Best Available Techniques
for Pollution Prevention and Control
in the European Fertilizer Industry

Booklet No. 1 of 8:

PRODUCTION OF AMMONIA

2000

EFMA
European Fertilizer Manufacturers' Association

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Best Available Techniques
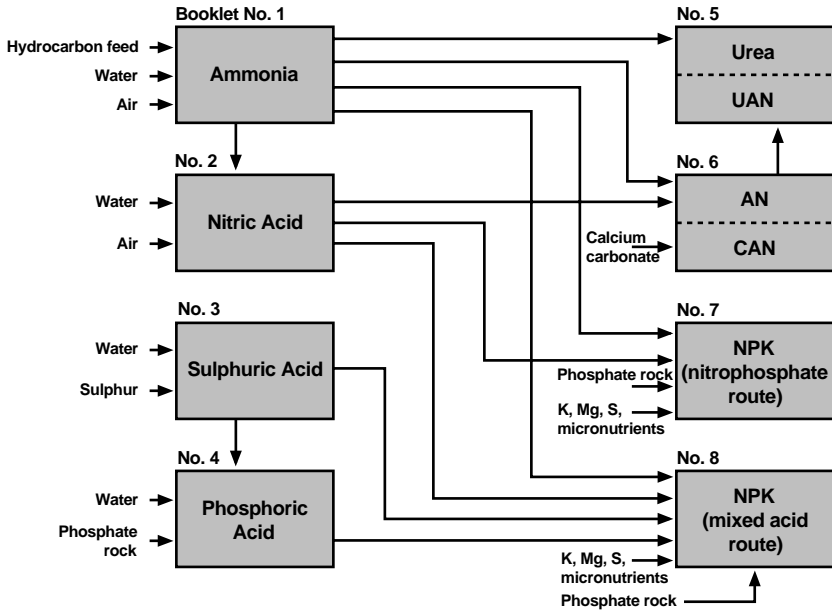for Pollution Prevention and Control
in the European Fertilizer Industry

Booklet No. 1 of 8:

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EFMA's BAT Booklets

Booklet No. 1

Hydrocarbon feed →
Water →
Air →
Ammonia

No. 2

Water →
Air →
Nitric Acid

No. 3

Water →
Sulphur →
Sulphuric Acid

No. 4

Water →
Phosphate rock →
Phosphoric Acid

No. 5

Urea
- - - - -
UAN

No. 6

AN
- - - - -
CAN

Calcium carbonate →

No. 7

NPK (nitrophosphate route)

Phosphate rock →
K, Mg, S, micronutrients →

No. 8

NPK (mixed acid route)

K, Mg, S, micronutrients →
Phosphate rock →

CONTENTS

PREFACE

In 1995, the European Fertilizer Manufacturers Association (EFMA) prepared eight Booklets on Best Available Techniques (BAT) in response to the proposed EU Directive on integrated pollution prevention and control (IPPC Directive). These booklets were reviewed and updated in 1999 by EFMA experts drawn from member companies. They cover the production processes of the following products:-

No. 1 Ammonia

No. 2 Nitric Acid

No. 3 Sulphuric Acid
(updated in collaboration with ESA)

No. 4 Phosphoric Acid

No. 5 Urea and Urea Ammonium Nitrate (UAN)

No. 6 Ammonium Nitrate (AN) and Calcium Ammonium Nitrate (CAN)

No. 7 NPK Compound Fertilizers by the Nitrophosphate Route

No. 8 NPK Compound Fertilizers by the Mixed Acid Route

The Booklets reflect industry perceptions of what techniques are generally considered to be feasible and present achievable emission levels associated with the manufacturing of the products listed above. The Booklets do not aim to create an exhaustive list of BAT but they highlight those most widely used and accepted. They have been prepared in order to share knowledge about BAT between the fertilizer manufacturers, as well as with the regulatory authorities.

The Booklets use the same definition of BAT as that given in the IPPC Directive 96/61 EC of 1996. BAT covers both the technology used and the management practices necessary to operate a plant efficiently and safely. The EFMA Booklets focus primarily on the technological processes, since good management is considered to be independent of the process route. The industry recognises, however, that good operational practices are vital for effective environmental management and that the principles of Responsible Care should be adhered to by all companies in the fertilizer business.

The Booklets give two sets of BAT emission levels:-
– For existing production units where pollution prevention is usually obtained by revamps or end-of-pipe solutions
– For new plants where pollution prevention is integrated in the process design

The emission levels refer to emissions during normal operations of typical sized plants. Other levels may be more appropriate for smaller or larger units and higher emissions may occur in start-up and shut-down operations and in emergencies.

Only the more significant types of emissions are covered and the emission levels given in the Booklets do not include fugitive emissions and emissions due to rainwater. Furthermore, the Booklets do not cover noise, heat emissions and visual impacts.

The emission levels are given both in concentration values (ppm, $mg.m^{-3}$ or $mg.l^{-1}$) and in load values (emission per tonne of product). It should be noted that there is not necessarily a direct link between the concentration values and the load values. EFMA recommends that the given emission levels should be used as reference levels for the establishment of regulatory authorisations. Deviations should be allowed as governed by:-

– **Local environmental requirements**, given that the global and inter-regional environments are not adversely affected
– **Practicalities and costs of achieving BAT**
– **Production constraints** given by product range, energy source and availability of raw materials

If authorisation is given to exceed these BAT emission levels, the reasons for the deviation should be documented locally.

Existing plants should be given ample time to comply with BAT emission levels and care should be taken to reflect the technological differences between new and existing plants when issuing regulatory authorisations, as discussed in these BAT Booklets.

