high pressure upstream	Close control valve a bit Reduce pressure in reactor

5.1.6 Operating pressure

The HazOp is identical for both the 2 and 7 bar cases. In general, the biggest risk is the release of ammonia. Although low, the risks are minimized by choosing the lowest operating pressure.

6 Economic evaluation

6.1 Ulrich method

The materials of the process equipment were determined by using a corrosion guide based on the properties of substances in contact with the equipment [24]. The cost of the equipment was estimated using the Ulrich method described below. The bare module cost, C_{BM} , describes the total cost of each piece of equipment in US\$ at year 2004:

$$C_{BM} = C_p \cdot F_{BM}^\alpha$$

where C_p is the purchased equipment cost and F_{BM}^α is the module factor which accounts for additional costs related to specific process conditions such as pressure and corrosion, as well as the cost for installation, auxiliaries, freight, insurance, engineering and installation overhead. The total Grass Roots Plant Cost is the sum of the bare module costs where fees, contingency and auxiliary facilities have been accounted for according to the equation below.

$$K_{\$,2004} = \left(\sum_{i=1}^n (C_{BM})_i \right) \cdot f_{\text{fees/contingency}} \cdot f_{\text{auxiliary facilities}}$$

The Grass Roots Plant Cost was updated to SEK at year 2016 by using the exchange rate from 2004, $(V_{GNP})_{2004}$, and the Swedish Producer Price Index at the relevant years, (I_{PP}) .

$$K_{SEK,2016} = K_{\$,2004} \cdot \frac{(I_{PP})_{2016}}{(I_{PP})_{2004}} \cdot (V_{GNP})_{2004}$$

6.2 Grass Roots Plant Cost

The calculations in this section are based on the bubble reactor design in section 4.1. Like in the process design, two cases are studied; 2 bar and 7 bar operation pressure inside the bubble reactor. The outcome of the economic evaluation decides the most desirable process condition. The equipment included in the economic analysis can be seen in Figure 16. One pump for the phosphoric acid (P1), one pump for the cooling water to the reactor (P2), and one pump for the cooling water to the condenser (P3) is included. In total there are three heat exchangers, one for condensation (VVX1, also referred to as the condenser), and two coils inside the reactor; one for cooling during operation (VVX2) and one for heating at startup (VVX3) of the process. Furthermore, there is also one reaction vessel like the one in Figure 9.

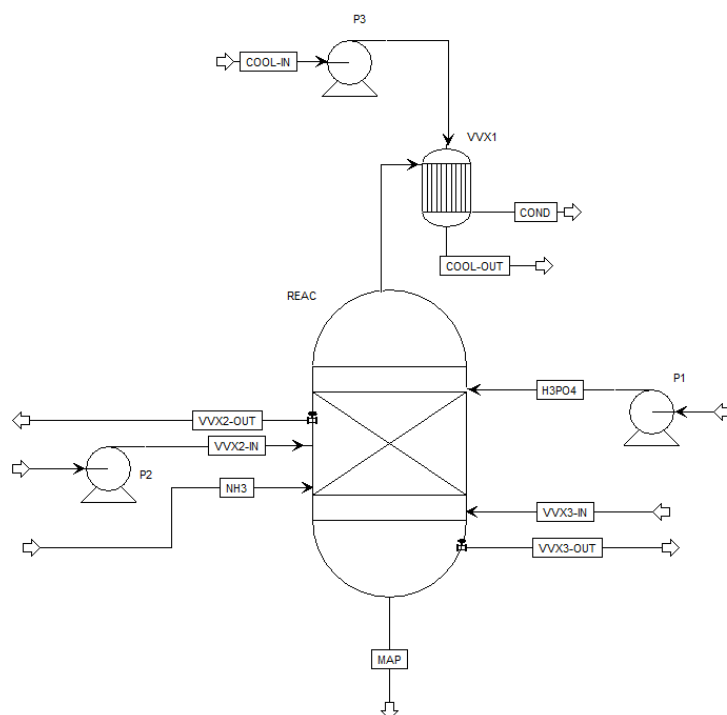


Figure 16. Process units relevant for the economic evaluation.

