German Notes on BAT of the production of

Large Volume Gaseous and Liquid Inorganic Chemicals

Federal Environmental Agency

March 2001

1 Contents

2

2. General Information

2.1 Production capacities

3 Description of processes for production of gaseous and liquid volume chemicals

3.1 Synthesis gas (carbon monoxide CO, hydrogen H_2)

3.1.1 Applied processes and techniques

Synthesis gases are mixtures from hydrogen and carbon monoxide. Raw materials are solid, liquid or gaseous fuels, which react under additivation of oxygen and / or steam at higher temperatures. Often the production of synthesis gas is a very economic recycling process of residues, which can provide the basis for basic chemical products, e.g. methanol. So heavy vacuum distillation residuals from refining processes are valuable raw materials. Before selection of a synthesis gas process the feedstock basis has to be considered first. The basic gasification processes for synthesis gas production are

- catalytic gasification of naphtha or natural gas,
- coal / coke gasification,
- heavy petroleum oil fraction gasification,

Synthesis gas is a raw material for further chemical synthesis and is used in different stages. *Methanol* using a mixture from hydrogen and carbon monoxide and *ammonia* using hydrogen from synthesis gas production are the most important chemical products. A further application for the carbon monoxide from synthesis gas is the production of hydrocarbons according the Fischer - Tropsch - process, isocyanates, carbonates, oxo-alkohols and -aldehydes, acryl- and propionacid and phosgene. Steam reforming with natural gas is the process most in use. 76 % of the produced hydrogen is provided of the basis of natural gas in the world.

The **gasification process** includes the following reaction steps

gasification process:	$-CH_2-$	+	$0{,}5\ O_2$	**->**	CO	+	H_2	-92 kJ/mol	partial oxidation
	$-CH_2-$	+	H_2O	**->**	CO	+	$2\ H_2$	+151 kJ/mol	reforming
conversion process	CO	+	H_2O	**->**	CO_2	+	H_2	-42,2 kJ/mol	watergas-reaction

The production of synthesis gas is an endothermal process with external energy supply (primary steam reforming process) or an exothermal process with partial combustion of educts for energy supply within the system (partial oxydation and secondary steam reforming). The catalyst most in use for processing of gaseous and liquid hydrocarbons is nickel on aluminium oxide. But a modificated heavy petrol oil gasification concept working with a catalyst has been described. A pretreatment of raw materials to seperate sulfuric compounds is an important prerequisite for catalytic processing. The higher part of synthesis gas in the world is produced by primary steam reforming.

A number of side reactions proceed beside the main process. These reactions may be undesired if they proceed uncontrolled but under a controlled regime they are used for final **conditioning** of the synthesis gas:

C	+	CO_2	**->**	2 CO			+172 kJ/mol	boudouard-balance
CO	+	$3\ H_2$	**->**	CH_4	+	H_2O	-206,7 kJ/mol	formation of methane
CO_2	+	$4\ H_2$	**->**	CH_4	+	$2\ H_2O$	-163,7 kJ/mol	formation of methane
2 CO	+	$2\ H_2$	**->**	CH_4	+	CO_2	-247,0 kJ/mol	formation of methane
C	+	$2\ H_2$	**->**	CH_4			-82,8 kJ/mol	formation of methane
2 C	+	$2\ H_2O$	**->**	CH_4	+	CO_2	-8,8 kJ/mol	formation of methane
H_2S	+	CO_2	**->**	H_2O	+	COS		H_2S/COS - balance
CO	+	$0{,}5\ O_2$	**->**	CO_2			-283 kJ/mol	CO - oxidation

The number of side reactions is the reason for a further **gas treatment** of the reaction products and **a treatment of the side products** after the main process.

The number of process steps for synthesis gas cleaning decrease in the following line:

solid > liquid > gaseous raw material.

The cleaning processes for synthesis gas are listed in the table below.

Contaminant	Process	Catalyst
Soot and dust	• Soot and vanadium/nickel removal with water (gasification of heavy petroleum oil fractions). Different processes have been developed. After water seperation and soot combustion a V- and Ni - containing ash with minimal soot content and ca. 70 % vanadium pentoxide (raw material for V – production) results. • Soot - water can be used as activated carbon to capture e.g. heavy metal compounds • Soot - recycling may be installed in some processes, but has the disadvantage of higher corrosion-/erosion - rates and probably a higher Ni - concentration in the waste water	
CO_2 (chemical raw material for further processes after cleaning)	• Hot K_2CO_3 - washing, • Physical washing, e.g. Rectisol – process (physical absorption with methanol) or Sepasol – process • MDEA – process (with methyldiethanolamine) • MDEA - scrubbing.	
Sulfur compounds (COS, H_2S, CS_2 , Mercaptane)	• Conversion of carbonoxidesulfide $COS - H_2O \rightarrow H_2S + CO_2$ • H_2S - removal by Sulfosolvan – washing • H_2S - removal by Sulfinol - washing (mixture of sulfolane, diisopropanolamine or methyldiethanolamine with H_2O) or MDEA – washing (ab-/desorption - methyldiethanol-amine with H_2O) and for example production of H_2SO_4 • H_2S - final cleaning by adsorption at $Fe(OH)_3$, or $Al(OH)_3$, ZnO • Catasulf - process, • Activated carbon desulfurisation, • Claus – process • Production of elementary sulfur by a redox-process (Sulferox – process, Low - Cat - process) • molecular sieves	Al_2O_3

Table 3-1: Processes for synthesis gas cleaning

Conditioning

The conditioning processes are performed to access the adequate component proportion, which is an important prerequesite for further chemical treatment :

- addition of steam (CO - conversion)
- methanisation (processing of CO, CO_2 H_2 into CH_4 , especially for NH_3 - synthesis)

3.1.2 Present consumption/emission levels

3.1.2.1 Gasification process

Atmospheric emissions are most important and depend on the raw material:

Coal:	dust, SO_x, NO_x H_2S, CO (many further anorganic compounds of coal)
Heavy petroleum oil fractions:	SO_x, NO_x H_2S, CO, V, Ni, COS, CS_2, NH_3 (dust can only come from flares at start up procedures)
Naphtha, natural gas:	NO_x, CO

As can be seen from this list, most atmospheric emissions arise from solid and liquid raw materials.

Atmospheric emissions demonstrated at the example of coal gasification /10/:

For the case of coal gasification atmospheric emissions arise from burning coal and fuel gas gasification, coal handling and preparation and fuel refining.

Combustion generated pollutants from the steam and utilities plant are primarily particulates, sulfur dioxide, nitrogen oxides, and volatile organic compounds. Other inorganic pollutants are found in coal including fluoride, beryllium, lead and mercury. The known technology for controlling pollution created by coal combustion is of course applicable here. Flue gas desulfurization units, electrostatic precipitators and bag houses can be used to control sulfur dioxide and particulates. Nitrogen oxides (NO_x) emissions can be minimized by combustion techniques or chemically, for example with selective catalytic reduction (SCR). The ash and sulfur contents depend on the characteristics of the coal. With appropriate design, indirect liquefaction plants can eliminate coal combustion for steam and utilities production. If gasifiers process feed coal, including fines, all the steam and power requirements could be met by combustion in gas turbines of a portion of the cleaned synthesis gas.

The crude gasification product contains almost 100% of the coal sulfur, mostly as hydrogen sulfide. The sulfur content must be reduced to ca. 1 mg/kg so as not to poison the catalyst. Various processes convert the hydrogen sulfide to elemental sulfur which is marketable. The most common of these are the Stretford, used at SASOL, and the Claus, used at several petroleum refineries. The Stretford process is used worldwide in over 50 plants. The Claus process has been well established in the refinery and natural gas industries for many years.

Particulates from coal *handling* and preparation can be controlled by enclosures, sprays, and bag houses. Gaseous pollutants from refining operations and vapor leakages can be controlled by recovery systems and proper maintenance.

Atmospheric emissions of heavy petroleum oil fraction gasification:

These are similar than those arising from coal gasification, but without typical dust pollutants.

Atmospheric emission figures:

Emissions from flares are usually calculated, as it is not possible to capture the exhaust gas stream for monitoring. The burn - off - rate is estimated to 99 % or even higher. The table below lists a summary of atmospheric emissions from synthesis gas production.

Pollutant	**Amount of emissions**			
	Raw material	**Heavy petr. oil**	**Raw material**	**Heavy petr. oil**

	gaseous or light HC[1] [mg/m^3]	**fract. or coal [mg/m^3]**	**gaseous or light HC[1] [g/t] [*]**	**fract. or coal [g/t][*]**
NO_x	200 - 300 mg/m^3	200 - 300 mg/m^3	250 g/t	250 g/t
SO_2	-		-	370 g/t
Dust	5 mg/m^3	50 mg/m^3		75 g/t
CO	< 100 mg/m^3	170 mg/m^3	100 g/t	-
V	-	5 mg/m^3	-	7,5 g/t
Ni	-	1 mg/m^3	-	1,5 g/t
VOC [1]		2 mg/m^3	2 g/t	
H_2S	-		-	2 g/t

[1] VOC = Volatile Organic Pollutants [*] Caculated from the emission concentration for 1500 m^3/t product

Table 3-2: Atmospheric emissions in synthesis gas production

Additionally to the emission data mentioned above a modificated heavy petrol oil gasification concept working with a sulfur - sensitive catalyst has been described; < 20 SO_2 g/t are emitted in this case, but about 300 g/t CO and 15 g/t VOC.

The table below lists atmospheric emission data for individual synthesis gas production plants:

No. of the production plant	**Emission data** (clean gas data - sum of all sources)
1. **Input:** Heavy oil gasification **Capacity:** 235 kt/a	SO_2 : 252 g/t CO: 165 g/t hydrocarbons: 2 g/t H_2S : 1 g/t
2. **Input:** Heavy oil gasification **Capacity:** 350 kt/a	SO_2 : 218 g/t CO: 96 g/t hydrocarbons: 3 g/t H_2S : 1 g/t
3. **Input:** 6391 t/a natural gas **Capacity:** 3250 kg/h	NO_x : 150 mg/m^3 CO: 10 mg/m^3 Dust: 5 mg/m^3
4. **Input:** natural gas **Capacity:** 0,045 t/h = 535 m^3/h (1 bar, 15 °C, 24 h/d)	NO_x : </= 200 mg/m^3 ; 270 g/h CO: </= 100 mg/m^3 ; 20 g/h **Waste:** within 10 years: 440 kg/a ceoliths, 240 kg/a activated carbon, 56 kg/a activated aluminas from waste water by demineralization: 1,6 kg/h salts
5. **Input:** natural gas **Capacity:** 55 x 10^6 Nm^3/ a; 12055x 10^6 Nm^3/ a	CO < 10 - 20 mg/m^3 NO_2 100 - 177 mg/m^3 VOC < 2 mg/m^3 SO_2 < 0,6 mg/m^3

Table3-3: Atmospheric emission data for synthesis gas production plants in Germany (source: local authorities, measured as ½ - h average)

The use of heavy petroleum oil fractions as raw material causes higher atmospheric emissions than the use of naphta or natural gas, but reduces a residual problem by processing in chemical synthesis.

The **Energy demand** depends on the raw material and on the desired content of CO and H_2.

3.1.3 Gas treatment

The processes for cleaning of synthesis gas depend on the used raw material. Gas treatment includes conditioning as well.