A wide variety of methods exist for monitoring emissions. The Booklets provide examples of methods currently available. The emission levels given in the Booklets are subject to some variance, depending on the method chosen and the precision of the analysis. It is important when issuing regulatory authorisations, to identify the monitoring method(s) to be applied. Differences in national practices may give rise to differing results as the methods are not internationally standardised. The given emission levels should not, therefore, be considered as absolute but as references which are independent of the methods used.

EFMA would also advocate a further development for the authorisation of fertilizer plants. The plants can be complex, with the integration of several production processes and they can be located close to other industries. Thus there should be a shift away from authorisation governed by concentration values of single point emission sources. It would be better to define maximum allowable load values from an entire operation, eg from a total site area. However, this implies that emissions from single units should be allowed to exceed the values in the BAT Booklets, provided that the total load from the whole complex is comparable with that which can be deduced from the BAT Booklets. This approach will enable plant management to find the most cost-effective environmental solutions and would be to the benefit of our common environment.

Finally, it should be emphasised that each individual member company of EFMA is responsible for deciding how to apply the guiding principles of the Booklets.

Brussels, April 2000

DEFINITIONS

The following definitions are taken from Council directive 96/61/EC of 1996 on Integrated Pollution Prevention and Control:-

"Best Available Techniques" mean the most effective and advanced stage in the development of activities and their methods of operation which indicate the practical suitability of particular techniques for providing, in principle, the basis for emission limit values designed to prevent or, where that is not practicable, generally to reduce emissions and the impact on the environment as a whole:-

"Techniques" include both the technology used and the way in which the installation is designed, built, maintained, operated and decommissioned.

"Available" techniques mean those developed on a scale which allows implementation in the relevant industrial sector under economically viable conditions, taking into consideration the costs and advantages, whether or not the techniques are used or produced inside the Member State in question, as long as they are reasonably accessible to the operator.

"Best" means most effective in achieving a high general level of protection for the environment as a whole.

1. INTRODUCTION

This Booklet covers Best Available Techniques (BAT) for ammonia production, storage, and transfer. The description is partly based on Reference [1].

Ammonia is produced basically from water, air, and energy. The energy source is usually hydrocarbons, thus providing hydrogen as well, but may also be coal or electricity. Steam reforming of light hydrocarbons is the most efficient route, with about 77% of world ammonia capacity being based on natural gas [2].

The total energy consumption for the production of ammonia in a modern steam reforming plant is 40-50% above the thermodynamic minimum. More than half of the excess consumption is due to compression losses. The practical minimum consumption is assumed to be about 130% of the theoretical minimum.

The typical size of a large single-train ammonia plant is 1,000-1,500t.d^{-1}, although capacities of 1,800t.d^{-1} and above are not uncommon for new plants. In this Booklet 1,500t.d^{-1} (500,000t.y^{-1}) will be considered as a standard capacity. The process and energy systems are integrated to improve overall energy efficiency. Further, the ammonia plant may stand alone or be integrated with other plants on the site, eg. a urea plant, but such integration is not covered in this Booklet.

Plant battery limits are generally feedstock and fuel supply by pipelines at sufficient pressure for reforming; untreated water and air; and ammonia product stored as liquid, either refrigerated at atmospheric pressure or non-refrigerated at ambient temperature. In the case of steam and/or carbon dioxide export those battery limit conditions will depend on the receiver's requirements.

The equipment and machinery used in today's large ammonia plants have achieved high reliabilities and technical on-stream factors in excess of 90% are common.

2. DESCRIPTION OF PRODUCTION PROCESSES

2.1 Production Processes in Operation in Europe

Two main types of production process for ammonia synthesis gas are currently in operation in Europe:-

- Steam reforming of natural gas or other light hydrocarbons (Natural Gas Liquids, Liquefied Petroleum Gas, Naphtha)
- Partial oxidation of heavy fuel oil or vacuum residue

In at least one partial oxidation unit, natural gas is used as feedstock. Coal gasification and water electrolysis are no longer in use in the European ammonia industry.

The ammonia synthesis process is principally independent of the type of synthesis gas production process, but synthesis gas quality influences the loop design and operating conditions.

A block diagram of the conventional steam reforming process is shown in Figure 1. (In some cases, a separate auxiliary boiler is required). About 85% of world ammonia production is based on steam reforming concepts [3]. A process description is given in 2.2.1.