The materials and specifications of the process equipment can be seen in Table 26. All pumps were regarded as rotary positive displacement pumps. An alternative possibility for the material choice of the bubble reactor could be titanium-clad carbon steel. According to the corrosion guide both titanium and glass are viable, but in this study glass has been the primary choice and the prices for titanium-clad equipment are presented in parenthesis.

Table 26: Materials and specifications of process equipment at operation pressures 2 and 7 bar inside the bubble reactor. SS-stainless steel, Ti-titanium, CS-carbon steel.

Unit	Description	Material	Specifications 2 bar	Specifications 7 bar
P1	Pump, phosphoric acid	SS	0.342 kW	2.05 kW
P2	Pump, cooling water reactor	SS	0.08 kW	0.18 kW
P3	Pump, cooling water condenser	SS	0.18 kW	0.4 kW
VVX1	Condenser, shell and tube	SS/SS	11.9 m ²	8.7 m ²
VVX2	Cooling coil reactor	SS/Ti	4 m ²	5 m ²
VVX3	Heating coil reactor ³	CS/Ti	11 m ² , (5 m ²)	22 m ²
REAC	Bubble reactor vessel	Glass-lined	h=3 m, d=1.86 m	h=3 m, d=1.02 m

³ For the 2 bar case it has been assumed that the heating coil is powered either by 6 or 19 bar steam and for the 7 bar case it has been assumed that the heating coil is powered by 19 bar steam. The number within brackets for the 2 bar case corresponds to 19 bar steam.

For each unit, the bare module cost was calculated, see Table 27. In calculations of $K_{\$,2004}$, $f_{fees/contingency}$ and $f_{auxiliary\ facilities}$ was assumed to be 18 % and 30 % respectively in accordance with the Ulrich method. For the cost update of the Grass Roots Plant Cost, $K_{\$,2004}$, $(I_{PP})_{2016}$ and $(I_{PP})_{2004}$ were 115 and 94.9 respectively and $(V_{GNP})_{2004}$ was 7.3. A summary of the Grass Roots Plant Cost can be seen in Table 28.

Table 27. The bare module cost for the process equipment.

Unit	C_{BM} 2 bar [US\$ ₂₀₀₄]	C_{BM} 7 bar [US\$ ₂₀₀₄]
P1	19500	35000
P2	2500	15000
P3	15000	20000
VVX1	24000	24000
VVX2	30800	37800
VVX3	45600, (23940) ⁴	102600
REAC	52500, (63000) ⁵	45000, (54000) ⁵
$\sum_{i=1}^n (C_{BM})_i$	199900	279400

Table 28. Grass Roots Plant Cost US\$₂₀₀₄ and SEK₂₀₁₆.

	2 bar	7 bar
$K_{\$,2004}$	307 000 [US\$ ₂₀₀₄]	429 000 [US\$ ₂₀₀₄]
$K_{SEK,2016}$	2.80 [MSEK]	3.92 [MSEK]

It can be seen that the case with 2 bar inside the bubble reactor is the cheapest choice when it comes to the Grass Roots Plant Cost.

6.3 Operating cost

The operating cost includes fixed capital, direct cost and indirect cost. Fixed capital consists of costs related to the storage of feed stock and product as well as spare parts. The cost for consumables and salaries as well as maintenance and repair are included in the direct cost. In this case, consumables include electricity, cooling water, and steam together with feed stock such as phosphoric acid and ammonia. The section of indirect cost consists of overhead expenses for personnel and administration costs. The calculations of operation costs are based on the prices of the consumables and the process dimensions. See price list in Appendix B. The results are displayed in Table 29.

