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# Exergy Analysis of Ammonium Nitrate Production Plants

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## Abstract:

Ammonium nitrate is a large volume industrial inorganic chemical, used mostly as a high grade (34% N) straight nitrogen fertilizer containing both ammonium and nitrate forms of nitrogen. Some complex fertilizers obtained by nitrophosphate route also contain ammonium nitrate.

Most fertilizer-grade ammonium nitrate is produced by direct neutralization of weak (up to 65%) nitric acid by gaseous ammonia. The neutralization is an exothermic process, but the reaction heat is used only to evaporate part of the water from the obtained ammonium nitrate solution. Thus additional steam is consumed to evaporate the solution to melt suitable to be solidified by prilling or granulation. The emissions of ammonium nitrate and ammonia to water and to atmosphere are the major problems of the existing technology and steam and electricity are consumed to purify the waste liquid and gaseous flows (process condensate, process steam and air from prilling towers or granulators).

Various ammonium nitrate synthesis processes are developed and used in modern plants, aiming at lower steam and electricity consumption and more efficient waste flows treatment.

In this work the exergy method is used to analyze and compare some basic design concepts of industrial ammonium synthesis in order to find opportunities for better utilization of the reaction's heat and therefore reduction of import steam consumption.

**Keywords:** Ammonium Nitrate, Efficiency, Environmental impact, Exergy Analysis

## 1. Introduction

Ammonium nitrate (AN) is the major straight nitric acid-based fertilizer with 34% nitrogen content, and the total production of 45 MM metric tons in 2011 worldwide. Along with calcium-ammonium nitrate (27% N) and complex NP and NPK fertilizers, produced by nitrophosphate process and containing about 35% ammonium nitrate, the total world ammonium nitrate production in 2011 is about 76 MM metric tons [1]. Ammonium nitrate is used as fertilizer worldwide, but is especially appropriate for the temperate zone climate and soils as it contains nitrogen in both ammonium (slow) and nitrate (quick) active forms. Thus most ammonium nitrate is traditionally produced and consumed in the northern hemisphere, but Latin America's consumption and production has recently increased rapidly [1].

In modern fertilizers industry ammonium nitrate as a single nitrogen fertilizer is produced from ammonia and weak nitric acid (55-65% HNO<sub>3</sub>) [2,3].

Ammonium nitrate synthesis is an exothermic process, but the neutralization heat is released at a low temperature level (135-180°C). As the weak nitric acid introduces a significant quantity of water in the process, the ammonium nitrate is obtained as a water solution. Hence about 300 to 400 kg water per ton AN has to be evaporated in order to obtain ammonium nitrate melt (>99% AN) which then is solidified by prilling or granulation. Despite that the major part of the water is evaporated using the reaction heat, some import MP or LP (1.0-1.6 MPa) steam is consumed in the production process. The obtained process steam and/or process condensate and also air used in the prilling or granulation processes contain some ammonia and ammonium nitrate and must be purified before being released into the environment or used in other processes at the same site. The purification processes also consume energy as heat and electricity [4].

The quantity and quality of the consumed energy depend on the design and basic parameters of the overall process and especially of the neutralizer and evaporator designs and also on the waste flows purification method. Safety is also the major consideration which restricts the choice of parameters and designs and is the reason of the limited energy-saving options of the AN production process. Therefore various designs and approaches are developed and used in modern ammonium nitrate plants in order to find a reasonable compromise between these contradictory requirements.

The exergy method [5] is considered to be the most appropriate and useful tool to estimate and compare different chemical processes from a Second Law-based point-of-view. However, the exergy method is used very rarely to analyse industrial ammonium nitrate production processes and plants [6,7] and no detailed analysis is available.

In a previous work [4] we used exergy analysis to compare various methods for the process steam and/or condensate purification with respect to their overall environmental impact. Three waste steam and/or condensate treatment methods are analyzed: absorption column with circulated acidified AN solution, 2-stage vacuum evaporation system and vacuum evaporation system with mechanical compressor (heat pump). In order to study the dependence of the energy and exergy consumption, the overall ammonium nitrate production site was included and some additional energy and exergy indices were defined.

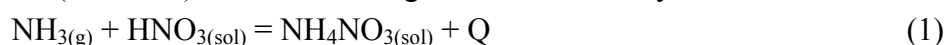
In a recent work [8] the exergy method is used to analyze the dependence of the primary energy consumption and GHG emissions in ammonium nitrate production complexes on basic parameters of the subsystems (ammonia, nitric acid and ammonium nitrate production units and CHP). However, the ammonium nitrate production subsystem is not analyzed in detail.

The goal of the present work is to use the exergy method to analyze and compare some basic concepts of industrial ammonium synthesis production processes, including various methods of reaction heat utilization and waste flows treatment.