Contaminants: Dust (coal), tar (heavy petroleum oil fractions, coal), soot (heavy petroleum oil fractions), O_2 (heavy petroleum oil fractions, coal), CN - compounds (heavy petroleum oil fractions, coal, NO_x (heavy petroleum oil fractions, coal), CO_2 (all raw materials), H_2S (in non - catalytical processes), NH_3 (all raw materials)

In the case of coke gasification tar and phenols are not formed.

Aqueous effluents /10/ or wastewaters arise principally from gasification wash waters, especially in coal and heavy petroleum oil gasification.

All the liquor produced by washing and cooling of the exit gases is combined in large separation vessels. This wastewater contains dissolved acid gas, organic acids, tar components, phenols, and ammonia. Phenols can be removed by solvent extraction, ammonia is stripped and the wastewater is then treated biologically by activated sludge, which, however, does not remove all chemical oxygen demand. Residual chemical oxygen demand is attributed to humic acid components, which are apparently harmless, but the remaining 1 mg/kg of phenol must he removed by adsorption on granular activated carbon.

Solid wastes /10/ arise from gasification residues (e.g. ash, slag, and char). Wastes generated by grinding and grading the coal; steam plant wastes, such as fly and bottom ash and flue-gas desulfurization residue; water treatment wastes, such as biosludge and salts from blowdowns; and spent catalysts.

The quantity and character of these solid wastes depend, largely, on the used gasification process used and the characteristics of the feed coal. Wastewater treatment sludge is usually incinerated and activated carbon regenerated. Concentrated inorganic salts from cooling tower blowdowns are hazardous and require disposal.

Pollution control is greatly simplified by the use of advanced entrained gasification. Some systems, for example, produces only carbon monoxide and hydrogen without tars, oils, or phenols, transforms the mineral matter in the coal to a glassy, nonleachable slag, and consumes minimal steam.

Removal of side products

Side products can be wastes, but valuable raw materials as well. These are:

- Sulfur -> raw material for further chemical synthesis,
- vandium/nickel - containing soot in heavy petroleum oil fraction gasification processes -> raw material for vanadium production in the metallurgical industry,
- tar, oil, phenols, cresols, ammonia and organic hydrocarbon acids from coking processes.

3.2 Phosgene ($COCl_2$) /6/

3.2.1 Applied processes and techniques

$$CO + Cl_2 \rightarrow COCl_2$$

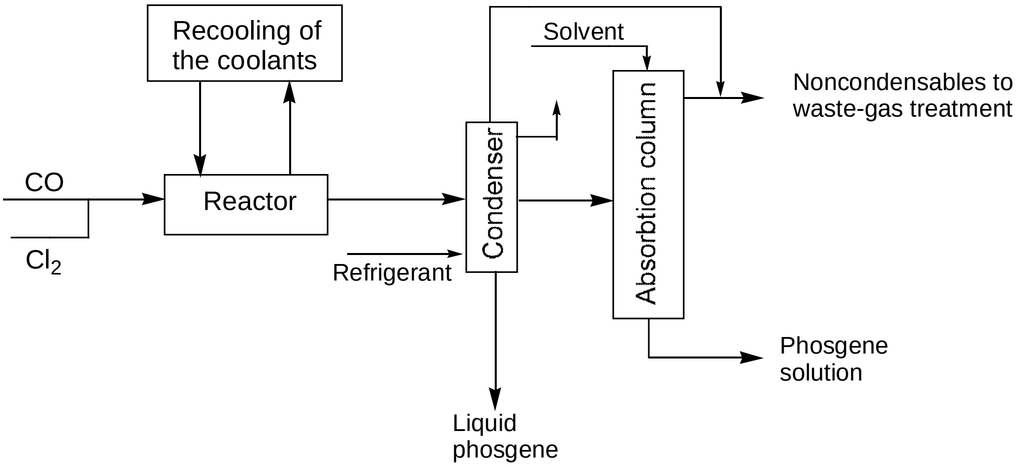

Abb.1: Block diagram of phosgene production

Phosgene is produced by reaction of carbon monoxid and chlorine over activated carbon. Pipe reaktors made from steel, filled with granulated catalyst and externally cooled with water or other cooling liquids are used. The diameter of the pipes is between 25 and 70 mm. The reaction starts at 40 - 50°C. The temperature in the pipes raises to about 400°C as a maximum and decreases rapidly afterwards. The temperature at the outlet should not be more than 100°C to prevend decomposition.

An excess of carbon monoxide is used to ensure the complete reaction of chlorine to a chlorine - free phosgene. The released gases are cooled for liquidation in cooling loops. The reaction can be performed without or under pressure. 2 - 3 bar are used in most cases to ensure the liquidation of the reaction product in the first cooling step. But the pressure should be controlled in a level, which prevend the liquidation of phosgene in the synthesis reactor.

The catalyst (normally charcoal) can be used over long time periods depending on the amount of contaminants in raw materials. To ensure a complete reaction in the case of decreasing contact efficiency as well a further reactor filled with activated carbon can be added. The used carbon can finally incinerated after elimination of the residual phosgene.

The needed carbon monoxide is obtained from a reformer process or CO/H_2 synthesis gas. Methane and hydrogen react with chlorine and result in local points of excess heat and possibly causing chlorine - iron fires.

3.2.2 Present consumption/emission levels

Operating requirements typical of those required for the production of phosgene in a modern plant are given below.

Input

Raw Material	**Quantity (in tons) per ton of phosgene**
Carbon Monoxide	0.306
Chlorine	0.732
Charcoal	0.00008
Steam (inc. distillation)	0.15 – 0.3
Process Water	2 – 5
Cooling Water *)	50 – 60
Power/Refrigeration *)	150 kWh

*) The cooling water requirement is reduced, and the refrigeration load is eliminated, if phosgene is fed directly from the reactor without condensation or further purification

Tabelle 3-4: Operating requirements typical for the production of phosgene in a modern plant

Atmospheric emissions and waste water

The residual gases of phosgene production and waste gases from phosgene processing have to be treated under destruction of the phosgene content. The removal of the high toxic phosgene contaminant from the waste gas is of special importance in this case.

An example for emission data is given below for a

phosgene - production plant as a single part of a MDA/MDI – production plant

Input:	Chlorine:	49.100 t/a
	Carbon monoxide:	22.200 t/a
Capacity:	68.000 t/a MDA	
	85.000 t/a MDI	
Emission data:	Waste gas:	
	phosgene:	6 kg/a
	Chlorine:	414 kg/a
	NO_2:	16,5 kg/a
	Organic carbon:	25.9 kg/a
	Waste water:	
	Amount:	489.700 t/a
	NaOH:	1.100 t/a
	NaCl:	44.800 t/a
	Na_2CO_3:	11.600 t/a

Waste gas treatment and monitoring /11/

The residual gases from phosgene production and the off-gases from plants for phosgene processing must be freed from phosgene in a decomposition unit. This is achieved by various methods.

Decomposition with alkaline scrubbing agents, mainly sodium hydroxide solution. The residual gas is led through packed towers, at the top of which sodium hydroxide solution is introduced. Make-up sodium hydroxide solution is added under pH control. Venturi scrubbers can also be used.

Decomposition in activated carbon towers. The residual gas is passed through towers that are filled with activated carbon and fed with water. Water and residual gas are usually fed cocurrently to avoid flooding of the packing. The water is usually recycled. If the concentration of hydrochloric acid which is formed by decomposition of phosgene exceeds 10 %, the decomposition effect is greatly reduced. Therefore a sufficient supply of fresh water must be assured. For safety reasons frequently two towers in series are used.

Combustion. The residual gases are burnt so as to convert phosgene to CO_2 and HCl only. An advantage of this method is that all remaining pollutants in the residual gas, such as solvents and carbon monoxide, are burnt together. Normally, the outlet gas from the phosgene destruction equipment is continuously monitored for residual phosgene content.

Safty issue

Phosgene is a very poisonous material effecting by inhalation. Phosgene is an especially insidious material in that human detection levels (about 0.5 – 1 ppm) are above those considered safe (0.1 ppm). After repeated exposures, human detection levels are elevated. In addition, phosgene is a gas that is heavier than air, so it accumulates in low areas. Operating areas need special safety provisions and have to be monitored by a variety of alarm and shutdown systems continuously. Operating personnel or others using areas where phosgene is employed usually wear phosgene indicator badges that change color upon exposure.

Different further measures are available */11/:*

Primary technical measures. The primary technical measures are aimed at preventing phosgene emission from the closed equipment. This is achieved by e.g., selection of resistant, highgrade materials for equipment and lines; careful testing of this equipment and lines, especially the welds; leak tests before resuming operation of plant units; the use of pumps which are hermetically sealed to the outside (canned motor pumps, magnetic pumps); the use of highgrade materials for flange gaskets; and regular inspections of equipment and lines. In the field of process control engineering, particularly high requirements are set for the quality and design of process control equipment. Plant equipment which are particularly important for safety have duplicated process control instrumentation. Automatic systems ensure immediate safe shutdown of the plant when important process parameters move outside a narrow bandwidth. In addition, the probability of phosgene emission and the emission potential are reduced further by continual optimization of the process system. In this way e.g. the number of vessels containing phosgene and their phosgene content are reduced.

Secondary technical measures. Secondary technical measures are used to detect leaks as soon as possible and to combat escaped phosgene. These measures include, e.g., continuously operating alarm systems for monitoring room air and ambient air, systems for combating escaped phosgene by chemical reaction (e.g. steam ammonia curtains in the case of gaseous emissions), jacked pipes, and complete containments for phosgene processing plants or plant units.

Organizational measures. The organizational measures ensure that the staff operate the plants safely and initiate rapid countermeasures following malfunctions or the detection of leaks. These measures include special training, routine plant inspection, training for exceptional situations, clear operating instructions, and regular safety discussions.

Personal safety precautions. The personal safety precautions ensure that the staff are protected from exposure during a possible release of phosgene into the atmosphere and that a possible exposure is detected early enough to prevent inhalation of a dose which would he dangerous to health. The staff are therefore equipped with escape masks or respirators.

3.3 Ammonia (NH_3) / Carbon dioxide (CO_2)

3.3.1 Applied processes and techniques for ammonia - production /1/

Extential discussion of different types of ammonia production were done in 1995/96 and process descriptions and results are included in the „Final BAT Reference Document on Ammonia Production“. The content of this document is repeated here only in the shortest version. The description of ammonia production plants includes installations in the range of common production capacities of 1 to 1,5 kt/d, but capacities up to 1,8 kt/d are not uncommon for new plants.

The different types of ammonia production installations can not be seperated to single aggregates and compared as parts of techniques isolated from each other, because of the highly integrated character of the whole process. The steam reforming is divided into the types:

ACP Advanced Conventional Process – with a fired primary reformer and excess air secondary reforming (stoichiometric H/N - ratio),

RPR Reduced Primary Reformer Process – with mild conditions in a fired primary reformer and excess air secondary reforming (under - stoichiometric H/N - ratio),

HPRHeat Exchange Primary Reformer Process - heat exchange autothermal reforming, with a process gas heated steam reformer (heat exchange reformer) and a seperate secondary reformer, or in a combined autothermal reformer, using excess or enriched air (under - stoichiometric H/N - ratio or stoichiometric H/N - ratio).

Additionally there is a further process technique in use:

POC Partial Oxidation Process – gasification of heavy petroleum oil fractions or vacuum residuals for production of synthesis gas.