The fixed capital related to storage was based on the time of storage and the value of the stored material. The average storage time at the site for phosphoric acid was assumed to be 3 days per campaign which is equivalent to 30 days per year. The same storage time was assumed for MAP. Since ammonia is consumed continuously, the average storage time was set to 5/6 days per campaign. Empirically derived flat-rates were used in calculations of the cost for storage of spare parts, the direct cost of maintenance and repair as well as the indirect costs for administration and overhead for personnel.

⁴ This price corresponds to the price of a heating coil run with 19 bar steam.

⁵ This price refers to titanium clad reactor material.

Table 29. The operating cost for fixed capital, direct cost, indirect cost and total operating cost. See price list of consumables per tonne in Appendix B.

Operating cost	2 bar [SEK/year]	7 bar [SEK/year]
Fixed capital		
Phosphoric acid	93 000	93 000
Ammonia	3 000	3 000
MAP	161 000	161 000
Spare parts	29 000	41 000
Sum	286 000	298 000
Direct cost		
Phosphoric acid	67.8 millions	67.8 millions
Ammonia	5.57 millions	5.57 millions
Electricity		
-Granulator	36 000	36 000
-Dryer	25 000	25 000
-Crusher	10 000	10 000
-Pumps	400	1600
Natural gas	1.52 million	1.52 million
Steam	200	100
Cooling water	155 000	199 000
Maintenance & repair	196 000	274 000
Salaries	1.25 millions	1.25 millions
Sum	76.6 millions	76.7 millions
Indirect cost		
Overhead personnel	825 000	825 000
Administration	206 000	206 000
Sum	1.03 millions	1.03 millions
Total operating cost	77.9 millions	78.1 millions

The distribution of fixed capital, direct cost and indirect cost can be seen in Figure 17.

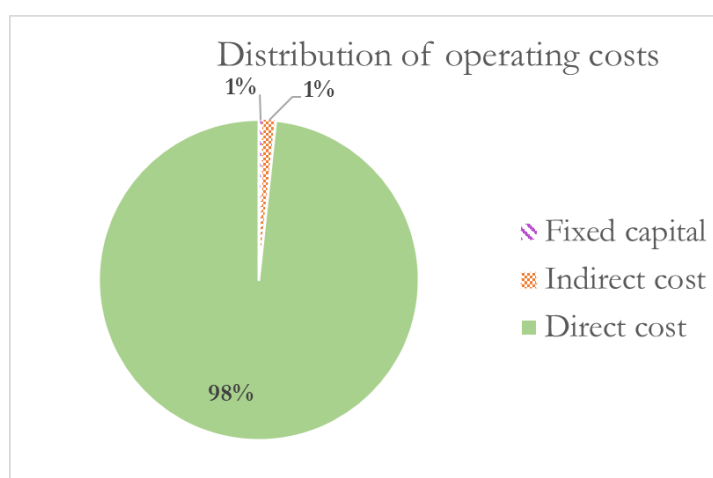


Figure 17. Distribution of operating costs.

From the results it can be concluded that the case with 2 bar pressure inside the bubble reactor gives the lowest operating cost, 77.9 [MSEK/year], as well as the lowest Grass Root Plant Cost, 2.80 [MSEK]. Even though the differences between the two cases are small, the case of 2 bar is chosen for further analysis since it is generally beneficial to keep the pressure as low as possible in aspects of safety.

6.4 Annuity method

The annual net revenue, N_I , is calculated with the equation below:

$$N_I = a_i - f_A \cdot G$$

where a_i is the difference between annual income and operating cost, G , is the Grass Roots Plant Cost and f_A is defined as:

$$f_A = \frac{X}{1 - (1 + X)^{-N}}$$

X is the interest rate and N is the economic life expectancy, 15 % and 10 years respectively. It can be of interest to know the total annual costs, N_C , which can be expressed as the annual net revenue minus the annual income according to:

$$N_C = U + f_A \cdot G$$

where U is the operating cost.