Natural gas

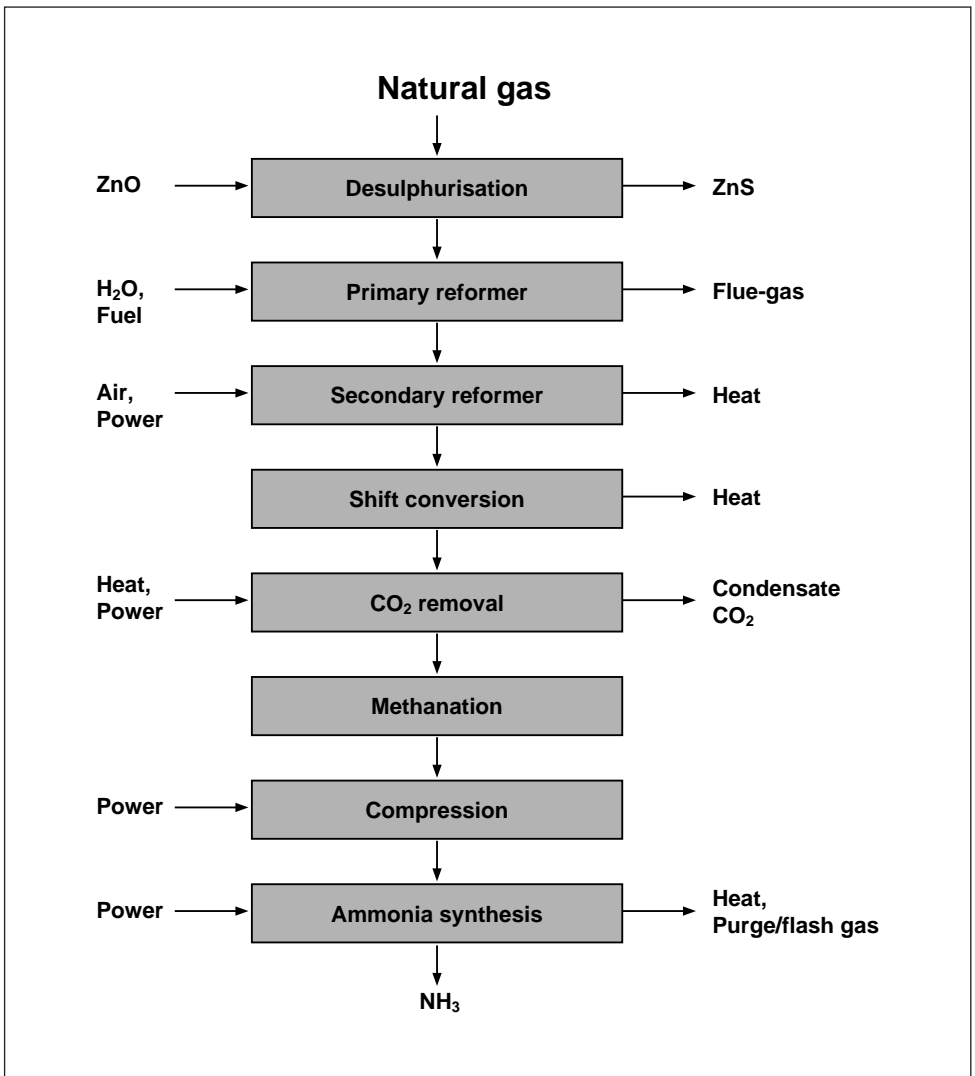|		
ZnO →	**Desulphurisation**	→ ZnS
H_2O, Fuel →	**Primary reformer**	→ Flue-gas
Air, Power →	**Secondary reformer**	→ Heat
	Shift conversion	→ Heat
Heat, Power →	**CO_2 removal**	→ Condensate CO_2
	Methanation	
Power →	**Compression**	
Power →	**Ammonia synthesis**	→ Heat, Purge/flash gas

NH_3

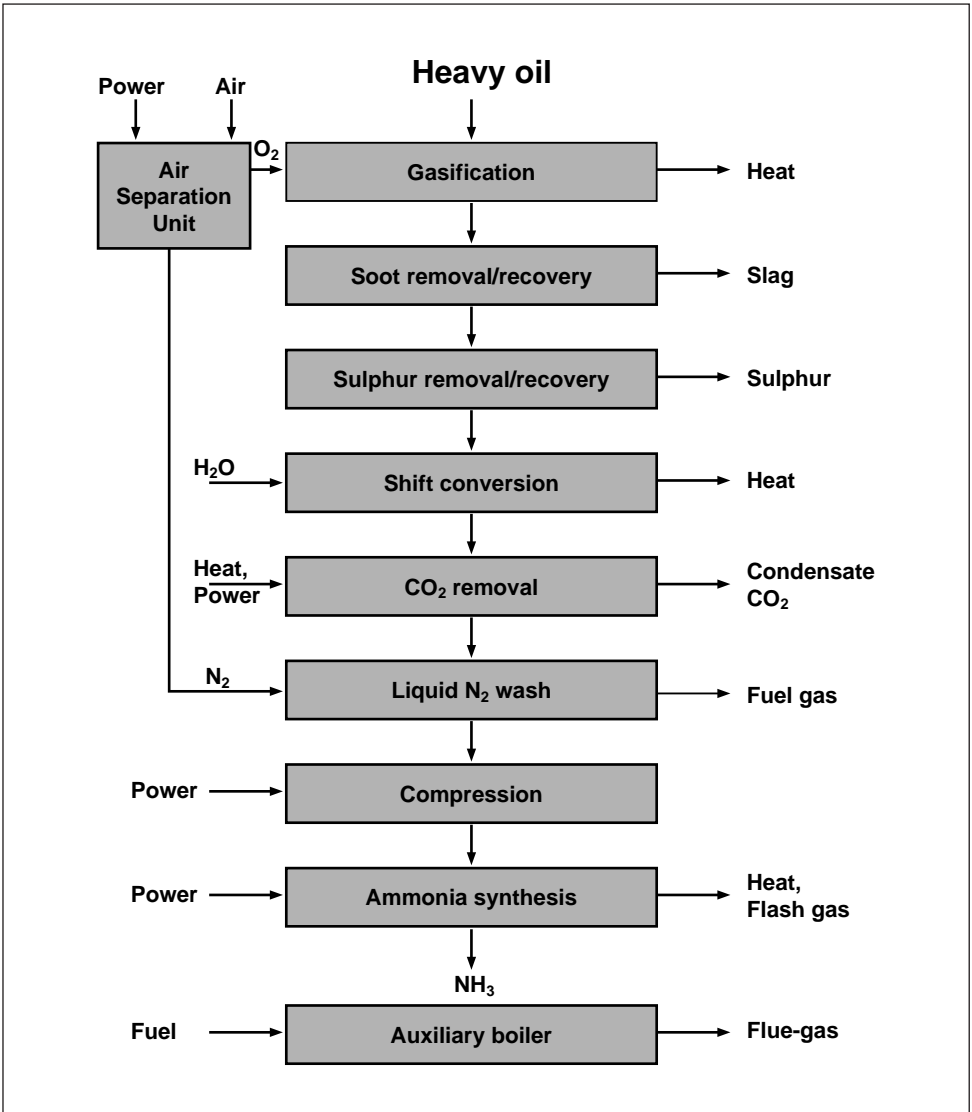*Figure 1 – Block diagram of the steam/air reforming process.*

Figure 2 – Block diagram of the partial oxidation process.