The most installations work on the basis of steam reforming using naphtha or natural gas. 3 % of the European plants are of the partial oxidation type.

3.3.2 Present consumption/emission levels

The main environmental concerns of ammonia production are atmospheric emissions and are caused by the energy demand and NO_X – emissions. The main emission source is the waste gas from the primary reformer. It includes NO_X, CO_2 and small amounts of SO_2 and CO. Little importance have other atmospheric emissions (ammonia), wastes (used catalysts) and waste water (condensates).

Energy demand and NO_X – emissions of existing installations are listed in the table.

Energy demand GJ/t				Atmospheric NO_X – emissions			
Steam reforming		Partial Oxidation		Steam reforming		Partial Oxidation	
feed	fuel	feed	fuel	g/t	mg/m^3	g/t	mg/m^3
existing installations							
22-25	4-9	29-34	6-20	600-1300	200-400	a) 200 – 500 b) 1300	a) 200 – 450 b) 700
new installations							
29,3		**36**		**450**	**200**	**a) 200** **b) 1300**	**a) 200** **b) 700**

a) Superheater b) Auxiliary Boiler

Table 3-5: Energy demand and NO_X – emissions of existing ammonia production installations according the existing NH_3 - BAT - description from 1996 /1/(capacities between 1 to 1,5 kt/d (500 kt/a))

Wastes (m^3/a – 1,35 kt/d)		Ammonia emissions (air – g/t)		Ammonia emissions (water – g/t)	
Steam Reforming	Partial Oxidation	Steam Reforming	Partial Oxidation	Steam Reforming	Partial Oxidation
existing installations					
57	40	40 – 20000		0 - 1500	0 – 1500
new installations					
0,2 kg/t		**c) 40** **a) 2**	**c) -** **a) 2**	**100**	

c) continuous emissions d) diffuse emissions

Tabelle 3-6: Further emissions in existing installations for NH_3 - production according to the existing NH_3 - BAT - Note - description from 1996 /1/ (capacities between 1 to 1,5 kt/d (500 kt/a))

Further descriptions were given by industry and are listed in th following tables:

Input

	Steam Reforming	**Partial Oxidation (POC)**
Energy – raw material		32,0 GJ /t
ACP	24,5 GJ/t	
RPR	26,0 GJ/t	
HPR	27,5 GJ/t	
Energy – fuel		6 - 10 GJ/t
ACP	8 - 10 GJ/t	
RPR	6 - 8 GJ/t	
HPR	4 - 8 GJ/t	
Energy - as a whole (for an isolated installation)	32 - 35 GJ/t	41 (39 – 42) GJ/t
Process air		4 kg air/kg NH_3 (air seperater)
ACP	0,85 kg N_2/kg NH_3 1,1 kg air/kg NH_3	
RPR	50 - 100 % higher	
HPR		
Process water	Condensates are recycled, processwater for steam production needed: 0,7 - 1,5 kg/kg NH_3	
Solvents	Solvents needed for CO_2 – separation: 0,01 - 0,02 kg/t NH_3 (monoethanolamin - MEA; activated methyl – diethanolamin - MDEA; potassium carbonate mixture; glycoldimethylether - Selexol)	

catalysts (plants of 1,5 kt/d)			
hydratisation of sulfur	1 m^3/a	(Co/Mo)	
separation of sulfur	5 m^3/a	(ZnO)	
primary reforming	5 m^3/a	(Ni/Cr - Leg.)	
secondary reforming	4 m^3/a	(Ni)	
(high temp. - CO - conv.)	10 m^3/a	(Fe/Cr-Oxid)	
(low temp. - CO - conv.)	20 m^3/a	(Cu/Zn-Oxid)	
methanisation	2 m^3/a	(Ni)	
synthesis	10 m^3/a	(Fe)	

Tabelle 3-7: Inputs for existing installations of NH_3 - production according to industry information /2/

Output

• Ammonia	1,0 - 1,5 kt/d / 300 - 500 kt/a (dry, technical - 99,5 %; ultra cleaned 99,8 %)
• CO_2	steam reforming of natural gas: 1,15 - 1,3 kg/kg NH_3 partial oxidation: 2 - 2,6 kg/kg NH_3 dependent on feedstock C/H ratio.
• Sulfur	production of elementary sulfur in Claus - plants, the produced amounts depend on the raw material
• Steam	export is possible

Atmospheric emissions

Waste gas type	**Emission component**
	Steam reforming
Waste gas of the primary reformer	Installation capacity: 1,5 kt/d; 200 kt/a waste gas with 3 % O_2 ; 8 % CO_2 (dry gas) = 500 kg CO_2/t NH_3 NO_x: 200 - 400 mg/Nm^3 (98 - 195 ppmv) 0,6 - 1,3 kg/t NH_3 (as NO_2) SO_2: 0,1 - 2 mg/Nm^3 (< 0,01 kg/t) dep. of fuel CO: < 10 mg/Nm^3 (< 0,03 kg/t)
Vent gas from CO_2 - removal	A part of the produced CO_2 is vented. The amount depend on the facilities for further processing or use at the production site (e.g. urea synthesis, facilities for filling of commercial technical gases)
Breathing gases of oil buffers	small contents of NH_3
Diffuse emissions	from Flanges etc.
Purge and flash gases (continuous emissions)	NH_3 (end - of pipe reduction techniques necessary, washing with H_2O, thermal combustion), NO_x - emissions in the case of thermal combustion.
The amount of waste gas and NO_x - and SO_2 – emissions are smaller in the heat exchange reforming process, because of the internal production of reformer heat. The waste gas volume can be reduced to 50 %.	
	Partial Oxidation

Steam production	SO_2: max. 500[(*)] mg/Nm^3 (dep. on the fuel) A partial oxidation plant may also have auxiliary boiler(s) for power steam production, if more efficiently off-site produced power is not available. The fuel to the auxiliary boiler/superheater together with possible scrubbing equipment determines the amount of SO_2 in the flue – gas. Tail gas from sulfur recovery will also contain sulfur oxides. This means that SO_2 emission from partial oxidation plants (max. 1500 mg/Nm^3) is higher than in the reformer flue – gas.
Further emissions according to steam reforming, excluding primary reformer	H_2S: 0,3 ppmv Methanol: 100 ppmv CO: 30 ppmv Dust: max. 50 mg/Nm^3 NO_X: max. 700 mg/Nm^3
Emissions to water: • process condensates from CO_2 – separation, • waste water from waste gas treatment contaminated with soot, Va and Ni	• 1 m^3 pro t NH_3 with 1 kg NH_3 and 1 kg Methanol pro m^3 – measure: recycling to the process, • soot can be recycled partially,
wastes – seperated soot in the case of heavy vacuum residuals	Seperated soot can be further used in metallurgical industry for vanadium production.

Table 3-8: Atmospheric emissions of existing plants for NH_3 - production according to industry information /2/, (*) SO_2 - emission postulated as BAT in Germany in this case

The table below lists atmospheric emission data for the Haber - Bosch part of NH_3 - production plants:

No. of the production plant	Emission data	
1	NH_3	14 g/t
2	NH_3	11 g/t
3	NH_3 CO Hydrocarbons:	32 g/t 6 g/t 9 g/t

Table 3-9: Atmospheric emission data for the Haber - Bosch part of NH_3 - production plants in Germany (source: local authorities)

3.3.3 *Techniques to be considered in the determination of BAT* /1/

The outcome of the ammonia - BAT - discussion in 1996 is referred in the following text:

The available information does not seem allow an isolated comparison. For existing installations, 3 whole - plant concepts may be considered as BAT. Though the RPR concept is superior from both an economic and environmental perspective, reconstruction of installations presently following other whole - plant concepts would seem to render limited benefits at high cost, if at all technically feasible - however more data would be required for a more comprehensive analysis.

In particular economic information on partial oxidation processes (POC) is insufficient to make an assessment. The environmental benefits to be gained here, however, are quite substantial. As an important aspect should be taken in mind, that heavy oil residuals are used as raw materials for chemical production.

For new installations, RPR whole - plant concept qualifies as BAT because of its environmental and economic superiority. Even though the HPR concept yields lower NO_x - emissions to the atmosphere, the performance of RPR on enegy consumption is deemed more important bearing in mind the conbtribution of ammonia production to both energy consumption and NO_x - emissions in a European context.

The summarising table shows environmental performance for ammonia production plants (typical size: 1,2 – 1,5 kt/d).

		Environmental performance			
Steam Reforming		energy GJ/t	NO_X g/t	waste kg/t	water g NH_3/t
	ACP	29,2	320	0,2	0 (28)
	RPR	28,9	300	0,2	0
	HPR	31,8	175	0,2	0 (80)
Partial Oxidation		38,7	1100	not relevant	130

Table 3-10: Environmental performance of best available techniques for ammonia production plants according to the BAT - Note /1/

The following block diagrams summarise the overall input / output- and emission data for ammonia production plants on the basis on steam reforming and partial oxidation.