For the case of 2 bar pressure inside the bubble reactor and 6 bar steam in heating coils, the annual net revenue, the total annual costs and the annual production cost per tonne of MAP is presented in Table 30.

Table 30. The annual net revenue, the total annual costs, the annual production cost per tonne of MAP and market price of MAP as of May 2016.

Annual net revenue	Total annual costs	Production cost per tonne	Market price MAP
-4.50 [MSEK]	78.5 [MSEK]	7746 [SEK/tonne]	7246 [SEK/tonne]

As can be seen, the annual net revenue is negative which means that the production is not profitable at the current price situation. The production cost per tonne shows what the price of MAP ought to be in order to break even. Thus, the selling price should be increased by at least 500 SEK/tonne in relation to the market price. Different price situations are investigated in the next section.

6.5 Sensitivity analysis

It was investigated how the annual net revenue, or the profitability of the process, is affected by price changes.

By varying the prices of phosphoric acid and MAP 20 % up and down in the model equations, it can be illustrated how the annual net revenue is affected, see Figure 18. As one parameter was analyzed, the other was kept constant. Price change necessary for breaking even is found where lines cross the x-axis. For phosphoric acid, the price must decrease by at least 8 % for the process

to be profitable and for MAP, the price must increase by at least 8 % for the process to generate profit.