For heavier feedstocks than naphtha, partial oxidation with oxygen is used in the synthesis gas production. A block diagram of a typical partial oxidation process is shown in Figure 2, and a process description is given in 2.2.5.

2.2 BAT Production Processes

No single process can be identified as BAT for the production of ammonia. In this chapter the characteristics of BAT processes based on available feedstocks are described. Other BAT processes may also exist.

Natural gas reforming with steam and air is the simplest and most efficient way of ammonia synthesis gas production. Comparing natural gas reforming, heavy oil and coal gasification gives the following approximate relative consumption figures, based on modern technological standards for each route, at European economic conditions:-

	Natural gas	Heavy oil	Coal
Energy consumption	1.0	1.3	1.7
Investment cost	1.0	1.4	2.4
Production cost	1.0	1.2	1.7

Based on the known resources of fossil raw materials, it is likely that natural gas will dominate as the feedstock for ammonia for the next 50 years at least. In the very long term, 50-200 years, one might expect coal to take over, based on world reserves and consumption rate. Heavy oil may be attractive under special environmental concerns, when natural gas is not available and the partial oxidation process could solve a waste problem (heavy residues, plastics recycle).

For the present time and the near future, the steam/air reforming concepts based on natural gas and other light hydrocarbons are considered to be the dominating group of BAT production processes. The BAT reforming processes can be divided into the following types:-

– Conventional steam reforming with a fired primary reformer and stoichiometric air secondary reforming (stoichiometric H/N-ratio)

– Steam reforming with mild conditions in a fired primary reformer and excess air secondary reforming (under-stoichiometric H/N-ratio)

– Heat exchange autothermal reforming, with a process gas heated steam reformer (heat exchange reformer) and a separate secondary reformer, or in a combined autothermal reformer, using excess or enriched air (under-stoichiometric or stoichiometric H/N-ratio)

For heavy feedstocks, partial oxidation is considered as the BAT production process.

All three reforming versions, and partial oxidation of heavy residues, are operated in Europe today.

The following description concentrates on presenting the conventional steam reforming process and only deviations and additions will be described for the other BAT processes.

2.2.1 Conventional steam reforming

2.2.1.1 Overall conversion

The theoretical process conversions, based on methane feedstock, are given in the following approximate formulae:-

$$0.88CH_4 + 1.26Air + 1.24H_2O \longrightarrow 0.88CO_2 + N_2 + 3H_2$$
$$N_2 + 3H_2 \longrightarrow 2NH_3$$
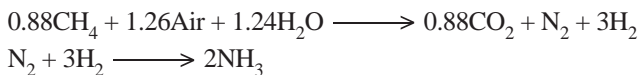
The synthesis gas production and purification normally take place at 25-35bar pressure. The ammonia synthesis pressure is usually in the range 100-250bar. For more detailed process flow sheets refer to Ullmann [3].

2.2.1.2 Feedstock desulphurisation

Most of the catalysts used in the process are sensitive to sulphur and sulphur compounds. The feedstock normally contains up to 5mg $S.Nm^{-3}$ as sulphur compounds. The feed-gas is preheated to 350-400°C, usually in the primary reformer convection section, and then treated in a desulphurisation vessel, where the sulphur compounds are hydrogenated to H_2S, typically using a cobalt molybdenum catalyst, and then adsorbed on pelletised zinc oxide:-

$$R\text{-}SH + H_2 \longrightarrow H_2S + RH$$
$$H_2S + ZnO \longrightarrow ZnS + H_2O$$
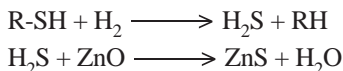
In this way, the sulphur is removed to less than 0.1ppm S in the gas feed. The zinc sulphide remains in the adsorption bed. The hydrogen for the reaction is usually recycled from the synthesis section.
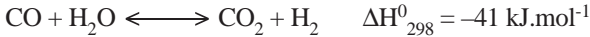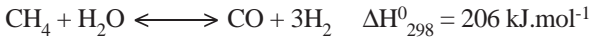
2.2.1.3 Primary reforming

The gas from the desulphuriser is mixed with process steam, usually coming from an extraction turbine, and the steam/gas mixture is then heated further to 500-600°C in the convection section before entering the primary reformer. In some new or revamped plants the preheated steam/gas mixture is passed through an adiabatic pre-reformer and reheated in the convection section, before entering the primary reformer. (Special pre-reformer catalysts are offered by several suppliers). Also, in some plants, part of the process steam is supplied by feed-gas saturation.

The amount of process steam is given by the process steam to carbon molar ratio (S/C-ratio), which should be around 3.0 for the BAT reforming processes. The optimum ratio depends on several factors, such as feedstock quality, purge gas recovery, primary reformer capacity, shift operation, and the plant steam balance. In new plants the optimum S/C-ratio may be lower than 3.0.

The primary reformer consists of a large number of high–nickel chromium alloy tubes filled with nickel-containing reforming catalyst. The overall reaction is highly endothermic and additional heat is required to raise the temperature to 780-830°C at the reformer outlet.

The composition of the gas leaving the primary reformer is given by close approach to the following chemical equilibria:-

$$CH_4 + H_2O \longleftrightarrow CO + 3H_2 \quad \Delta H^0_{298} = 206 \text{ kJ.mol}^{-1}$$
$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{ kJ.mol}^{-1}$$

The heat for the primary reforming process is supplied by burning natural gas or other gaseous fuel, in the burners of a radiant box containing the tubes.