## 2. Ammonium Nitrate Synthesis Background: Parameters and Designs

The AN production process comprises three main unit operations [2,3]:

- Neutralization of weak (55 - 65%) nitric acid with gaseous ammonia by the reaction:



- Evaporation of obtained ammonium nitrate solution up to > 99% melt;
- Solidification of ammonium nitrate melt by prilling or granulation.

Although AN production seems a simple sequence of the above three processes, the industrial implementation of the ammonium nitrate synthesis is strongly limited by some very specific properties of ammonium nitrate, mainly, by ammonium nitrate self-decomposition at higher temperatures, acidic environment and presence of some metals and organic matter. As the self-decomposition concerns not only solid ammonium nitrate, but also the AN solutions obtained in the production process, their acidity gradually increases and if ammonia is not added continuously to maintain the neutral pH, the risk of an accident increases.

Thus the basic parameters of the AN production process are specified mainly with a view to the safety requirements and the various designs of the above three main process stages are developed in order to find a reasonable compromise between the safety limitations and the energy consumption.

The basic parameters and designs of the main stages of the modern ammonium nitrate production processes are shown in Table 1. A simplified block flow diagram of an ammonium nitrate production plant with 2-stage atmospheric neutralisation is shown in Fig. 1.

Table 1. Basic process parameters and designs in ammonium nitrate production plants [2, 3]

Ammonium nitrate synthesis (neutralization)				
Neutralization pressure, MPa	Atmospheric processes (about 0.1 MPa)		Pressure processes (0.3 - 0.5 MPa)	
Neutralization temperature, °C	150-170		178-185	
Neutralization stages	1 stage or 2 stages		1 stage or 2 stages	
Neutralization pH: - 1 <sup>st</sup> stage - 2 <sup>nd</sup> stage	1.5-2.5 4.5-5.5		5.5-6.0 4.5-5.5	
Neutralizer design	Atmospheric reactor with internal natural or forced circulation	Pipe reactor with atmospheric flash separator	Pressure reactor with external forced circulation	Pipe reactor with pressure flash separator
Ammonium nitrate solution evaporation and melt solidification				
Evaporation pressure and design	Vacuum falling film evaporator 1 or 2 stages	Atmospheric falling film evaporator with hot air stripping	Vacuum falling film evaporator 1 or 2 stages	Atmospheric falling film evaporator with hot air stripping
Solidification method	Prilling or granulation			

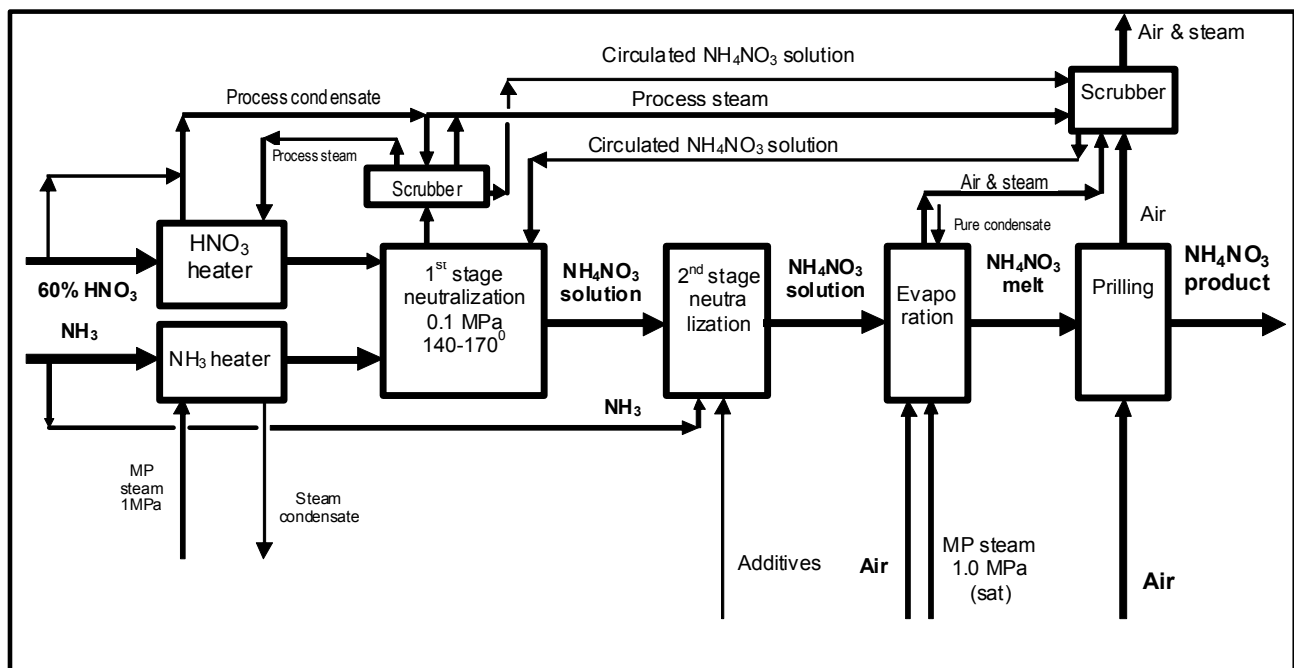


Fig. 1. Block flow diagram of ammonium nitrate production plant with 2 stage atmospheric neutralization and atmospheric falling film evaporator with hot air stripping