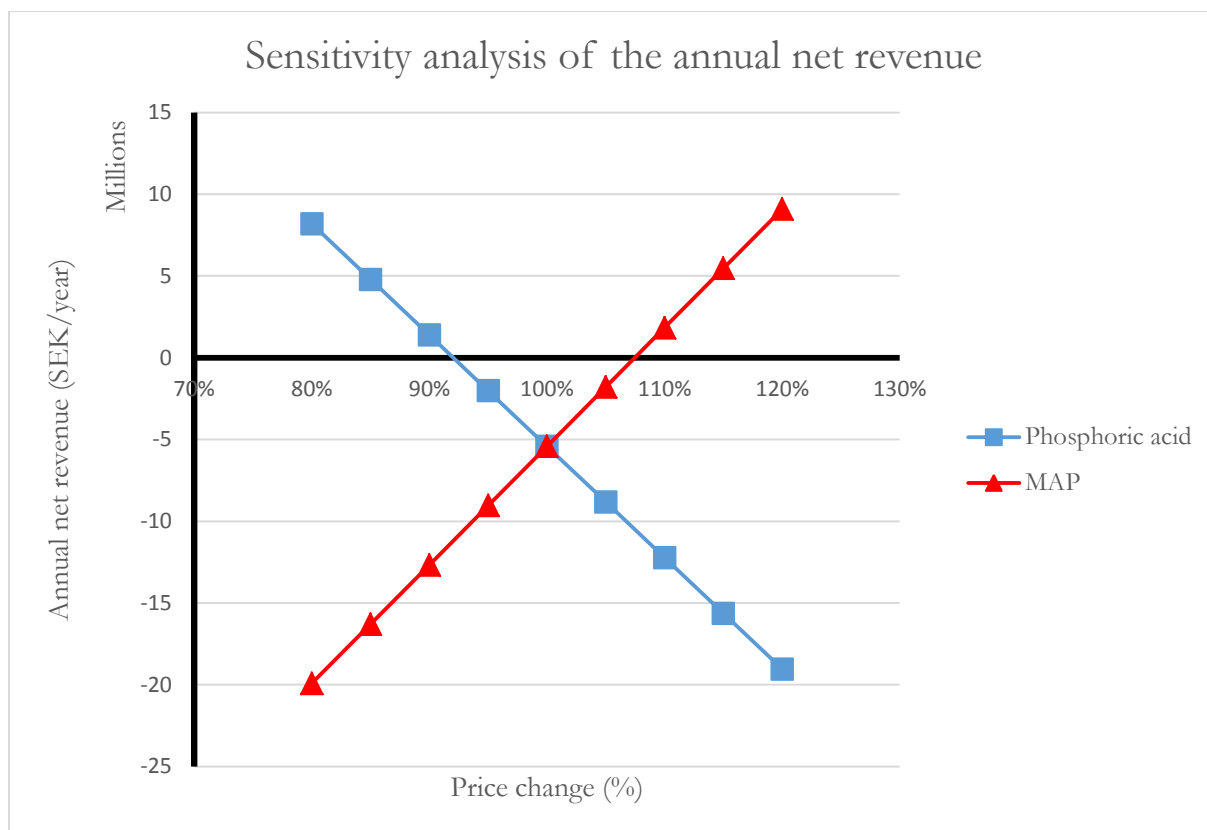


Figure 18. Sensitivity analysis of the annual net revenue. Only one parameter (price for MAP or Phosphoric acid) was changed at the time as the other was kept constant.

If both prices are varied at the same time, see Figure 19, different scenarios can be considered. For example, if the price of phosphoric acid is decreased by 20 %, the selling price of MAP can actually be decreased with almost 10 % and still generate profitability. It can be concluded that the profitability is sensitive to increased phosphoric acid prices. For increases of the price of phosphoric acid above 20 %, the selling price of MAP has to be increased significantly.