The flue-gas leaving the radiant box has temperatures in excess of 900°C, after supplying the necessary high level heat to the reforming process. Thus only about 50-60% of the fuel's heat value is directly used in the process itself. The heat content (waste heat) of the flue-gas is used in the reformer convection section, for various process and steam system duties. The fuel energy requirement in the conventional reforming process is 40-50% of the process feed-gas energy.

The flue-gas leaving the convection section at 100-200°C is one of the main sources of emissions from the plant. These emissions are mainly CO_2, NO_x, with small amounts of SO_2 and CO.

2.2.1.4 Secondary reforming

Only 30-40% of the hydrocarbon feed is reformed in the primary reformer because of the chemical equilibria at the actual operating conditions. The temperature must be raised to increase the conversion. This is done in the secondary reformer by internal combustion of part of the gas with the process air, which also provides the nitrogen for the final synthesis gas. In the conventional reforming process the degree of primary reforming is adjusted so that the air supplied to the secondary reformer meets both the heat balance and the stoichiometric synthesis gas requirement.

The process air is compressed to the reforming pressure and heated further in the primary reformer convection section to around 600°C. The process gas is mixed with the air in a burner and then passed over a nickel-containing secondary reformer catalyst. The reformer outlet temperature is around 1,000°C, and up to 99% of the hydrocarbon feed (to the primary reformer) is converted, giving a residual methane content of 0.2-0.3% (dry gas base) in the process gas leaving the secondary reformer.

The process gas is cooled to 350-400°C in a waste heat steam boiler or boiler/superheater downstream from the secondary reformer.

2.2.1.5 Shift conversion

The process gas from the secondary reformer contains 12-15% CO (dry gas base) and most of the CO is converted in the shift section according to the reaction:-

$$CO + H_2O \longleftrightarrow CO_2 + H_2 \quad \Delta H^0_{298} = -41 \text{ kJ.mol}^{-1}$$
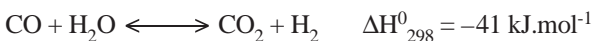
In the High Temperature Shift (HTS) conversion, the gas is passed through a bed of iron oxide/chromium oxide catalyst at around 400°C, where the CO content is reduced to about

3% (dry gas base), limited by the shift equilibrium at the actual operating temperature. There is a tendency to use copper containing catalyst for increased conversion. The gas from the HTS is cooled and passed through the Low Temperature Shift (LTS) converter.

This LTS converter is filled with a copper oxide/zinc oxide-based catalyst and operates at about 200-220°C. The residual CO content in the converted gas is about 0.2-0.4% (dry gas base). A low residual CO content is important for the efficiency of the process.

2.2.1.6 CO_2 removal

The process gas from the low temperature shift converter contains mainly H_2, N_2, CO_2 and the excess process steam. The gas is cooled and most of the excess steam is condensed before it enters the CO_2 removal system. This condensate normally contains 1,500-2,000ppm of ammonia 800-1,200ppm of methanol. Minor amounts of amines, formic acid and acetic acid could be present in the condensate. All these components should be stripped from the condensate and/or recycled in BAT processes. The heat released during cooling/condensation is used for:-

 – The regeneration of the CO_2 scrubbing solution
 – Driving an absorption refrigeration unit
 – Boiler feedwater preheat

The amount of heat released depends on the process steam to carbon ratio. If all this low-level heat is used for CO_2 removal or absorption refrigeration, high-level heat has to be used for the feedwater system. An energy-efficient process should therefore have a CO_2 removal system with a low heat demand.

The CO_2 is removed in a chemical or a physical absorption process. The solvents used in chemical absorption processes are mainly aqueous amine solutions (Mono Ethanolamine (MEA), Activated Methyl DiEthanolamine (aMDEA) or hot potassium carbonate solutions. Physical solvents are glycol dimethylethers (Selexol), propylene carbonate and others. The MEA process has a high regeneration energy consumption and is not regarded as a BAT process.

For new ammonia plants the following CO_2 removal processes are currently regarded as BAT:-

 – aMDEA standard 2-stage process, or similar
 – Benfield process (HiPure, LoHeat), or similar
 – Selexol or similar physical absorption processes

Concepts such as Pressure Swing Adsorption (PSA) should also be regarded as BAT in some new plants but in such cases CO_2 removal is not the only function of the PSA unit.

The typical range of heat consumption in the modern chemical absorption process is 30-60MJ.kmol^{-1} CO_2. The physical absorption processes may be designed for zero heat consumption, but for comparison with the chemical processes, the mechanical energy requirements have also to be considered.

Residual CO_2 contents are usually in the range 100-1,000ppmv, dependent on the type and design of the removal unit. Contents down to about 50ppmv are achievable.

2.2.1.7 Methanation

The small amounts of CO and CO_2, remaining in the synthesis gas, are poisonous for the ammonia synthesis catalyst and must be removed by conversion to CH_4 in the methanator:-

$$CO + 3H_2 \longrightarrow CH_4 + H_2O$$
$$CO_2 + 4H_2 \longrightarrow CH_4 + 2H_2O$$
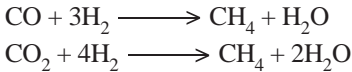
The reactions take place at around 300°C in a reactor filled with a nickel containing catalyst. Methane is an inert gas in the synthesis reaction, but the water must be removed before entering the converter. This is done firstly by cooling and condensation downstream of the methanator and finally by condensation/absorption in the product ammonia in the loop or in a make-up gas drying unit.

2.2.1.8 Synthesis gas compression and ammonia synthesis

Modern ammonia plants use centrifugal compressors for synthesis gas compression, usually driven by steam turbines, with the steam being produced in the ammonia plant. The refrigeration compressor, needed for condensation of product ammonia, is also usually driven by a steam turbine.