## 2.1. Heat of Reaction, Problems and Limitations

The neutralization is a highly exothermic process. The heat of the reaction is used to evaporate as much water as possible from the AN solution. The quantity of water in the AN solution depends mainly on the concentration of the used nitric acid and in modern plants it ranges from 300 to 400 kg/t AN. As some pure water is added to the process in order to remove the ammonia and ammonium nitrate emissions from the contaminated air and process steam, the quantity of water that needs to be evaporated is slightly (10-20%) more than the above values.

The temperature of the neutralization process depends on the process pressure and concentration of the obtained AN solution. In most ammonium nitrate plants the neutralization is performed at atmospheric (or slightly lower or higher) pressure and thus the temperature varies in the range of 150<sup>0</sup> to about 170<sup>0</sup>C (Table 1). As this temperature is low, the only way to use the reaction heat is the direct evaporation of water from the solution simultaneously with the reaction itself. In order to fit the heat balance of the neutralizer, the feedstocks are preheated: nitric acid to 60<sup>0</sup>-80<sup>0</sup>C and ammonia up to 150<sup>0</sup>C. Thus the AN solution concentration at the neutralizer outlet can reach 90-96% AN. The generated process steam is used partly to preheat nitric acid, but the process steam temperature is not enough high to preheat ammonia.

To use the reaction heat at a higher temperature level, in some ammonium nitrate plants the neutralization is performed at a higher pressure, up to 0.5 MPa and respectively at a higher temperature up to 185<sup>0</sup>C. Thus some quantity of LP (0.4 - 0.5 MPa) process steam (contaminated) or clean steam is generated. The upper limit of the process pressure is defined by the safety requirements, as at temperatures over 180<sup>0</sup>C the risk of the ammonium nitrate self-decomposition increases [2,3].

The neutralization is implemented as a single stage or a double stage process. The pH of the solution in a single stage neutralizer should be close to neutral, in order to decrease the risk of self-decomposition, but in this case ammonia losses are high. Thus the double stage process is preferable as different pH can be specified in the consecutive neutralization stages. If the 1<sup>st</sup> neutralizer is atmospheric, the solution is preferable to be acidic (pH = 1.5 to 2.5) so the ammonia losses are lower; a higher pH (4.5 – 5.5) is obtained in the 2<sup>nd</sup> neutralizer by addition of some ammonia. If the neutralization stage is implemented at elevated pressure, some ammonia excess is preferable in the 1<sup>st</sup> stage, in order to prevent possible self-decomposition of the solution; in this case some nitric acid is added in a small second neutralizer [9-12].

Various neutralizer designs are used in modern ammonium nitrate plants. The classical and the most widespread until recently were the neutralizers ensuring intensive natural or forced, internal or external circulation of the obtained ammonium nitrate solution [9-12]. The intensive circulation prevents the solution from local temperature raise and thus ensures the safety of the process. In the last three decades a new design of the neutralizer – the pipe reactor - is being increasingly used in new and in old ammonium nitrate plants, due to the very intensive process in the reactor [13-15].

The overall heat generated in the neutralization process depends on the concentrations of both solutions: weak nitric acid used as feedstock and obtained ammonium nitrate solution. The nitric acid concentration is determined from the nitric acid production technology and in modern nitric acid plants is in the range from 55 to 65%. The ammonium nitrate solution concentration depends mainly on the nitric acid concentration, but also on the process pressure, ammonia and nitric acid input temperatures and the neutralizer design (Table 2).

Table 2. Heat of reaction of ammonia and nitric acid in ammonium nitrate synthesis

Process	Heat of reaction (-ΔH, 25 <sup>0</sup> C, 101325 Pa)			
	kJ/mol NH <sub>4</sub> NO <sub>3</sub>		GJ/t NH <sub>4</sub> NO <sub>3</sub>	
Ammonium nitrate (solid) synthesis from gaseous ammonia and liquid nitric acid (100%) by reaction (1)	145.1		1.814	
Heat of dissolution of nitric acid to 60% (mass)	-21.2		-0.275	
Ammonium nitrate (solid) from gaseous ammonia and weak nitric acid (60%)	123.9		1.549	
Concentration of ammonium nitrate solution (% mass)	90%	95%	90%	95%
Heat of dissolution of ammonium nitrate	-4.8	-2.4	-0.060	-0.030
Ammonium nitrate (solution) from gaseous ammonia and weak nitric acid (60%)	119.1	121.5	1.489	1.519

## 2.2. Environmental Problems: Process Steam and Condensate Purification

The process steam generated in the neutralizer and the evaporator, contains rather high concentrations of ammonia and AN up to 3000 ppm w/w, depending on the neutralizer and the evaporator design and parameters [16]. Also the air from prilling towers contains ammonia and AN fume. Ammonium nitrate emissions from neutralizers and prilling are very difficult to remove because the AN particles are very fine. According to the requirements concerning new BAT plants, the waste gaseous flows (air and process steam) emitted from prilling must contain no more than 10 mg/m<sup>3</sup> ammonia and 15 mg/m<sup>3</sup> AN particulates, and from other points (e.g., evaporation) up to 30 and 50 mg/m<sup>3</sup>, respectively [3]. Emissions to water are limited up to 100 mg N/l (0.2 kg N/t product [3].