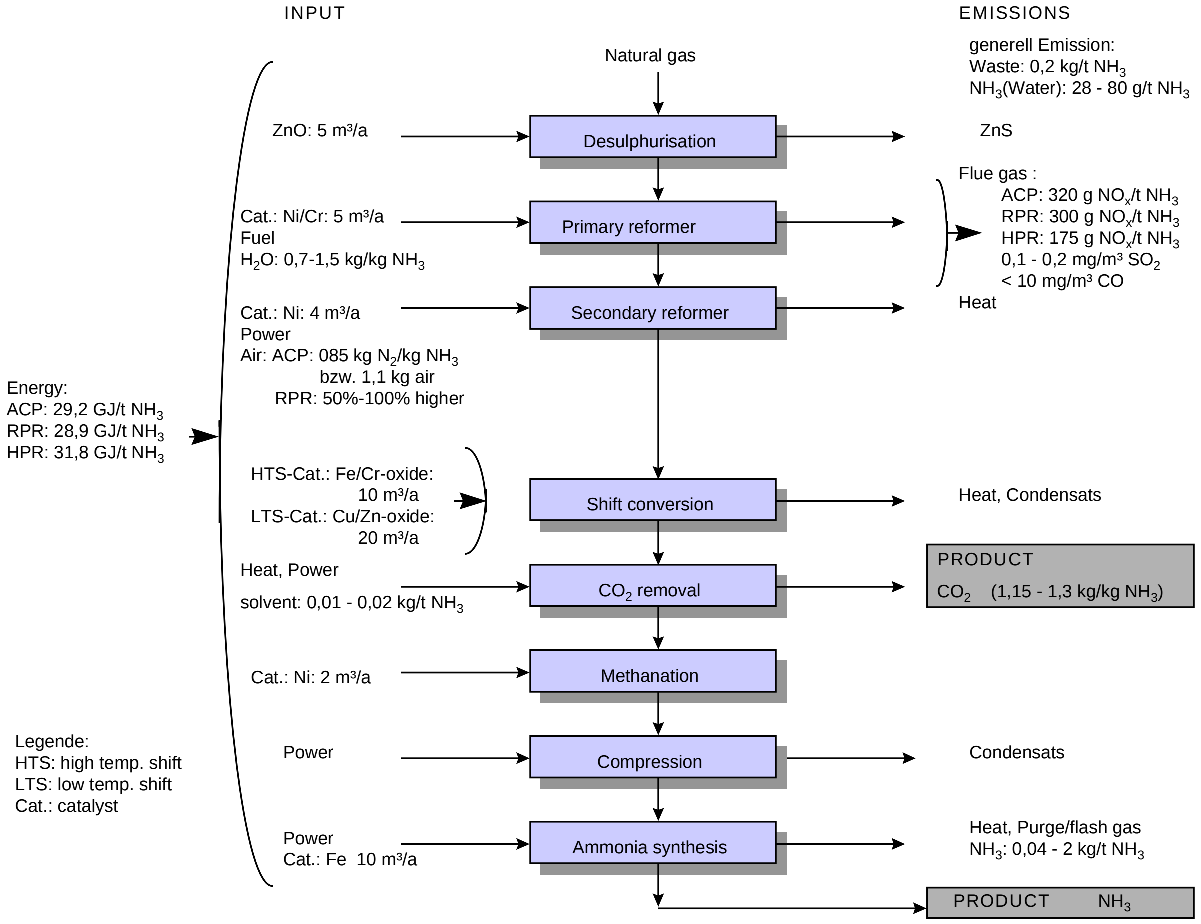

Abb.2: Block diagram of ammonia production on the basis of steam reforming

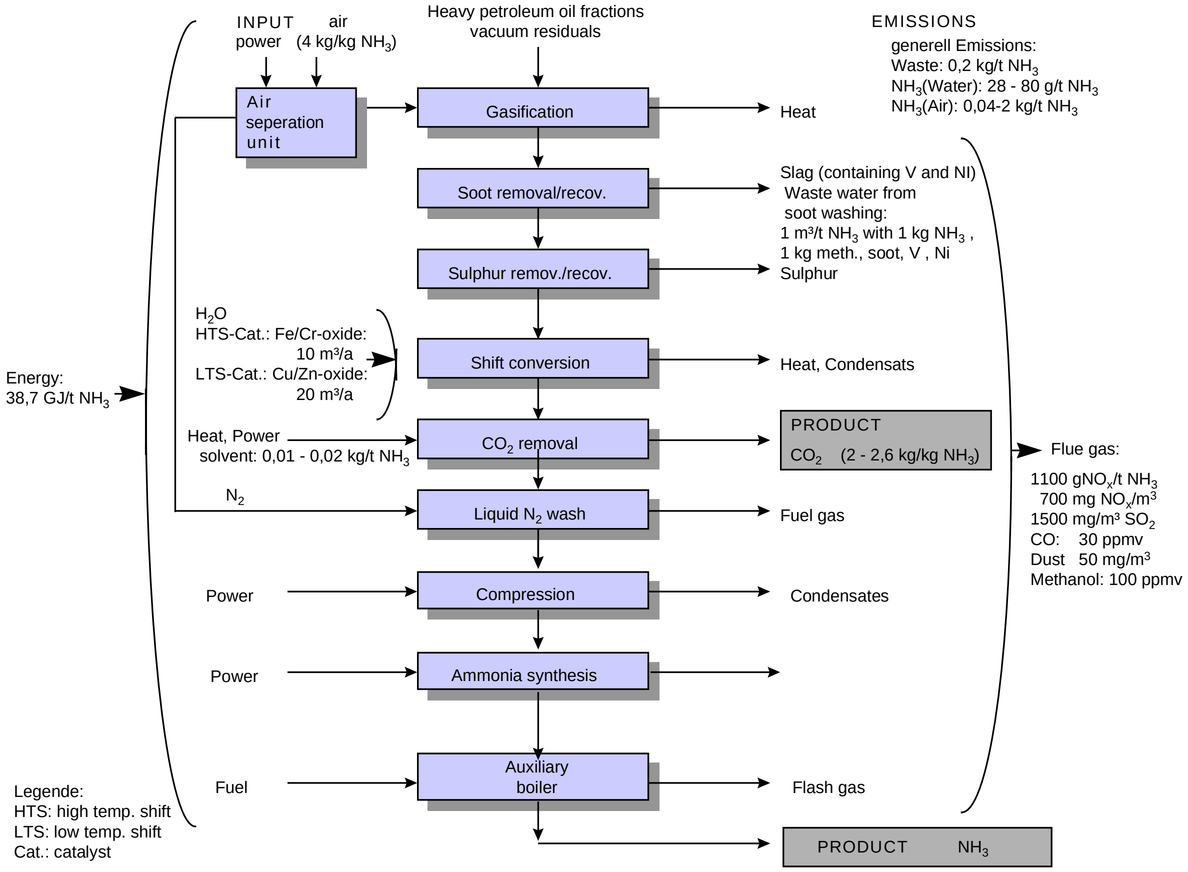

Abb. 3: Block diagram of ammonia production on the basis of partial oxidation

3.3.4 Applied processes and techniques for carbon dioxide production

Shift conversion /1/

Carbon monoxide in the process gas from the secondary reformer of the ammonia production contained at 12 - 15 % (dry gas base) reacts catalytically with steam, still present in surplus quantity in the gas , to hydrogen and carbon dioxide. To achieve a high conversion and a low residual CO content the exothermal reaction is accomplished in two steps with intermediate heat removal. In the first step, starting at an inlet temperature of around 360 - 380 ^{o}C the gas is passed through a high temperature shift reactor using a bed of an iron oxide/chromium oxide catalyst. Because of the adiabatic process design the temperature of the reaction gas rises by about 70^{o}C, with around 3 % CO content, which is close to equilibrium. After cooling to about 200^{o}C to 220^{o}C, for example by raising steam and preheating boiler feed water, the conversion is further performed in the low - temperature shift reactor using a copper - zinc oxide catalyst. Because of the more favourable equilibrium at the lower temperature, a residual CO concentration of 0,2 - 0,4 % can be attained. According to new developments isothermal shift one - step conversion can also take place by means of internal cooling of the process gas with cooling tubes running through the catalyst layers.

CO_2 - removal /1/

CO_2 removed from the reaction gas corresponds to nearly all carbon introduced as feed gas into the overall process. The residual CO_2 content is usually in the range of 100 - 1000 ppmv, depending on the solvent and design of the CO_2 removal unit. CO_2 concentrations down to 50 ppmv are achievable. Emissions from this operation occur directly through the CO_2 removed and vented to the atmosphere. The vented CO_2 contains traces of several substances such as removal solvents, hydrocarbons, H_2 , and CH_4. In cases where the CO_2 is used as a feedstock for urea production, these emissions are prevented. Apart from the emissions, the CO_2 removal section contributes significantly to the energy consumption of the plant and improvements of this step are becoming increasingly available.

The CO_2 is absobed by a solvent which has chemical and/or physical absorption characteristics. Generally, chemical solvents remove CO_2 to a higher extend but require more energy than physical solvents. The solvents used in chemical absorption processes are mainly aqueous amine solutions with special promoters (e.g. activated - monoethanolamine) and hot potassium carbonate solutions. Some solvents, like activated methyldiethanolamine are intermediate in their absorption behaviour.

The scrubbing is performed in packed columns in counter current with the gas stream. The CO_2 is recovered in almost pure form, and vented or used in other production processes, e.g. urea production. The performance of this process step depends on the regeneration characteristics of the solvents and include the energy requirements and solvent losses. When chemical solvents are used, the energy consumption of the process is mainly heat required for the regeneration of the solution. In all processes mechanical energy is needed for the circulation of the solvent. Typical range of heat consumption in the modern chemical absorption process is 30 - 60 MJ/kmol CO_2. The physical absorption processes are mostly designed for zero heat consumption, but for a fair comparison with chemical processes, the total of mechanical energy and heat requirements should be considered.

An other emerging process is the Pressure Swing Adsorption (PSA). This process has the potential to combine in one step both the classical CO_2 removal and the methanation in the ammonia production process. This is valid for all cases where the CO_2 purity has no priority. However, if pure CO_2 is needed as product, then it can be recovered by a classical solvent scrubbing process of the low - pressure off - gas of the PSA.

The table below summarizes the described process for CO_2 formation and removal.

Contaminant	**Process**	**catalyst**
carbon monoxide	• CO + H_2O -> CO_2 + H_2 high temperature conversion • low temperature conversion • methanisation of CO CO - 3 H_2 -> CH_4 - H_2O • copper sole washing	10 m ^{3}/a Fe_2O_3/Cr_2O_3 20 m ^{3}/a $ZnO/CuO/Cr_2O_3$ Ni/Cr_2O_3
carbon dioxide	• absorption with K_2CO_3/H_2O - solutions, water washing under pressure • Solvents needed for CO_2 – seperation: 0,01 - 0,02 kg/t NH_3 (monoethanolamin - MEA; • activated methal – diethanolamin - AMDEA; • potassium carbonate mixture; • glycoldimethylether - Selexol)	

Table 3-11: Processes for cleaning of synthesis gas for the ammonia production under seperation of carbon dioxide

3.4 Sulfuric acid (H_2SO_4)

3.4.1 Applied processes and techniques

There are three steps for the production of sulfuric acid:

1. Production of SO_2,
2. Conversion of SO_2 to SO_3,
3. SO_3 absorption

The figure below gives a summary of the process steps for H_2SO_4 production:

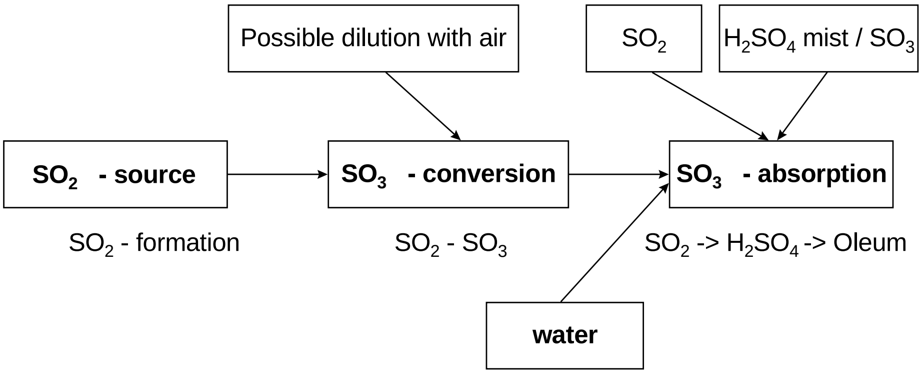

Abb. 4: Block diagram of H_2SO_4 production

3.4.1.1 SO_2- production

There are different processes for H_2SO_4 – production using different sources for SO_2. Typical SO_2 – sources are shown in the block diagram and in the table below. Beside of these there are high capacity H_2SO_4 – production plants using waste gases from other industrial processes, e.g. from copper- plumbum -, iron - and other ore treatment, from power stations and sinter plants. Because of different SO_2 – concentrations and contaminants different processing methods resulting in a wide range of emission concentrations are in use.

Reaction	**Process**
From elemental sulfur: $S + O_2 \rightarrow SO_2$	Combustion of sulfur, which is obtained either from natural deposits or from de - sulfurisation of natural gas or crude oil, is carried out in one - stage or two - stage sulfur combustion units at between 900°C and 1800 °C. Combustion units consist of a combustion chamber followed by a process gas cooler. The SO_2 content of combustion gases is generally up to 18 % by volume and the O_2 content is low (but higher than 3 %).