The synthesis of ammonia takes place on an iron catalyst at pressures usually in the range 100-250bar and temperatures in the range 350-550°C:-

$$N_2 + 3H_2 \longleftrightarrow 2NH_3 \quad \Delta H^0_{298} = -46 \text{ kJ.mol}^{-1} NH_3$$

Only 20-30% is reacted per pass in the converter due to the unfavourable equilibrium conditions. The ammonia that is formed is separated from the recycle gas by cooling/condensation, and the reacted gas is substituted by the fresh make-up synthesis gas, thus maintaining the loop pressure. In addition, extensive heat exchange is required due to the exothermic reaction and the large temperature range in the loop. A newly developed ammonia synthesis catalyst containing ruthenium on a graphite support has a much higher activity per unit of volume and has the potential to increase conversion and lower operating pressures.

Synthesis loop arrangements differ with respect to the points in the loop at which the make-up gas is delivered and the ammonia and purge gas are taken out. The best arrangement is to add the make-up gas after ammonia condensation and ahead of the converter. The loop purge should be taken out after ammonia separation and before make-up gas addition. This configuration is dependent on the make-up gas being treated in a drying step before entering the loop. A make-up gas containing traces of water or carbon dioxide must be added before ammonia condensation, with negative effects both to ammonia condensation and energy.

Conventional reforming with methanation as the final purification step, produces a synthesis gas containing inerts (methane and argon) in quantities that do not dissolve in the condensed ammonia. The major part of these inerts is removed by taking out a purge stream from the loop. The size of this purge stream controls the level of inerts in the loop to about 10-15%. The purge gas is scrubbed with water to remove ammonia before being used as fuel or before being sent for hydrogen recovery.

Ammonia condensation is far from complete if cooling is with water or air and is usually not satisfactory (dependent on loop pressure and cooling medium temperature). Vapourising ammonia is used as a refrigerant in most ammonia plants, to achieve sufficiently low ammonia concentrations in the gas recycled to the converter. The ammonia vapours are liquified after recompression in the refrigeration compressor.

2.2.1.9 Steam and power system

Steam reforming ammonia plants have high-level surplus heat available for steam production in the reforming, shift conversion, and synthesis sections, and in the convection section of the primary reformer. Most of this waste heat is used for high pressure steam production for use in turbines for driving the main compressors and pumps and as process steam extracted from the turbine system.

A modern steam reforming ammonia plant can be made energetically self-sufficient if necessary, but usually a small steam export and electricity import are preferred.

2.2.2 Steam reforming with excess air secondary reforming

2.2.2.1 Process flowsheet

Some processes are designed for reduced primary reforming by moving some of the duty to the secondary reformer because of the marginal low efficiency of the primary reformer.

A brief description is given of features diverging from the conventional concept in the following paragraphs. These features are:-

– Decreased firing in the primary reformer
– Increased process air flow to the secondary reforming
– Cryogenic final purification after methanation
– Lower inert level of the make-up syngas

2.2.2.2 Decreased firing in the primary reformer

Decreased heat supply in the primary reformer means that the process outlet temperature is lowered (to about 700°C), the firing efficiency increases, and the size and cost of the primary reformer are reduced. The milder operating conditions prolong catalyst, catalyst tube and outlet header service lives. The extent of reforming is reduced according to the lower heat supply and lower temperature. Generally, a slight decrease in steam to carbon ratio is acceptable, compared to the conventional concept.

2.2.2.3 Increased process air supply to the secondary reformer

Decreased heat supply in the primary reformer means that increased internal firing is necessary to achieve approximately the same degree of total reforming. A somewhat higher methane slip, and thus a lower secondary reformer outlet temperature is acceptable and preferable in this type of process, as methane is removed in the final purification step.

The process air requirement is about 50% higher than in the conventional process. This means increased compression capacity and energy. The process air compressor is usually driven by a gas turbine with the exhaust gas from the turbine being used as combustion air in the primary reformer. Some excess steam is available for export when using a gas turbine.

2.2.2.4 Cryogenic final purification

In the cryogenic purifier all the methane and the excess nitrogen are removed from the synthesis gas as well as a part of the argon. The cooling is produced by depressurisation and no external supply is needed. The purified syngas is then practically free of all impurities, except for a small amount of argon. The cryogenic unit also receives the purge from the synthesis section and delivers an off-gas for fuel.

2.2.2.5 Lower syngas inert level

The removal of essentially all impurities from the make-up synthesis gas is a significant improvement, compared to the conventional purification by methanation only. Higher conversion per pass and reduced purge flow, together result in a more efficient process.

2.2.3 Heat exchange autothermal reforming

From a thermodynamic point of view it is wasteful to use the high-level heat of the secondary reformer outlet gas and the primary reformer flue-gas, both at temperatures around 1,000°C, simply to raise steam. Recent developments are to recycle this heat to the process itself, by using the heat content of the secondary reformed gas in a newly-developed primary reformer (gas heated reformer, heat exchange reformer), thus eliminating the fired furnace. Surplus air or oxygen-enriched air is required in the secondary reformer to meet the heat balance in this autothermal concept.

Emissions to the atmosphere are reduced significantly by eliminating the flue-gas from the primary reformer. NO_x emissions may be reduced by 50% or more, depending on the extent of auxiliary combustion in the plant, compared to conventional steam reforming.

Two processes of this kind are in operation, and some others are at the pilot stage. All these processes are considered as BAT production processes. Recently it has been reported that capacities in the range of $1,800 t.d^{-1}$ can be built.