Thus the problem is to determine if the water evaporated from the AN solution should be emitted as process steam into the atmosphere or as process condensate into the water. It is clear that if the process steam would be condensed, the heat of condensation could be used in the plant itself and thus the steam export could be decreased or eliminated.

In most AN plants with atmospheric neutralization, the latent heat of the process steam is used partially to preheat nitric acid and partly ammonia and thus some process condensate is formed. However, only up to 20% of the process steam condensation heat can be used in this way. The rest is condensed in water coolers and some quantity of cooling water is consumed. Also, if one or two-stage vacuum evaporation is used, the latent heat of a part of the process steam could be used in this way.

In the old AN plants the obtained process condensate was recycled to the nitric acid plant and was used again in the absorption column. However, this is not admissible in the modern nitric acid plants with absorption at elevated pressure up to 1.4 MPa.

Various techniques are used for the process steam and condensate treatment. The most widespread is the absorption of AN and ammonia from the process steam with recycled solution containing 15-25% AN and some nitric acid. The recovered ammonia and AN are recycled back into the process. However, this method can not ensure the ammonia and AN concentration in the treated process steam lower than about 100 ppm w/w. Thus an additional treatment stage is used in modern plants in order to obtain lower emissions level. Certainly more efficient abatement techniques are recommended to be used in new plants: two or three stage vacuum evaporation systems [4,16], membrane separation (reverse osmosis) and ion-exchange process [18-20]. All these processes consume additional energy as steam and electricity and so additional emissions are generated [4]. But the purified condensate can be re-used as demineralised water in the nitric acid plant or as BFW after polishing.

To avoid process condensate purification problems, another approach is used in some AN production plants: the process steam is added to the air outgoing prilling tower, the steam&air mixture is treated in an absorption/stripping column by recycled 15-25% AN solution and then the purified mixture is emitted to the atmosphere. The process condensate obtained in the nitric acid preheater is also added to the scrubbing liquor and is evaporated there, as the prilling air is not saturated. Thus no liquid effluents are emitted and no cooling water is used (Fig. 1). The shortcoming of this design is that water, incoming in the plant from nitric acid, is not recovered and so the demineralized water consumption in other plants in the site is much higher [11,12].

## 3. Exergy Analysis of Ammonium Nitrate Plants: Approaches, Results and Discussion

Subject of the analysis are two kinds of ammonium nitrate plants, both with atmospheric pressure neutralization. The first one is provided with an internal natural circulation neutralizer and has no liquid effluents [11,12]. The second operates with a pipe reactor and a RO process condensate purification system [13-15].

The exergy of the material flows is calculated by the method proposed by Szargut as a sum of chemical and physical (thermal and mechanical) exergy [5]. The environment parameters are assumed as follows:  $P_0 = 101325$  Pa,  $T_0 = 298.15$  K and relative humidity 0.301. Some data obtained in previous works of the author [4,8] on the exergy analysis of ammonium nitrate production processes are also used.

### 3.1. Reaction's heat utilization

As in most chemical processes, the chemical exergy of the material flows is very high and so the physical (thermal and mechanical) exergy changes seem negligible. The process itself seems high efficient, as the exergy degree of perfection appears high, so based only on this it may be incorrectly concluded that no energy saving opportunities exist.

Ammonium nitrate synthesis process is an especially characteristic example of the above, as the chemical exergies of ammonia and ammonium nitrate are high and the physical exergy changes are much lower due to the low pressures and low temperatures implemented in the industrial process. Also, utility (steam and power) consumption is small, relative to the energy intensive processes such as, for example, ammonia production.

However, ammonium nitrate is a large volume chemical and the average energy consumption in Europe is about 0.7 GJ/t [2]. Thus, if we assume the same value as a world average, about 25 PG/year as MP (1 MPa) steam are consumed worldwide in this process.

That is why in this work special attention is paid to the utilization of the reaction heat. In Table 3 an example of the MT and LT heat balances of an ammonium nitrate production unit is presented. The basic parameters are typical for the most widespread atmospheric processes: weak nitric acid concentration 60%, AN solution output neutralizer 92%, solidification by prilling. The process steam and condensate treatment are not included. The data in Table 3 do not refer to pipe neutralizers. To estimate the exergy efficiency of the reaction heat utilization, the exergy of each available and consumed heat is also shown and exergy balances of the exergy of MT and LT heat utilization are shown in Table 4.