From metal sulfid roasting/smelting: $ZnS + 1{,}5\ O_2 \rightarrow ZnO + SO_2$ $PbS + O_2 \rightarrow Pb + SO_2$ $CuFeS_2 + SiO_2 + 3\ O_2 \rightarrow$ $Cu + 2SO_2 + FeSiO_3$	Roasting of ore concentrates in smelters. Mainly in a fluidized bed roaster or alternatively in a sinter plant. The SO_2 content of the gases is about 5 to 10 %. Belt sinter machines in those cases, where a shaft furnace is the actual smelting step or in flash or bath smelting furnace in the other processes. From continuous operations, such as sinter machines, the SO_2 - content is about 6 and 9 %. Pyrometallurgical copper extraction is based on the decomposition of complex iron - copper sulfide minerals into copper sulfides, followed by selective oxidation, seperation of the iron portion as slag and final oxidation of the remaining copper sulfide. These steps are roasting, smelting and converting.
From hydrogen sulfide: $2\ H_2S + 3\ O_2 \rightarrow 2\ SO_2 + 2\ H_2O$	Recycling of waste gases of the viscose process.
From sulfides (e.g. Pyrit): $4\ FeS_2 + 11\ O_2 \rightarrow 2\ Fe_2O_3 + 8\ SO_2$ $3\ FeS_2 + 8\ O_2 \rightarrow Fe_3O_4 + 6\ SO_2$	Roasting of pyrit concentrate at 650 - 800 ^{o}C in various furnaces, e.g. multiple - hearth furnace, rotary kiln, fluid bed roaster. The SO_2 content of the gases is generally 6 - 14 % and the O_2 - gas is zero.
regeneration of spent acid: $2\ H_2SO_4 \rightarrow 2\ SO_2 + 2H_2O + O_2$ $\Delta H = +\ 202$ kJ/mol	Destruction of used sulfuric acids by heat gas injection or injection in a hot gas stream or a moving bed of solids, such as coke, sand or ore
from sulfates: $CaSO_4 + C + ½\ O_2 \rightarrow CaO + SO_2 + CO$ $2\ FeSO_4 \rightarrow Fe_2O_3 + 2\ SO_2$	Modificated MÜLLER - KÜHNE - process Regeneration of pickling liquors or as a side product in the TiO_2 process via the sulfate route. Decomposition in a fluid - bed pyrite roasting furnace at 900^{o}C. The gases contain about 7 % by volume of sulfur dioxide.
combust. of S - containing comp.	Combustion at 800 – 1200^{o}C in a muffle furnace

Table 3-12: Processes for production of sulfur dioxide (SO_2) /3/

3.4.1.2 SO_2 - conversion to SO_3

The design and operation of a sulfuric acid plant are focused on the following gas phase chemical equilibrium reaction with a catalyst:

$$SO_2 + ½\ O_2 \rightarrow SO_3 \qquad \Delta H = +\ 99 \text{ kJ/mol}$$

This reaction is characterised by the conversion rate, which is defined as follows:

$$\text{conversion rate} = \frac{SO_2 \text{ in } - SO_2 \text{ out}}{SO_2 \text{ in}} \times 100\ \%$$

For SO_2/SO_3 systems, the following methods are available to maximise the formation of SO_3:

- heat removal with decreased temperature (exothermic process),
- increase of oxygen concentration,
- removal of SO_3 (as in the case of the double absorption process),
- raise of the system pressure,
- sufficient residence time,
- a selected catalyst to reduce the working temperature.

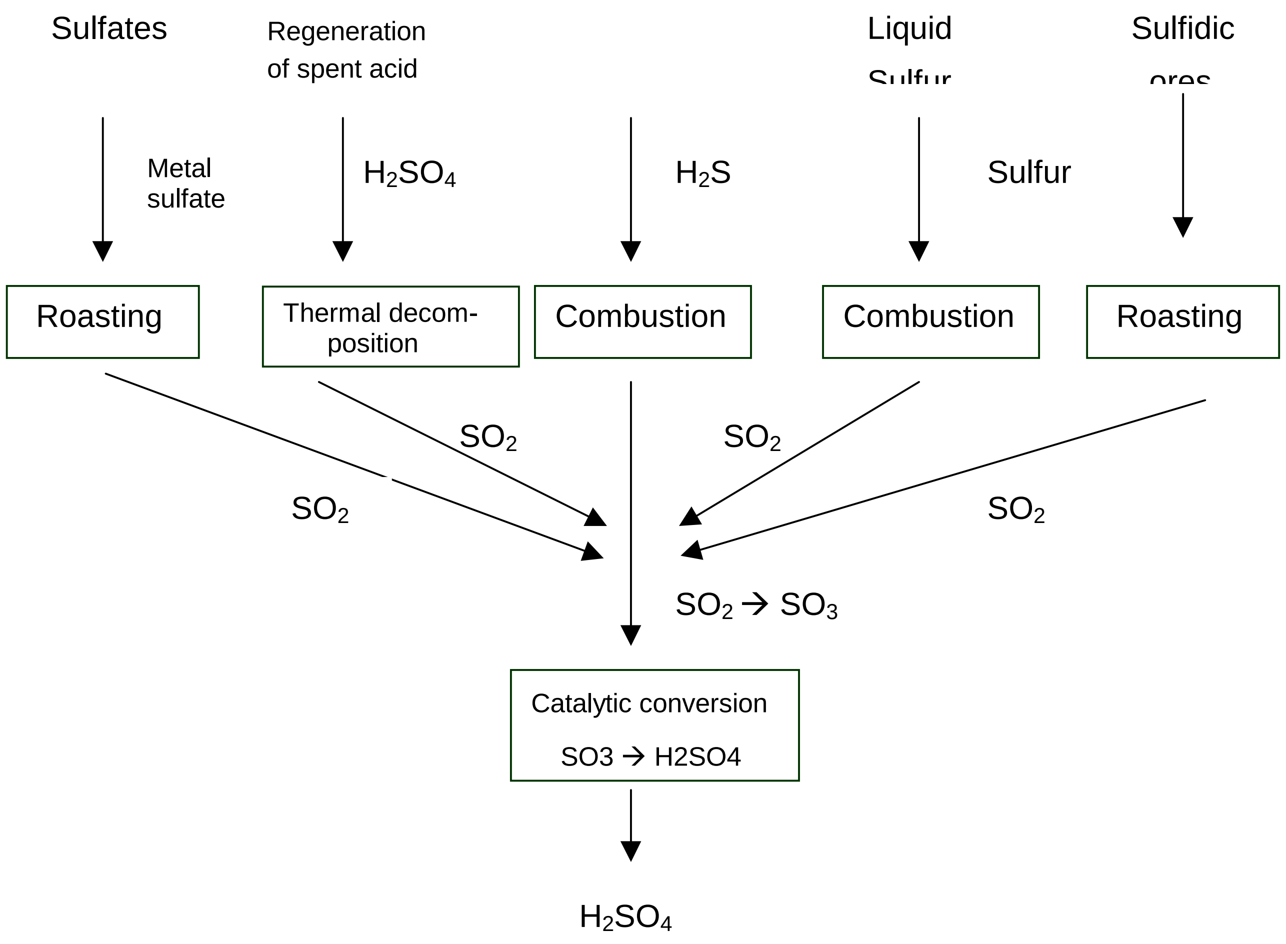

Abb. 5: Block diagram of SO_2 production from different raw materials

An optimal overall system behaviour requires a balance between reaction velocity and equilibrium. However, this optimum depends also on the SO_2 concentration in the raw gas and on its variability in time.

Different substances have been tested as catalysts for their catalytic activity toward sulfur dioxide oxidation. Vanadium compounds, platinium and iron oxide have been proven to be technically efficient. Vanadium pentoxide is used almost exclusively today. Ring (or star - ring) shaped catalysts, which are mostly used today, give a lower pressure drop and are less sensitive to dust blockage. There is a lower temperature limit at 410 - 430°C for conventional catalysts and 380 - 390°C for caesium doped catalysts. The upper temperature limit is 600 - 650°C. Above this limit catalytic activity decrease due to the reduction of the internal surface.

3.4.1.3 Absorption of SO_3 - H_2SO_4 - production

Sulfuric acid is obtained from the absoption of SO_3 and water into H_2SO_4 (with a concentration of at least 98 %).

The efficiency or the absorption step is related to:

- the H_2SO_4 concentration of the absorbing liquid (98,5 - 99,5 %),

- the temperature range of the liquid (normally 70°C - 120°C) and the temperature of the inlet gas,
- acid distribution technique,
- raw gas humidity (mist passes the absorption equipment),
- mist filter,
- the co - current or counter - current character of the gas stream in the absorbing liquid.

For production of sulfuric acid the following processes are used:

a) Single contact process,

The SO_2 - containing gases, which have been carefully cleaned and dried, are oxidised to sulfur trioxide in the presence of catalysts containing alkali and vanadium oxides. Sulfur trioxide is absorbed by concentrated sulfuric acid in absorbers, if necessary preceded by oleum absorbers. In these absorbers sulfur trioxide is converted to sulfuric acid by the water in the absorber acid. The absorber acid is kept at the desired concentration of approximately 99 % by wt. by adding water or diluted sulfuric acid. The single contact process is nowadays only used in new plants to process gases with low and widely varying SO_2 - contents.

b) Double contact process,

In the double contact process a primary conversion efficiency of 80 % to 93 %, depending on the arrangement of the contact beds and of contact time, is obtained in the primary contact stage of a converter preceding the intermediate absorber. After gas cooling to 190°C in a heat exchanger, the sulfur trioxide already formed is absorbed in the intermediate absorber by sulfuric acid with a concentration of 98,5 to 99,5 % by wt. The intermediate absorber is preceded by a oleum absorber if required. The absorption of the sulfur trioxide results in a considerable shift in the reaction eqilibrium towards the formation of SO_3, effecting considerably higher overall conversion efficiencies when the residual gas is passed through one or two secondary contact beds. Sulfur trioxide formed in the secondary stage is absorbed in the final absorber.

c) Pressure contact process,

Pressure contact processes have been developed in which the sulfur combustion, sulfur dioxide conversion and sulfur trioxide absorption stages are effected at elevated pressure. Several parameters can influence the conversion efficiency by modifying the chemical equilibrium. The oxidation of SO_2 is favoured by pressure in the conversion part only. The concept of operating a contact process under pressure is not new but so far, it has only been embodied in one industrial double - absorption plant (Fa. PCUK) in France with a capacity of 550 - 575 t/d H_2SO_4. The maximum pressure in this plant is 5 bar and it came into operation in 1972 first.

The advantages are listed below:

- position of chemical equilibrium in SO_2 more favourable, allowing a higher efficiency (99,8 - 99,85 %),
- small SO_2 - emissions (200 - 250 ppmv),
- smaller equipment,
- reduced investment cost by 10 - 17 % compared with the double contact process.

Disadvantages are:

- higher formation of NO by higher temperatures in the S - combustion furnace,
- higher demand for electric energy and lower steam export,
- higher demands for process safety.

Tailgas processes:

a) Wet contact process,

The process is not sensitive to the water balance and has been used to treat off - gas from a molybdenium smelter as well as being installed in two desulfurisation plants.