2.2.4 BAT reforming processes for new plants

The modern versions of the conventional steam reforming and excess air reforming processes will still be used for new plants for many years to come. Developments are expected to go in the following directions:-

– Lowering the steam to carbon ratio

– Shifting duty from primary to secondary reformer

– Improved final purification

– Improved synthesis loop efficiency

– Improved power energy system

– Low NO_x burners

– Non iron based ammonia synthesis catalyst

The new autothermal concepts are expected to be developed further, and will continue the developments outlined above.

2.2.5 Partial oxidation of heavy oils

2.2.5.1 Process description

The partial oxidation process is used for the gasification of heavy feedstocks such as residual oils and coal. Extremely viscous hydrocarbons and plastic wastes may also be used as fractions of the feed. The partial oxidation process offers an alternative for future utilisation of such wastes.

An air separation unit is required for the production of oxygen for the partial oxidation step. The nitrogen is added in the liquid nitrogen wash to remove impurities from the synthesis gas and to get the required hydrogen/nitrogen ratio in the synthesis gas.

The partial oxidation gasification is a non-catalytic process taking place at high pressure (>50bar) and temperatures around 1,400°C. Some steam is added for temperature moderation. The simplified reaction pattern is:-

$$-CH_n- + 0.5O_2 \longrightarrow CO + n/2H_2$$
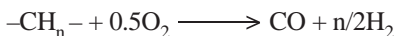
Carbon dioxide, methane and some soot are formed in addition. The sulphur compounds in the feed are converted to hydrogen sulphide. Mineral compounds in the feed are transformed into specific ashes. The process gas is freed from solids by water scrubbing after waste heat recovery and the soot is recycled to the feed. The ash compounds are drained with the process condensate and/or together with a part of the soot. In at least two units in Europe, the soot is separated from soot water in a mainstream filtration stage, to avoid ash build-up in the gasification cycle downstream units. The heavy metals, such as V, Ni and Fe are recovered. The hydrogen sulphide in the process gas is separated in a selective absorption step and reprocessed to elementary sulphur in a Claus unit.

The shift conversion usually has two high temperature shift catalyst beds with intermediate cooling. Steam for the shift conversion is supplied partially by a cooler-saturator system and partially by steam injection.

CO_2 is removed by using an absorption agent which might be the same as that in the sulphur removal step. Residual traces of absorption agent and CO_2 are then removed from the process gas, before final purification by a liquid nitrogen wash. In this unit practically all the impurities are removed and nitrogen is added to give the stoichiometric hydrogen to nitrogen ratio.

The ammonia synthesis is quite similar to that used in steam reforming plants, but simpler and more efficient, due to the high purity of synthesis gas from liquid nitrogen wash units and the synthesis loop not requiring a purge.

2.2.5.2 Steam and power system

Auxiliary boilers are required if the compressors are steam-driven. The flue-gas from these power plants is the main source of emissions which are mainly SO_2, NO_x, and CO_2. The site emissions are very low if the compressors are driven by imported electric power.

No major improvements are to be expected concerning process efficiency and plant invest-ment costs. However, partial oxidation will continue to be interesting in the future, due to its feedstock flexibility. The separation and disposal of the soot and especially the ashes are nec-essary to adapt to deteriorating residue qualities or alternative raw material sources.

3. DESCRIPTION OF STORAGE AND TRANSFER EQUIPMENT

3.1 Introduction

Liquefied ammonia from production plants is either used directly in downstream plants or transferred to storage tanks. From these the ammonia can be transferred to road tankers, rail tank cars or ships.

Ammonia is usually stored by using one or other of three methods:-

– Fully refrigerated storage in large tanks with a typical capacity of 10,000 to 30,000 tonnes (up to 50,000)

– Pressurised storage spheres or cylinders up to about 1,700 tonnes

– Semi-refrigerated tanks

Emissions during normal operation are negligible. Major leaks of ammonia from storage tanks are almost unknown with most of the leaks which do occur being during transport or transfer.

A well designed, constructed, operated and maintained installation has a very low probabil-ity of an ammonia leak of hazardous proportions. However, even though the residual risk is small, the effects of a major leak on areas of high population density could be very serious. It is therefore good practice to build ammonia storage and handling installations at a sufficient distance from domestic housing, schools, hospitals or any area where substantial numbers of people may assemble. In some countries there are planning procedures or regulations which control the siting of ammonia storage installations and similar establishments.

Where there are no formal controls, the siting of ammonia storage facilities should be given serious consideration at the design stage.

It is undesirable for ammonia storage tanks to be sited close to installations where there is a risk of fire or explosion, since these could increase the possibility of a release of ammonia.

3.2 Storage Tanks

Anhydrous ammonia is stored in three types of tank as outlined above:-

– Fully refrigerated at a temperature of about –33°C, these tanks are provided with refrig-eration equipment

– Non-refrigerated tanks in which the ammonia is stored at ambient temperature

– Semi-refrigerated spheres

Refrigerated storage is preferred for storage of large quantities of liquid ammonia. The initial release of ammonia in the case of a line or tank failure is much slower than with pressurised ammonia.

There are several construction types for the storage of refrigerated liquid products. The most important types are:-

– Single containment: a single-wall insulated tank, normally with a containment bund around it

– Double containment: this type of storage tank has two vertical walls, both of which are designed to contain the stored amount of liquid and withstand the hydrostatic pressure of the liquid. The roof rests on the inner wall

– Full containment: the two walls of this closed storage tank are also designed to contain the stored amount of liquid, but in this case the roof rests on the outer wall

The tank must be constructed in conformity with an agreed code for the construction of pressure vessels or storage tanks and taking account of its pressure and operating temperature. The design and materials of construction of the tank should be checked by consulting an appropriate national, or recognised international, standard. These could make demands on the blast resistance of storage tanks in some cases.