The neutralization reaction is highly exothermic. Depending on the input temperatures of ammonia and nitric acid (concentration above 60%) in the neutralizer, theoretically it is possible to evaporate the water up to the ammonium nitrate melt (99%) without steam import. Indeed, there exists a design, known as Carnit (now Amnit) process, where this concept is implemented, but the pressure neutralization, clean steam generation, two stage vacuum evaporation, etc., make this process very complex [21]. As shown in Table 3, in the atmospheric AN processes, obtaining concentrated 92-93% solution from 60% nitric acid is a practical maximum of the reaction heat utilization by direct evaporation, as the temperatures of nitric acid (70<sup>0</sup>C) and ammonia (120<sup>0</sup>C) preheating reach the practical maximum.

As the evaporation and the reaction are performed at the same temperature inside the neutralizer, the temperature approach is near zero and the exergy losses are very low (Tables 3 and 4). Thus the direct evaporation is indeed the most efficient method for the ammonium nitrate synthesis reaction heat utilization. The exergy losses in this process depend on the preheating temperatures of ammonia and nitric acid and are the lower the higher these temperatures are.

However, it is impossible to preheat both feedstocks to neutralization temperature which leads to some problems. The first one is that preheating of ammonia to temperature above 70-80<sup>0</sup>C is impossible by the process steam and preheating of nitric acid above 70-80<sup>0</sup>C causes significant corrosion.

The second problem concerns the subsequent utilization of the process steam heat. As it is clear from Table 3, only part of the process steam is used for preheating of nitric acid. The major part is unusable as the subsequent evaporation of the AN solution to melt requires much higher temperature, up to 180<sup>0</sup>C. Thus, the only available high temperature source is the import MP steam (1-1.3 MPa). There are some options to use the process steam heat in the waste fluids treatment

processes (e.g. 2- and 3 stage vacuum evaporation [16], but the rather complex treatment units and the additional generated emissions make these options not so valuable [4].

Table 3. Medium and low temperature (MT&LT) heat balances of an ammonium nitrate production plant

Production process	Standard heat of reaction (-ΔH, 25 <sup>0</sup> C, 101325 Pa)		Average reaction temperature <sup>0</sup> C	Exergy of heat GJ/t AN
	kJ/mol AN	GJ/t AN		
1. Heat balance and exergy of reaction heat utilization in the neutralizer				
Exothermic process - available MT heat in the neutralizer				
Ammonium nitrate (92% solution) synthesis from gaseous ammonia and weak nitric acid (60%)	120.1	1.501	159	0.4654
Endothermic processes - consumed MT heat in the neutralizer				
Direct water evaporation in the neutralizer, incl:				
- Water from 60% HNO <sub>3</sub>	74.1	0.926	159	0.2872
- Water from recycled 20% AN solution	13.3	0.167	159	0.0517
Total water evaporation in the neutralizer	87.4	1.093	159	0.3389
Input flows heating to the reaction temperature:				
- Nitric acid from 70 <sup>0</sup> C	27.1	0.339	113	0.0772
- Ammonia from 120 <sup>0</sup> C	1.5	0.019	139.5	0.0053
- Recycled solution from 90 <sup>0</sup> C	1.9	0.023	124.5	0.0058
Total input flow heating	30.5	0.381	-	0.0767
Heat losses in the neutralizer	2.2	0.027	159	0.0084
Total MT heat consumption in the neutralizer	120.1	1.501	-	0.4240
Losses of heat exergy	-	-	-	0.0414
Exergy degree of perfection of the neutralization heat utilization	-	-	-	0.9110
2. MT heat consumption in other processes for 99.7% AN melt production				
Water evaporation from AN 92% solution to AN 99.7% melt in atmospheric falling film evaporator	14.2	0.178	180	0.061
AN 92% solution heating from 159 to 180 <sup>0</sup> C	4.2	0.053	169.5	0.017
Air preheating from 25 to 190 <sup>0</sup> C	7.0	0.087	101.5	0.018
Total heat for AN solution evaporation	25.4	0.318	-	0.096
Ammonia preheating from 20 to 120 <sup>0</sup> C	4.5	0.056	67	0.007
Heating of AN melt and solution piping	8.0	0.100	180	0.034
Total MT heat consumption for AN 99.7% melt	37.9	0.474	-	0.137
Import MP steam (1.3 MPa)	37.9	0.474	192	0.170**
Losses of heat exergy	-	-	-	0.033
Exergy degree of perfection of the import MT heat utilization	-	-	-	0.8059
3. LT heat utilization balance				
Exothermic process – available LT heat				
Condensation of a part of the process steam	27.1	0.339	100	0.068
Endothermic process - consumed LT heat				
Nitric acid preheating from 25 to 70 <sup>0</sup> C	27.1	0.339	47	0.023
Losses of LT heat exergy	-	-	-	0.045
Exergy degree of perfection of the LT heat utilization	-	-	-	0.3382
4. Not utilized LT heat				
Solidification of AN melt (prilling)	11.1	0.139	170-40	0.028
Condensation of the rest process steam	63.2	0.790	100	0.159
Total not utilized LT heat	74.3	0.929	-	0.187

\*Neutralization at atmospheric pressure, internal natural circulation. No liquid effluents. \*\*Only thermal exergy of steam.