In this process the SO_2 - gases are converted at the contact to sulfuric acid without the need to dry the gas first. The formed SO_3 is converted to H_2SO_4 in the same gas phase immediately and condensed after that.

b) Process based on NO_x,

The Modified Lead Chamber Process is able to treat gases with a low content of SO_2 from 0,5 - 8 % as well as gases containing a mixture of SO_2 and NO. The process is a development of lead chamber technology in which nitrogen oxides are used to promote sulfuric acid production from sulfur dioxide directly, through the formation of the intermediate nitrosyl sulfuric acid. A disadvantage of this process is the low concentration of sulfuric acid with 75 - 80 %.

c) Hydrogen peroxide process.

Conversion of SO_2 to SO_3 can be achieved by the use of hydrogen peroxide. The conversion efficiency is higher than 99 % but the costs of hydrogen peroxides makes this an expensive process for sulfuric acid production. The energy demand for H_2O_2 production as a raw material for this process should be considered. The process leaves no waste and emissions.

d) Activated carbon process.

In the activated carbon process the SO_2 content of waste gases is adsorbed with activated carbon and converted with O_2 in a wet catalytic direct oxidation process to H_2SO_4. The catalytic reaction is performed after thermal regeneration of the activated carbon. The desorbed SO_2 is mixed with H_2O.

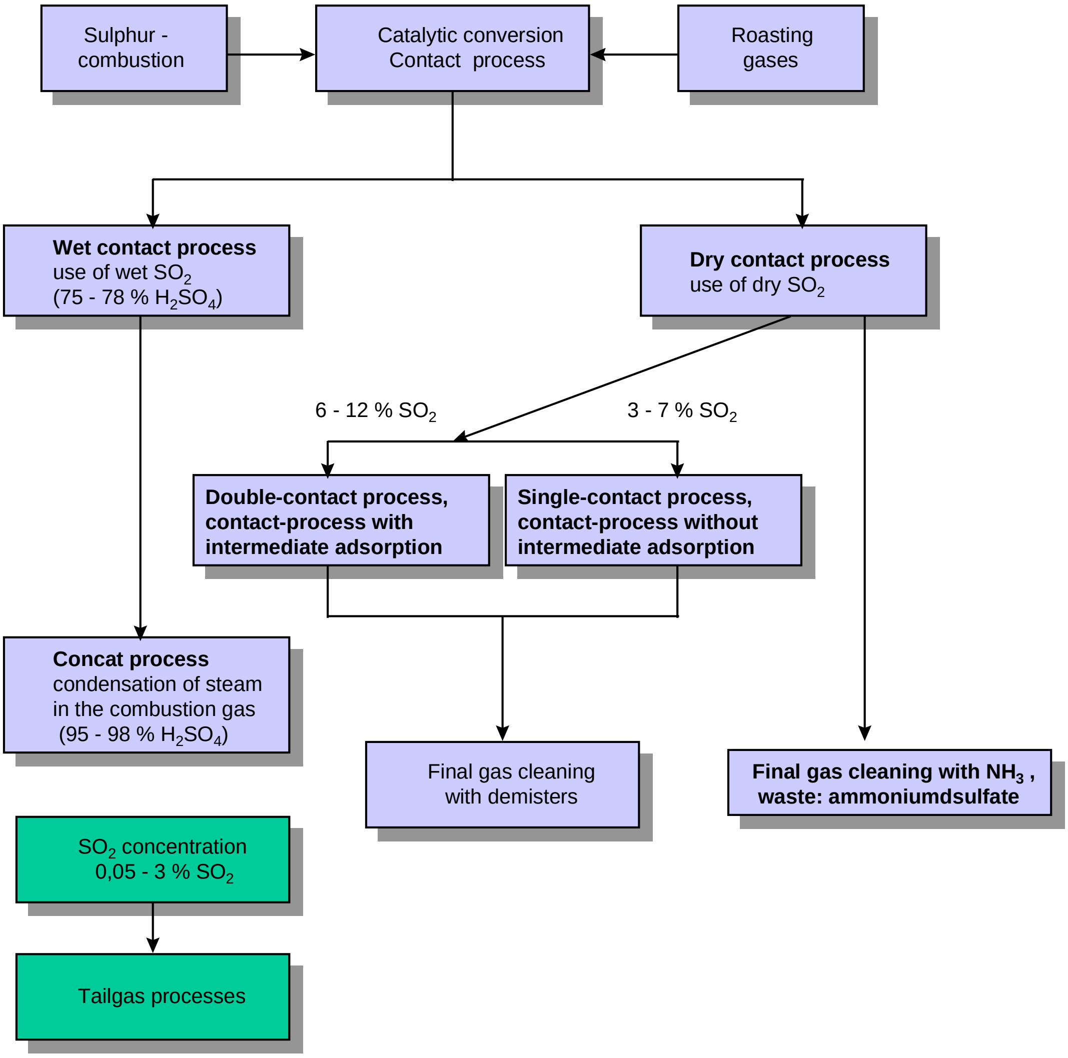

Abb. 6: Types of the contact process for production of sulfuric acid

3.4.2 Present consumption/emission levels

3.4.2.1 Input /3/

Raw materials:	Solid and liquid sulfur, pyrite and other metal sulfides, metal sulfates, used sulfuric acid or sulfur compounds. Most of the raw materials come from the desulfurisation of mineral oil and natural gas or from mining.
Auxiliary materials:	Commercial catalysts contain 4- 9 wt% vanadium pentoxide. V_2O_5 is combined with alkali - metal sulfate promoters. Potassium sulfate is used normally, but caesium sulfate has been used more and more in recent years. Life time of the catalyst is 10 years as a maximum. Service life is generally determined by catalyst losses during screening for dust removal.
Water:	Process water is needed for acid cooling and for adjusting the acid concentration after SO_3 - absorption. The amount of cooling water depend on the type of the heat exchange system. Closed circuits for cooling purpose are used. In some installations cooling is done by air. Additionally demineralized water is needed for steam production. Demineralization is performed by anion/cation - exchanger and water conditioning with ammonia or sodiumhydroxide, hydrazine or phosphates. Ca. < 95 % of water is used for steam production. The rest boiler water (alkaline in most cases) can

given after neutralization in the water drainment system. All fractions of uncontaminated water should be collected to supply the steam production system.

3.4.2.2 Output /3/

The production installation of the European sulfuric acid production industry is between 0,125 and 1,4 kt/d expressed as 100 % H_2SO_4. Most of the installations have a capacity between 0,3 bis 0,9 kt/d.

0,33 t S is needed for production of one t 100 % H_2SO_4. 1,2 t steam is produced, which can be used for steam export (ca. 1500 MJ/t).

Example for input/output - table of an individual H_2SO_4 - production plant on the basis of sulfur burning and an double absorption process in Germany/9/:

Input:	SO_2	9,5 - 11,5 %
	O_2	9,5 - 11,5 %
	CO_2	0 %
	Water	< 100 mg/m^3
Output:	Energy	3450 MJ net balance
	Emissions to air:	
	SO_2	1,4 - 1,8 kg SO_2/t 100 % H_2SO_4
	$H_2SO_4 + SO_3$	0,07 kg SO_3/t 100 % H_2SO_4
	NO_x	10 - 35 mg NO_2/Nm^3
	Emission to water:	no emissions
	Solid wastes:	120 g/t spent catalyst
	Conversion rate:	97,5 - 98,5 %
	Emissions with the final product:	
	As	< 0,01 ppm
	Hg	< 0,01 ppm
	Se	< 0,01 ppm
	F	< 0,01 ppm
	SO_2	< 20 ppm
	NO_x	< 30 ppm
	HCl	< 2 ppm
	organic carbon	< 5 ppm

3.4.2.3 Atmospheric emissions

The atmospheric emission are to be considered in the context of the whole production concept. According to information from local authorities atmospheric emissions should be not higher than:

0,1 kg SO_3/t H_2SO_4 and
5 kg SO_2/t H_2SO_4 .

The table below lists atmospheric emission data for different typs of H_2SO_4 - production plants:

Type of H_2SO_4 - production plant - SO_2 - source	Emission data	
Residual acids and salts from TiO_2 – production	SO_2	1588 g/t
	SO_3	210 g/t
Sulfur compounds	SO_2	1174 g/t
	SO_3	53 g/t
Residual acids and salts from TiO_2 – production	SO_2	855 g/t
	SO_3	56 g/t

Waste gas from a sinter plant	SO_2 SO_3	5362 g/t 17g/t
Zinc ores	SO_2 SO_3	2734 g/t 61 g/t
Pyrit, Sulfur	SO_2 SO_3 NO_x as NO_2 HCl HF	2617 g/t 31 g/t 9 g/t 5 g/t 3 g/t
SO_3 from Sulfur containing residuals and Sulfur burning	SO_2 H_2SO_4	78 g/t 94 g/t
	SO_2 SO_3	1524 g/t 80 g/t

Table 3-13: Atmospheric emission data for different individual typs of H_2SO_4 - production plants in Germany (source: local authorities)

Example for atmospheric emission data for an individual H_2SO_4 - production plant in Germany:

part a) Pyrit roasting. SO_3 formation by the separate double contact plant with intermediate absorption. Waste gases are released after the final absorber.

- pyrit roasting, process gas cleaning, contact process plant, absorption, sulfur combustion of c).

part b) Liquid sulfur combustion. SO_3 formation by the double contact process with intermediate ab sorption by the use of a V - containing catalyst. Waste gases are released after the final absorber.

- sulfur combustion, contact process plant, absorption.

part c) Liquid sulfur combustion and use of the contact part of a)

Capacity:	a)	250 t H_2SO_4 100 % /d
	b)	150 t H_2SO_4 100 % /d
	c)	100 t H_2SO_4 100 % /d
Conversion rate:	a) - c)	max. 99,6 %
Emission data SO_3:	a)	28 mg/m^3
	b)	35 mg/m^3
	c)	42 mg/m^3
Emission data SO_2:	a)	1450 mg/m^3
	b)	1450 mg/m^3
	c)	560 mg/m^3

The next table summarises data for new production plants, based on a O_2/SO_2 - ratio of 1,2.

	SO_2 in feed gas [%vol]	**conversion rate [daily ave.%]**	**SO_3 - emissions 1)**
Single contact (Waste gas vol.: 110x10^3 Nm^3/h, Kap.: 0,9 kt/d H_2SO_4)	6 - 10	98,5	0,4 kg/t (10-12 kg SO_2/t H_2SO_4)
	3 - 6	97,5 - 98,5	
Double contact (Waste gas vol.: 87x10^3 Nm^3/h, Kap.: 1 kt/d H_2SO_4)	6 - 12	99,7 2)4)	0,15 kg/t (2-3 kg SO_2/t H_2SO_4)
Tailgas processes			
Wet contact process	0,05 - 7	98,0	< 10 ppmv
NO_x based process	0,5 - 8	nearly 100 3)	no data

H_2O_2 – process		> 99,0	very low

[1] SO_3 + H_2SO_4 expressed as SO_3 [2] when sulfur is burned [3] emissions of NO_x possible [4] According to BREF „Non-ferrous metals industry“

Table 3-14: Output/input - and emission data for pure production of sulfuric acid according to industry information /3/

3.4.2.4 Solid wastes

Solid wastes are from packing / lining and spent V - Catalysts, which are recycled. The vanadium (or other metal) content can be reclaimed for further use. The arsenic content has to be as low as possible for recycling demands. The metal is removed as vanadium salts or as ferrovanadium for steel production.

Large quantities of solid products can be caused, if SO_2 - production does not operate on the base of sulfur combustion.