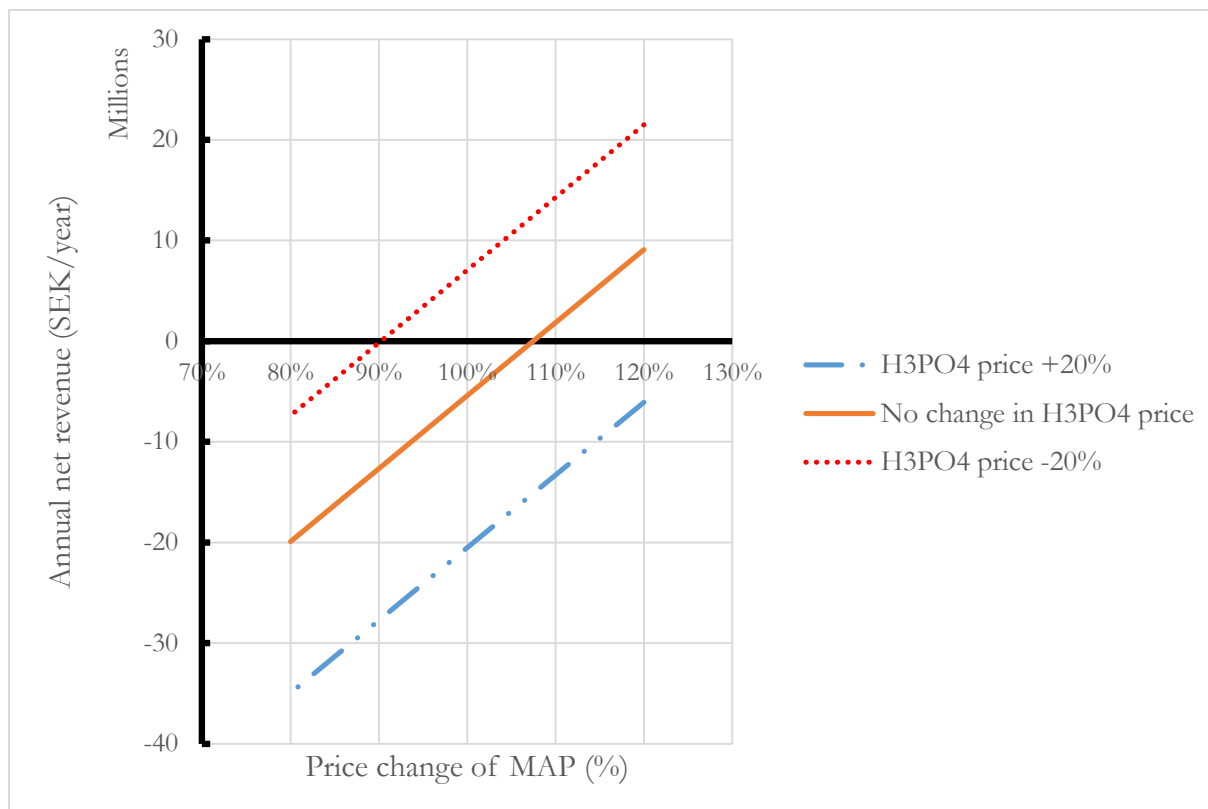


Figure 19. Analysis of how the price change of MAP affects the annual net revenue at different price levels of phosphoric acid (H₃PO₄).

7 Conclusion

In the literature study it was found that the reaction where MAP is formed is instantaneous and highly exothermic. The process can be controlled by cooling the reactor since this affects the moisture content and thereby the granulation as well. Important characteristics of the MAP were found in the literature study such as its tendency to clog cold spots in the process and the solubility at different N to P ratios. Seeding of the system was found to favor granulation in the production of MAP.

The reactor and process design was based on the concepts developed in the literature study. The study has proven that the most suitable design for Yara's site in Helsingborg is the bubble reactor since it can be implemented with a low amount of modifications to the existing equipment. However, if a new factory is to be constructed, alternative process designs might be considered. For example, the pipe-reactor process or a process with a spray dryer which can produce both powder and granules depending on whether a granulator is installed or not. This design can be interesting to investigate in future work.

Estimations and assumptions were made in the calculations, thus the results should not be regarded as exact facts, but rather an indication. In the reactor design many assumptions were made when estimating the dimensions and properties. The mass transfer was estimated from the two film theory and the bubble rise velocity and bubble diameter was derived using empirical equations. Since extensive safety margins were included it is not likely that the errors arising from estimations and assumptions will have an impact on the functionality of the reactor. For example, the reaction zone was calculated to approximately one decimeter but in the design it was chosen to one meter. As for the economic evaluation there are more uncertainties related to the method since flat rates were used to estimate operation costs and parameters in the Ulrich method.

Since both the economic evaluation and the risk assessment promotes the case with 2 bar operating pressure inside the bubble reactor this case is recommended. This process design is considered to have a low risk of incidents. However, a concern is release of ammonia. The operating cost was found to be large compared to the investment cost. The biggest contribution to the operating cost is the cost of raw material, especially phosphoric acid. This is due to the large consumption of phosphoric acid along with its high market price. Since this parameter strongly affects the annual net revenue, or the profitability, it can be valuable to study the sensitivity of the market price of phosphoric acid.

The study has shown that the process is not profitable at the current price situation. However, both a small decrease of the market price of phosphoric acid and a small increase of the market price of MAP will give positive annual net revenue. Since the investment cost is small in relation to the operating cost, even a small potential profit will quickly pay back the investment cost.

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9 Appendix

9.1 Appendix A

Calculation of the enthalpy of reaction for MAP.

The enthalpy of formation of the substances are displayed in Table 31.

Table 31. ΔH_f^0 at 298.15 K and 1 atm.

Substance	ΔH_f^0 [kJ/mol]
NH ₃	-45.940 [25]
H ₃ PO ₄	-1278.999 [26]
MAP	-1445.07 [27]

ΔH_R is calculated with:

$$\Delta H_R = \sum \Delta H_f(\text{products}) - \sum \Delta H_f(\text{reactants})$$

Thus, ΔH_R for the reaction below is -120.131 kJ/mol.



9.2 Appendix B

A price list for the consumables used in the process can be found in Table 32.

Table 32. Price list consumables, as of may 2016 [28].

	Price
NH ₃	3716 SEK/tonne
H ₃ PO ₄	6503 SEK/tonne
MAP	7246 SEK/tonne
Steam 6 and 19 bar	325 SEK/tonne
Electricity	500 SEK/MWh
Natural gas	500 SEK/MWh
Cooling water	10 SEK/m ³