Table 4. Exergy balance of medium and low temperature (MT&LT) heat utilization in an ammonium nitrate production plant (data from Table 3)

Exergy input		Useful exergy output	
Exergy flows	GJ/t	Exergy flows	GJ/t
<b>Exergy balance of MT reaction heat utilization in the neutralizer</b>			
Exothermic process – exergy of the available MT heat in the neutralizer	0.465	Total exergy of the MT heat consumption in the neutralizer	0.424
		Exergy losses	0.041
		Exergy degree of perfection, $\eta_e$ , %	91.10
<b>Exergy balance of MT heat utilization in other processes for 99.7% AN melt production</b>			
Exergy of import MP steam (1.3 MPa)	0.170	Total MT heat consumption for AN 99.7% melt	0.137
		Exergy losses	0.033
		Exergy degree of perfection, $\eta_e$ , %	80.59
<b>Exergy balance of LT heat utilization</b>			
Exergy of the available LT heat from condensation of process steam	0.068	Exergy of the LT heat consumption in nitric acid preheating from 25 to 70°C	0.023
		Exergy losses	0.045
		Exergy degree of perfection, $\eta_e$ , %	33.82
<b>Exergy of not utilized LT heat</b>			
Exergy of not utilized LT heat	0.187	External exergy losses	0.187
<b>Total exergy balance of MT and LT heat utilization in the AN plant</b>			
Total exergy input with MT and LT heat	0.890	Total exergy output with MT and LT heat consumption	0.584
		Total exergy losses	0.306
		Exergy degree of perfection, $\eta_e$ , %	65.62

### 3.2. Exergy balances of some AN plants

The neutralization of ammonia and nitric acid is a quite irreversible reaction. In order to distinguish and estimate the irreversible losses due to the chemical reaction, the exergy balances of two theoretical cases are shown in Table 5. The first case is a hypothetical reaction between gaseous ammonia and liquid 100% nitric acid (at environmental temperature and pressure) to solid ammonium nitrate. The second case is a nearly real reaction between gaseous ammonia and weak (58%) nitric acid also to pure solid ammonium nitrate.

Table 5. Exergy balances of theoretical ammonium nitrate production processes

Exergy input			Exergy output		
Mass and energy flows	GJ/t	%	Mass and energy flows	GJ/t	%
Theoretical ammonium nitrate synthesis from NH <sub>3</sub> and HNO <sub>3</sub> (100%)					
Ammonia (gaseous)	4.281	88.30	Ammonium nitrate solid (100%)	3.731	76.96
Nitric acid liquid (100 %)	0.567	11.70	Total useful exergy output	3.731	76.96
Total exergy input	4.848	100.0	Exergy losses	1.117	23.04
			Exergy degree of perfection	η <sub>e</sub> = 76.96 %	
Theoretical ammonium nitrate synthesis from NH <sub>3</sub> and diluted HNO <sub>3</sub> (58%)					
Ammonia (gaseous)	4.281	87.82	Ammonium nitrate (100%)	3.731	76.53
Nitric acid solution (58 %)	0.594	12.18	Total useful exergy output	3.731	76.53
Total exergy input	4.875	100.0	Exergy losses	1.144	23.47
			Exergy degree of perfection	η <sub>e</sub> = 76.53 %	

The exergy losses in the first case are due only to the chemical reaction and are rather high: 23% from the exergy input. But the exergy degree of perfection is also high (77%), as the chemical exergy of ammonium nitrate and ammonia are very high. The heat of the reaction is not used. It is accepted to be removed from the system and treated as an external exergy loss. The second case shows very similar values of these exergy indices, the difference due to the irreversibility of the mixing of water and nitric acid and also due to the exclusion of the obtained water from the useful exergy output. In both cases the heat of the reaction is not used and is. However, in the real ammonium nitrate production process it is exactly the separation of water from obtained ammonium nitrate that is the key source of the irreversibility and consequently of the additional exergy consumption.

Two versions of the exergy balance of a relatively old ammonium nitrate plant with atmospheric pressure and internal natural circulation neutralizer [11] are shown in Table 6 [17]. The process parameters are very similar to these, shown in Table 3. The two versions differ mainly by the additives used, in the first version the additives are acids, thus the consumption of nitric acid is slightly lower, and of ammonia – slightly higher, than in the second version, where the additive is nearly neutral. The steam and electricity consumption are nearly equal and the exergy degree of perfection and exergy losses values are similar. It is clear from Table 6 that the exergy of steam and power is only about 6% from the total exergy input.