3.4.2.5 Waste water

The table below lists waste water emission data for different individual typs of H_2SO_4 - production plants:

Typ of H_2SO_4 - production plant - SO_2 - source	**Emission data (data from raw water)**			
Residual acids and salts from TiO_2 – production	Sulfate:	2910 g/t	CSB:	445 g/t
	Fe:	23 g/t	Cr:	no information
	Pb:	0,1 g/t	Zn:	no information
	As:	no information	Cu:	0,16 g/t
	Ni:	no information	Hg:	0,002 g/t
	Cd:	no information		
Residual acids and salts from TiO_2 – production	Sulfate:	2380 g/t	CSB:	19 g/t
	Fe:	90 g/t	Cr:	0,38 g/t
	Pb:	0,38 g/t	Zn:	1 g/t
	As:	0,24 g/t	Cu:	0,1 g/t
	Ni:	0,05 g/t	Hg:	0,02 g/t
	Cd:	0,005 g/t		
Müller - Kühne - process on the basis of thermal recycling of spent sulfuric acid	Sulfate:	no information	CSB:	48.960 kg/a
	N_{ges}:	18.000 kg/a	Fe:	no information
	Cr:	360 kg/a	Pb:	2.880 kg/a
	Zn:	8.640 kg/a	As:	no information
	Cu:	173 kg/a	Ni:	187 kg/a
	Hg:	26 kg/t	Cd:	173 kg/a

Table 3-15: Waste water emission data for different individual typs of H_2SO_4 - production plants in Germany (source: local authorities)

3.5 Nitric acid (HNO_3)

3.5.1 Applied processes and techniques

HNO_3 production proceeds over two process steps:

a) **Oxidation** of NH_3 to NO and
b) **Conversion** of NO to NO_2 and **absorption in / reaction** with H_2O.

The detailed information about the process is described below:

3.5.1.1 Catalytic oxidation of ammonia

A mixture of ammonia and air at an ammonia to air ratio of 1:9 is oxidised in the presence of a platinum catalyst alloyed with rhodium and/or palladium at a temperature between 800 and 950 ^{o}C. The related reaction, according to the 'Ostwald'-process, is:

$$4\ NH_3 + 5\ O_2 \rightarrow 4\ NO + 6\ H_2O$$

Simultaneously, nitrogen, nitrogen oxide and water are formed by the following undesired sidereactions:

$$4\ NH_3 + 3\ O_2 \rightarrow 2\ N_2 + 6\ H_2O$$

$$4\ NH_3 + 4\ O_2 \rightarrow 2\ N_2O + 6\ H_2O$$

All three ammonia oxidation reactions are exothermal and heat may be recovered to produce steam for the process and for export to other plants and/or to preheat the tail gas. The reaction water is condensated in a cooler - condenser during the cooling of the reaction gases and led to the absorption column.

The catalyst consists of several knitted or woven gauzes, containing approximately 90 % platinum, alloyed with rhodium for greater strength and sometimes with palladium. Air pollution and contamination from ammonia can poison the catalyst. Poisoning as well as poor ammonia/air mixing and poor gas distribution across the catalyst may reduce the nitric monoxide yield by about 10 %. During the reaction, some of the platinum and rhodium from the catalyst vaporises and a platinum recovery system is installed below the catalyst in most cases. Such a system call recover 60 to 80 % of the catalyst loss.

3.5.1.2 Oxidation of nitrogen monoxide

Nitrogen oxide reacts to nitrogen dioxide according to the following equation:

$$2\ NO + O_2 \rightarrow 2\ NO_2$$

Nitrogen dioxide dimerises to form an equilibrium mixture with the liquid dinitrogen tetroxide:

$$2\ NO_2 \rightarrow N_2O_4$$

The reaction is exothermal and the conversion of NO to NO_2 increases with falling temperature. Hence, the reaction will not be near completion until the waste gas enters the absorption section.

3.5.1.3 Absorption process

The mixture of nitrogen dioxide with its dimer is pumped into the bottom of the absorption tower. Water produced by ammonia oxidation (according to reactions 1 to 3) is condensed in the cooler - condenser, forming a weak acid by the absorption of present nitrogen dioxide, and is then transferred to the absorption column, in which it flows counter-currently to the NO_2/N_2O_4 gas mixture. The absorption of nitrogen dioxide in water takes place according to the following reaction:

$$3\ NO_2 + H_2O \rightarrow 2\ HNO_3 + NO$$

This reaction is exothermal and the heat released necessitates continuous cooling of the acid within the absorber. Furthermore, nitrogen monoxide is formed. A secondary air stream is introduced into the column which oxidises NO and removes also NO_2 from the product. Modem counter - flow absorption towers use high efficiency tray designs with the spacing between the trays progressively increasing towards the top of the tower to allow for the increasing contact times necessary to oxidise NO to NO_2. Many of the trays are equipped with internal cooling coils for removing the heat of reaction from the absorption of NO_2.

Low pressure at the ammonia oxidation stage slightly favours more efficient NO production while high pressure in the absorption stage favours the oxidation of NO to NO_2 and the absorption of NO_2 in water. The design of nitric acid production plants has therefore met these conflicting requirements by developing along two separate lines: single pressure or dual pressure operation.

Three pressure ranges can be distinguished:

low pressure (N)	< 1,7 bar	810 – 850 ^oC	97 % NO
medium pressure (M)	1,7 – 6,5 bar	850 – 900 ^oC	96 % NO
high pressure (H)	6,5 – 13 bar	900 – 940 ^oC	95 % NO

Basing on these pressure ranges single pressure – and dual pressure installations referring both process steps are used /5/.

The types installed in Europe are listed below:

single pressure – M/M	22 installations	existing installations
single pressure – H/H	11 installations	new installations
dual pressure – L/M	9 installations	existing installations
dual pressure – L/H	1 installations	existing installations
dual pressure – M/H	36 installations	new installations.

The typical installation has a capacity of 1 kt/d. Emission data do not depend on the capacity generally.

In the mentioned installations nitric acid is produced with concentrations of 50 – 70 % (weak acid). Higher concentrated acids are produced in so - called Hoko – plants or indirectly with drying agents. The chapter describes the production of weak acid.

3.5.2 Present consumption/emission levels/4/

3.5.2.1 Atmospheric emissions

The major emission sources of NO_x - emissions are listed in the table below.

Production process	Major emission source
Medium concentration nitric source	Absorption column
High concentration nitric acid:	
- Extractive distillation using H_2SO_4	Final tower
- Distillation of superazeotropic acid	Weak acid absorption column

Table 3-16: The major emission sources of NO_x - emissions in different types of nitric acid production processes /secondary source from /8/

Most emissions are released with waste gases. The main contaminants are NO_X and N_2O.

NO_X	100 to 2000 ppmv (200 - 4000 mg/m^3)

In Germany emission concentration levels down to 160 mg/m^3 NO or NO_2 can be reached.

N_2O	300 to 3500 ppmv (600 - 7000 mg/m^3)
O_2	1 to 4 vol%
H_2O	0,3 to 0,7 vol%
N_2	equlibrium
conversion rate	3130 to 3300 Nm^3/t 100% HNO_3 3925 to 4180 kg/t 100% HNO_3

Emissions are influenced by process parameters significantly. NO_X - emission concentrations are much lower in efficient installations, working with high pressure compared with medium pressure in the absorption step.

The following parameters contribute to decrease the NO_x - emissions:

- sufficient air supply to the oxidiser and absorber,
- high pressure, especially in the absorber,
- low temperatures in the cooler/condenser and absorber,
- operation at optimum throughput rates,
- as most as little faulty equipment such as compressores and pumps for reduction of diffuse emissions.

The minimum emission levels currently achieved in a modern plant without added pollution abatement are:

for medium pressure absorption:	1000 - 2000 ppmv
for high pressure absorption:	100 - 200 ppmv

Best available technique are installations with emission levels not higher than 200 mg/m^3 NO_x. This emission standard can be reached by

- high pressure plants with absorption pressures above 80 000 Pa or
- medium pressure plants with SCR.

When SCR is used as waste gas reduction measure, up to 30 ppmv NH_3 may slip through and occur in the off - gas.

NSCR as NO_x - abatement can not be defined as BAT in the case of using hydrocarbons as reduction agents because of hydrocarbon - emissions. When using NSCR the emission of hydrocarbons can be higher as 4000 ppmv (total carbon) in the case of using hydrocarbons as reduction agents.

A start - up will lead to higher NO_x - emissions in the range of 200 to 1000 kg. Closing down will lead to NO_x - emissions of ca. 50 bis 100 kg.

Transient conditions will occur ca. 2 to 4 times per year for replacement of the catalyst and 0 to 6 times per year due to malfunktioning or unforeseen breakdown of the plant. The NO_x - emissions from transient conditions can therefore be estimated between 0,5 (minimum) and 11 (maximum) tons per year.

The table below lists atmospheric emission data for individual HNO_3 - production plants working on the basis of ammonia combustion:

No. of the production plant	Emission data
1	NO: 307 g/t NO_2 33 g/t NO_x (as NO_2) 1 g/t NH_3 2 g/t
2	NO_2 413 g/t HNO_3 19 g/t NH_3 3 g/t
3	NO_2 1100 g/t NH_3 136 g/t
4 part of a aniline - production plant **Input:** 180 kg NH_3 for production of 1000 kg HNO_3 (65%) **Capacity:** 150 kt/a (0,4 kt/d)	**Emission reduction measure:** selective catalytic reduction (SCR) **Emission data:** 15 - 75 mg NO_x /m^3 (1/2 h-average)

Table 3-17: Atmospheric emission data for individual HNO_3 - production plants working on the basis of ammonia combustion in Germany (source: local authorities)

N_2O – emissions are between 600 – 1500 ppm. Selective catalysts for the reduction of N_2O have already been developed for the waste gases of adipic acid production and for fluidized bed combustion. However, these catalysts are developed for temperature conditions between 400°C to 600°C. These temperature are reached following from the burning of higher N_2O - concentrations in the waste gas in adipic acid production. When applying these catalysts in nitric acid production, much energy is needed to pre - heat the waste gas to the temperatures needed. Desirable would be to develop a low - temperature selective catalyst for the reduction of N_2O at nitric acid plants. It is estimated that such a catalyst might be developed.

Another option for N_2O reduction has been installed in an reference plant of the Hydro Agri Europe in Norway. By application of an expended reaction chamber a N_2O reduction of at least 85 % to about 400 mg/m^3 were reached. This option is described as a most suitable concept for new plants. /4/

3.5.2.2 Waste water

A single data from a HNO_3 production plant in Germany was given with < 500 g NO_3-N /t NH_3 (before biological treatment) by local authorities.

Waste water emissions does not appear continuously. Water present in the liquid ammonia (typically) 0,5 %) concentrates in the ammonia vaporiser and periodic blow - down generates a small gaseous ammonia release.

The resulting sodium nitrite - nitrate solution in the case of wet scrubbing from the neutralisation reaction is a liquid effluent and may present a disposal problem. Therefore, this NO_x - emission reduction option is only attractive if the effluent can either be of any further use or eliminated without causing subsequent environmental pollution.

3.5.2.3 Solid wastes

Solid wastes are used catalysts

In the case of emission reduction with molecular sieve adsorption a solid waste is generated via the deactivated molecular sieves, which have to undergo disposal.