Exergy balances of two versions of another design of ammonium nitrate plant are shown in Table 7. The neutralisation is going in a pipe reactor and the subsequent process pressure is atmospheric [15,16]. It is correct to compare the previous balances with the second version only, as the first one refers to the obtained 96% AN solution, not to the solid product. The exergy efficiency of this design is slightly higher than that of plant No.1, mainly due to the lower consumption of the import MP steam. In this plant a higher degree of the process steam heat utilization is achieved in evaporation of the recycled diluted solutions. Also the purified process steam condensate is a useful by-product and so the exergy losses are lower and the exergy degree of perfection is higher than in the first design. As the result of the waste flows treatment is also the recycling of the pollutants (ammonia and ammonium nitrate) back into the production process, the overall effect includes also some reduction of feedstock and energy consumption. Thus, despite the lower concentration of ammonium nitrate solution at the neutralizer section output, the exergy indices in this design are better than in the first plant, mainly due to the deeper purification of the process condensate.

Table 6. Exergy balances of an ammonium nitrate production plant (No. 1\*)

Exergy input			Exergy output		
Mass and energy flows	GJ/t	%	Mass and energy flows	GJ/t	%
Version 1					
Ammonia	4.410	82.63	Ammonium nitrate	3.724	69.78
Nitric acid (58%)	0.594	11.13	Clean steam condensate	0.038	0.71
Additives	0.011	0.20	Total useful exergy output	3.762	70.49
Steam (1.6 MPa)	0.239	4.48	Exergy losses total, incl.:	1.575	29.51
Electricity	0.083	1.56	- external losses	0.332	6.22
Total exergy input	5.337	100.0	- internal losses	1.243	23.29
			Exergy degree of perfection	$\eta_e= 70.49\%$	
Version 2					
Ammonia	4.389	82.70	Ammonium nitrate	3.671	69.17
Nitric acid (58%)	0.594	11.19	Clean steam condensate	0.038	0.72
Additives	0.010	0.19	Total useful exergy output	3.709	69.89
Steam (1.6 MPa)	0.231	4.35	Exergy losses total, incl.:	1.598	30.11
Electricity	0.083	1.57	- external losses	0.395	8.59
Total exergy input	5.307	100.0	- internal losses	1.203	21.52
			Exergy degree of perfection	$\eta_e= 69.89\%$	

Table 7. Exergy balances of an ammonium nitrate production plant (No. 2\*)

Exergy input			Exergy output		
Mass and energy flows	GJ/t	%	Mass and energy flows	GJ/t	%
Version 1					
Ammonia	4.300	84.70	Ammonium nitrate (99 % melt)	3.774	74.34
Nitric acid (60%)	0.585	11.52	Clean steam condensate	0.041	0.71
Additives	0.003	0.06	Purified process steam condensate	0.073	1.44
Steam (1.6 MPa)	0.126	2.48	Total useful exergy output	3.868	76.19
Electricity	0.063	1.24	Exergy losses	1.209	23.81
Total exergy input	5.077	100.0	Exergy degree of perfection	η= 76.19 %	
Version 2					
Ammonia	4.300	84.40	Ammonium nitrate (solid)	3.706	72.74
Nitric acid (60%)	0.585	11.48	Clean steam condensate	0.041	0.80
Additives	0.003	0.06	Purified process steam condensate	0.073	1.43
Steam (1.6 MPa)	0.126	2.47	Total useful exergy output	3.820	74.98
Electricity	0.081	1.59	Exergy losses	1.275	25.02
Total exergy input	5.095	100.0	Exergy degree of perfection	η= 74.98 %	

\*Neutralization at atmospheric pressure, pipe reactor. Solidification by prilling. Steam condensate is purified by RO.

In Table 8 a comparison is made of the exergy losses distribution in the plant No 1 and the data from an investigation concerning US chemical industry [7]. Unfortunately, no data are shown in [7] about the features of the processes and design of the studied AN plants. Despite some differences concerning exergy losses distribution between external and internal, the main source of losses in both cases is the neutralization process. Having in mind that the pipe reactors are used firstly in US chemical plants, the neutralization in the studied AN plants is presumably implemented in pipe neutralizers. So this could be the explanation of the similarity of the total exergy values in Plant No. 2 and in referred US plant [7]. The external exergy losses in the plant No. 1 are due only to the air and process steam flow outgoing the prilling tower (Fig. 1). In the referred US plants [7] the external losses from the neutralization stage are due probably to the exergy of the condensation heat of the process steam which is removed by cooling water. In the same plant the external losses from the evaporator are due to the exergy of the hot air and process steam emitted from the evaporator.

Table 8. Exergy losses distribution in ammonium nitrate production plants

Exergy losses source	AN plant No. 1, Version 1* [17]		AN plant No. 2	AN plant [7]			
				GJ/t			%
	GJ/t	%		GJ/t	External	Internal	Total
Neutralization 1 <sup>st</sup> and 2 <sup>nd</sup> stages	1.028	65.27		0.272	0.698	0.970	80.03
Prilling tower & process steam and prilling air treatment scrubbers	0.155	9.84	-	-	0.068	0.068	5.61
Evaporation unit	0.027	1.71	-	0.084	0.084	0.167	13.78
Nitric acid preheater	0.027	1.71	-	-	-	-	-
Ammonia preheater	0.006	0.38	-	-	-	-	-
Finishing	-	-	-	-	0.007	0.007	0.58
<b>Total internal exergy losses</b>	<b>1.243</b>	<b>78.92</b>	-	-	<b>0.856</b>	--	<b>70.63</b>
<b>External losses total</b>	<b>0.332</b>	<b>21.08</b>	-	<b>0.356</b>	-	-	<b>29.37</b>
<b>Total exergy losses</b>	<b>1.575</b>	<b>100.00</b>	<b>1.275</b>	-	-	<b>1.212</b>	<b>100.00</b>

A simplified Grassmann exergy flows diagram is shown in Fig. 2. The diagram is based on the exergy balances data from Table 6 [17]. The width of some flows (e.g. steam, electricity) is not proportional to the real exergy flows, as the difference between the flows, containing exergy of chemical substances and these containing nearly only physical exergy, is too big. Yet the diagram shows graphically the transformations of the exergy flows in the major stages of the technological chain. It is interesting to see that the recycle AN solution, used in prilling air & steam treatment at the final stage of the process, is going back to neutralizer in order to recover the AN from the waste flows. But it is clear that part of the reaction heat must be used to evaporate once again the water from this diluted (20%) solution. As shown in Table 4, about 15% of the reaction heat is consumed for evaporation of the water in the recycled solution.

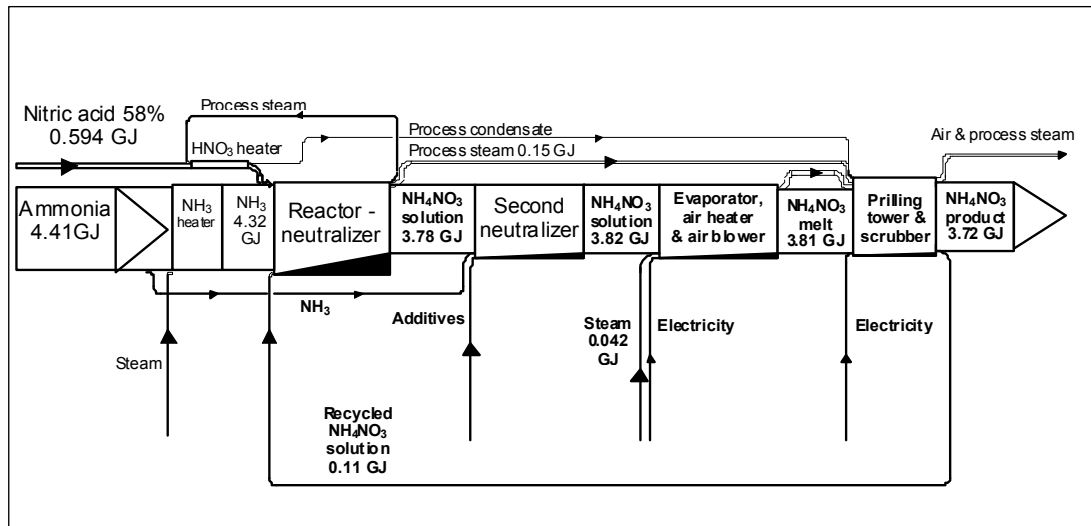


Fig. 2. Grassmann exergy flow diagram of ammonium nitrate production plant No.1, Version 1

## 4. Conclusions

The exergy method is used to analyze two basic designs of industrial ammonium nitrate production plants. As it could be expected, the irreversible chemical reaction – neutralization of ammonia with nitric acid - is the main reason of the exergy losses. In spite of that, the comparison of the analyzed plants shows that there exist some opportunities for a possible reduction of the middle (1 – 1.3 MPa) pressure steam import by better low temperature heat utilization and water recovery. The external exergy losses can be reduced with about 20% if the steam condensate would be purified (ammonia and AN content down to below 10 ppm w/w), recycled to the water treatment plant and then (after polishing) used as boiler feed water. The purification of all process steam and condensate has as a result also almost full recycling of ammonia and AN back into the production process and in consequence of this, some reduction of the feedstock consumption.

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## Nomenclature and abbreviations

<i>AN</i>	Ammonium Nitrate	<i>MT</i>	Middle Temperature, °C
<i>E</i>	Exergy	<i>Q</i>	Heat of reaction (-ΔH)
<i>LP</i>	Low Pressure, MPa	<i>RO</i>	Reverse osmosis
<i>LT</i>	Low temperature, °C	<i>η<sub>e</sub></i>	Exergy Efficiency
<i>MP</i>	Middle Pressure, MPa		

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