3.5.2.4 Energy

Energy production of a dual pressure nitric acid plant is estimated at 1,7 GJ/t 100% HNO_3. This includes (40 bar) steam production of 2,4 GJ/t 100% HNO_3 and an electricity consumption of 31 kWh/t 100% HNO_3.

Electricity is consumed mainly by the compressors, turbines and pumps. The electricity consumption depends on the type of plant, the dimensions and properties of the absorption column and the presence and type of NO_x - abatement.

3.5.3 Reduction Measures for waste gas treatment

The following text refers different emission reduction measures available for nitric acid production /8/.

Primary Emission Reduction Measures

Extended Absorption

The primary NO_x-abatement technique which can be applied to both medium and high concentration nitric acid plants is extended absorption.

Reduction of nitrogen oxides can be achieved either by increasing the efficiency of the existing process by extending the height of an existing absorption tower or by adding a further absorption tower in series with the existing unit. As a consequence, both the oxidation volume and the number of trays are increased, leading to a larger amount of NO_x being recovered as nitric acid and subsequently reducing the emission levels.

In the case of an additional absorption tower, the tail gas from the first tower is routed to the base of the second tower and flows counter-currently to a chilled process water feed to form weak nitric acid. This weak acid is then cycled to the upper trays of the first tower, absorbing the rising NO, gases from the ammonia oxidation stage and producing the product acid at the tower bottom. In order to minimise the size of the additional absorption tower, the inlet gas requires to be pressurised with additional refrigeration cooling provided for the liquid on the trays. Extended absorption offers an attractive method of meeting NOx - emission limit values (500 g/Mg nitric acid (100 % acid) may be achieved), but may require considerable integration with heat and power recovery in order to achieve a satisfactory operating efficiency.

Economic aspekts

Currently, no information is available as regards the costs for an additional absorption tower. In the case of retrofit, cost data can hardly be given in general terms, as the necessary modifications are very plant - specific.

Secondary Emission Reduction Measures

For both medium and high concentration nitric acid, two waste gas cleaning techniques are in use in the nitric acid production sector: selective and non-selective catalytic reduction. Two further alternatives,. seldom implemented, are molecular sieve adsorption and wet scrubbing

Selective Catalytic Reduction (SCR)

The reducing agent, ammonia, is injected into the tail gas from the absorption tower, where it reacts with the nitrogen oxides in the presence of a catalyst to form water and molecular nitrogen. Catalysts commonly used are vanadium pentoxide, platinum. iron/chromium oxide mixtures or zeolites. The inlet temperature of the waste gas depends on the catalyst applied and is generally around 200 ^{o}C. The operating pressure has only a minor effect on the overall efficiency. For efficient NO_x-abatement, an excess amount of ammonia may sometimes be necessary, depending on catalyst type (e. g. for catalysts other than zeolithes). The excess ranges from 5 - 50 % beyond the stoichiometric equilibrium, depending on the catalyst and other process conditions. NO_x emissions of less than 100 g/Mg nitric acid are achievable.

The permanent availability of ammonia at a nitric acid production plant makes the SCR technology particularly attractive. Currently, the SCR technology is applied at three plants in the Netherlands, four plants in Sweden, fifteen plants in France, as well as at plants in Germany, and UK.

Economic Aspects

Investments are reported ranging between 770,000 and 3 million E for retrofitting an installation with a production capacity of 1,000 Mg/d nitric acid with a SCR unit. The investments for an integrated SCR unit for a new 1,000 Mg/d plant are estimated to be much lower: around 0.5 million E.

Associated operating costs include costs incurred by ammonia consumption, steam consumption, electricity consumption, catalyst replacement, maintenance and repair, insurance and taxes, and eventually personnel, administration and catalyst disposal.

Non-Selective Catalytic Reduction (NSCR)

Here, the waste gas is mixed with a reducing agent, which can be hydrogen and/or hydrocarbons, e.g. natural gas, waste gas from ammonia plants or naphta, but they must be free of sulphur to avoid premature deactivation of the catalyst. Hydrogen has the advantage of operating at a significantly lower temperature than methane or other hydrocarbons, and cannot introduce CO or hydrocarbons into the tail gas as hydrocarbons do. The fuel gas is injected into the tail gas and this homogenised mixture is then passed onto a catalyst. The composition and form of the catalyst are relevant parameters as regards operation flexibility, abatement efficiency, efficiency of fuel combustion, and catalyst lifetime. Currently, honeycomb-based systems are widely used, because they show a high activity, a low pressure drop and a satisfying lifetime. The activity of the catalyst is particularly important when methane is used as reducing fuel, since the methane molecule is very stable and difficult to oxidise. Platinum has a high stability combined with a satisfying activity and also under reducing conditions do's 'lot cause carbon formation, which may occur with palladium-based systems.

An excess of fuel is necessary to ensure reducing conditions. The gas leaving the catalyst reactor consists predominantly of nitrogen gas and water vapour and contains reduced concentrations of nitrogen oxides and oxygen; this hot gas leaving the system at a temperature up to 750 'C can be used to generate steam. NO_x emissions of 500 g/Mg nitric acid are achievable, and in the Netherlands NO_x emission values below 205 mg/m^3 (100 ppmv) are achieved at a plant with a medium pressure absorption unit. However, in the case of hydrocarbons as reducing agents this option cannot be considered as best available technology, since the mixture of various by-products is emitted.

When hydrocarbons are used as reducing agent, the waste gas may contain carbon monoxide as well as hydrocarbons in a non-converted or partially converted state. These by-products have to be removed. Besides NO_x also N_20 produced in the catalytic ammonia oxidation reactor can be significantly reduced (typically by 70 %).

Molecular Sieve Adsorption

The tail gas is brought into contact with an active molecular sieve, which catalytically oxidises NO to NO_2 and selectively absorbs NO_2. Afterwards, NO_2 is thermally stripped from the molecular sieve and returned to the absorber. A drawback of this denitrification technique is related to the fouling potential of the sieve bed.

In the USA, this NO_x - removal technique has found successful application in existing plants. However, for new plants, this option is usually not applied, as investment and energy costs are relatively high. In Europe, this technique is still under development and currently there is no commercial application of this technique at nitric acid plants.

Wet Scrubbing (Neutralisation with Sodium Hydroxide Solution)

Wet scrubbing means waste gas treatment with an aqueous solution of alkalihydroxides or -carbonates, ammonia, urea, potassium permanganate, or caustic chemicals. The nitrogen oxides (NO and NO_2) are absorbed, and formation of sodium nitrite ($NaNO_2$) is observed when sodium hydroxide is used.

This technique is able to achieve a 65 % - reduction, providing the pressure is in excess of $4{,}5\ 10^5$ Pa and the molar ratio of NO/NO_2 is close to unity; however, this technique cannot meet stringent emission limits on its own.

3.6 Fluorine hydrogen (HF)

3.6.1 Applied processes and techniques

The production of fluorine hydrogen is done on the basis of calcium fluoride with sulfuric acid following the main reaction

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2\,HF$$

and include the following process steps:

a) CaF_2 – drying,
b) transport of CaF_2,
 c) calcination
  or alternatively
 c) pre - reaction of CaF_2 with H_2SO_4 and Oleum in a pre - reactor (100 - 150°C),
d) main reaction of CaF_2 with H_2SO_4 under formation of HF in a rotating furnace (200 - 250 °C),
e) washing of reaction gases with H_2SO_4 for separation of high boiling components (H_2SO_4 + HF are given back to the rotating furnace),
f) HF - condensation,
g) waste gas washing (SiF_4 is washed with diluted HF to form H_2SiF_6 , which can be further used for other purposes such as production of cryolith),
h) HF – atmospheric distillation for separation of other gases (residuals of the distillation process are given back to the rotating furnace),
i) final condensation and packaging (storing under normal pressure and temperature)

3.6.2 Present consumption/emission levels

3.6.2.1 Atmospheric emissions

Possible emissions are HF, SO_2 SiF_4 and dust.
Waste gas abatement techniques are used:

a) filtration of CaF_2 – dust,
b) scrubbing with H_2SO_4 for HF - seperation,
c) scrubbing with H_2O for HF and SiF_4 – separation,
d) alkaline scrubbing for fine cleaning of the waste gas.

As a main point should be mentioned, that all parts of the production line should be under slight vacuum to prevent diffuse HF - emissions.

Most important are atmospheric emissions (yearly average values). Waste gas components are listed below and according to information from local authorities atmospheric emissions are not higher than:

HF (as F)	< 5 mg/m^3	5 g HF/t HF
SO_2	20 mg/m^3	17 g SO_2/t HF
Dust	5 mg/m^3	70 g dust/t HF

SO_2- Emissions are much higher if water scrubbing is used for waste gas abatement only, which is the case in different European plants. With fine gas cleaning by alkaline scubbing the mentioned values can be reached.
The table below lists atmospheric emission data for individual HF - production plants:

No. of the production plant	Emission data

1	SO_2 :	10 g/t
	NO:	325 g/t
	NO_2 :	56 g/t
	CO	54 g/t
	HF:	2 g/t
2	SO_2 :	7 g/t
	HF:	5 g/t
4	SO_2 :	17 g/t
	HF :	2 g/t

Table 3-18: Atmospheric emission data for individual HF - production plants in Germany (source: local authorities)

3.6.2.2 Waste water

There is no waste water in HF production itself, but waste water results from waste gas treatment behind the different parts of the HF – production. The contaminants of these waste water include inorganic components only, no organics. Waste water cleaning steps include usually:

a) neutralisation with lime,
b) addition of coagulation agents,
c) sedimentation,
d) filtration.

3.6.2.3 Solid wastes

The main solid waste is $CaSO_4$. This can be further used as a market product in cement industries or as binders for floor screed. This use reduces the amount of waste for disposal. Further wastes are SiO_2 and CaF_2 from waste water treatment. H_2SiF_6 may be used for other purposes such as cryolith – production.

Residuals from the HF – washing with H_2SO_4 and the bottom from HF - distillation are given back to the main reactor.

4 References

/1/ Summary of Draft Final BAT Reference Document on Ammonia Production with Commission Conclusion (24. – 25.09.96)

/2/ BAT für Pollution Prevention and Control in the European Fertilizer Industry Production of Ammonia (EFMA, 1995)

/3/ BAT für Pollution Prevention and Control in the European Fertilizer Production of Sulphuric Acid (EFMA, 1995)

/4/ Dutch Notes on best Available Techniques for Pollution Prevention and Control in the Production of Nitric Acid (VROM 9/95)

/5/ BAT für Pollution Prevention and Control in the European Fertilizer Industry Production of Nitric Acid (EFMA, 1995)

/6/ Ullmanns Enzyklopädie der technischen Chemie, 4. Neubearbeitete Auflage, Bd. 18, S. 275 ff.

/7/ T. A. Ryan; C. Ryan, E. A. Seddon and K. R. Seddon „Phosgene and related carbonyl halides“, Elsvier, 1996, p. 169.

/8/ O.Rentz, S. Nunge, M. Leforsch, T. Holtmann, „Tchenical background document for the actualisation and assessment of UN/ECE protocols related to the abatement to the transboundary transport of nirtogen oxides from stationary sources“, Karlsruhe, 1999

/9/ Information from chemical industry

/10/ Ullmanns Enzyclopedia, Vol. A 7, p. 218 f.

/11/ Ullmanns Enzyclopedia, Vol. A 19, p . 416 f.