The storage tank must be safeguarded against high pressure and in the case of refrigerated liquid ammonia also against a pressure below the minimum design pressure. The ingress of warm ammonia into cold ammonia must be avoided to eliminate risk of excessive evaporation and the "roll-over" phenomenon. All storage tanks should be equipped with two independent level indicators, each having a high level alarm.

An automatic cut-off valve, operated by a very high level alarm instrument, should be installed on the feeding line.

In cases of refrigerated liquid ammonia, storage tanks must be equipped with a recompression installation to liquefy the boil-off. There should be at least two refrigeration units to allow proper maintenance and to prevent the emission of ammonia via the relief valves. Furthermore, an installed alternative power supply may be necessary. An automatic discharge system to a flare may be provided in case of failure of the refrigeration equipment. The flare must be located at a suitable distance from the tanks.

Relief valves should be provided, appropriate for the duty using an adequate margin between operating and relief pressure.

3.3 Transfer Equipment

Liquid or gas pipelines should be fitted with isolation valves. The main isolation valves should be backed up by remotely operated valves. The remote systems should be of such a type that closure is automatic in case of a power failure. Liquid ammonia has a high thermal coefficient of expansion and, therefore, some means of safe venting should be provided on pipelines in which any significant quantity can be trapped between valves, etc.

Liquid ammonia pipelines should be fitted with remotely operated valves at suitable intervals to minimise the loss in the event of a line failure.

Ammonia is transported in road tankers, rail tank cars (both pressurised) and ships (pressurised or refrigerated).

3.3.1 Railroad and road loading

Loading and unloading of rail tank cars and road tankers is usually done by loading arms. During (un)loading both the liquid supply and vapour return lines must be connected to the transport medium. The ammonia vapours can be transferred during (un)loading to a storage tank, an ammonia vapour network of the site or to a scrubber/absorber, to prevent emissions to the atmosphere.

Before disconnection of equipment after (un)loading the liquid ammonia in these parts must be removed to one of the reservoirs. Preferably, this should be done by using a pressurised inert gas such as nitrogen or ammonia vapour. If inert gas is used, attention should be paid to avoid getting inert gas into tankers and storage tanks. There should be a scrubbing system or a flare in the event of venting inert gas.

A weigh check must be carried out after the loading, to ensure that the maximum allowable content has not been exceeded. Modern road and rail car loading stations are equipped with a safeguard against overfilling.

3.3.2 Ships

Loading and unloading of ships is only permitted at sites which are authorised for this purpose. During (un)loading a minimum safety distance to other ships must always be maintained around the ship (eg. 30m).

Both liquid and vapour return lines should be present for import and export terminals. A vapour return line is not necessary when the ship has sufficient refrigeration capacity or for the import of ammonia only.

Both liquid and vapour connections must be equipped with isolation valves as near to the ship as possible. It must be possible to close these valves quickly under all conditions and the connection between tank and liquid line must be equipped with an isolation valve.

The ends of loading and unloading arms should be equipped with dry break couplings. The isolation valves must be closed automatically, when these couplings are disconnected or when the (un)loading arms are too far out of position.

After each loading-unloading operation, liquid ammonia contained within loading arms must be collected in a suitable evaporation tank connected to the storage tank through the vapour line. Loading arms are then purged by inert gas or ammonia vapour. If inert gas is used, attention should be paid to avoid getting the inert gas into tankers and storage tanks. There should be a scrubbing system or flare in case the inert gas has to be vented.

4. ENVIRONMENTAL DATA

Environmental data for the BAT production processes are generally known with a high degree of reliability, while data for storage and transfer are more uncertain and of much less importance. Hence, data for production will be given the highest attention.

4.1 Production Input Requirements

4.1.1 Feedstock

The typical feedstock requirements for modern plants are (approximately):-

Conventional reforming: 22.1 GJ(LHV*).t^{-1} NH_3
Excess air reforming   : 23.4 GJ(LHV).t^{-1} NH_3
Autothermal reforming : 24.8 GJ(LHV).t^{-1} NH_3
Partial oxidation   : 28.8 GJ(LHV).t^{-1} NH_3
* Lower Heating Value

4.1.2 Fuel

Assuming an efficient stand-alone plant with no energy export and no other import than feedstock and fuel, the fuel requirements are (approximately):-

Conventional reforming: 7.2-9.0 GJ(LHV).t^{-1} NH_3
Excess air reforming   : 5.4-7.2 GJ(LHV).t^{-1} NH_3
Autothermal reforming : 3.6-7.2 GJ(LHV).t^{-1} NH_3
Partial oxidation   : 5.4-9.0 GJ(LHV).t^{-1} NH_3

The uncertainty in autothermal reforming is mainly due to the type of compressor drives.

4.1.3 Water and air

In the steam reforming processes process steam is taken from the plant steam system, usually from an extraction turbine. The net consumption according to the stoichiometic conversion is 0.6-0.7kg.kg^{-1} NH_3, the total supply at a S/C ratio of 3.0 will be about 1.5kg.kg^{-1} NH_3. In partial oxidation much less steam is fed to the gasification reactor, but additional steam is needed in shift conversion (1.2kg.kg^{-1} NH_3 in total).

Process air supply: In conventional reforming the nitrogen supply equals the ammonia nitrogen content plus the purge losses, ie. about 0.85kg N_2.kg^{-1} NH_3 or about 1.1kg air.kg^{-1} NH_3. In the excess air reforming and gas heated reformer cases the process air requirements are about 50% and 100% higher, respectively. In the partial oxidation process the amount of air fed to the air separation unit is approximately 4kg.kg^{-1} NH_3, based on the oxygen requirement.

Boiler feedwater: Assuming all steam condensates are recycled, only the process steam consumption has to be replaced by outside water. This will be 0.7-1.5kg.kg^{-1} NH_3 (see above), depending on process condensate recycle or not. Small additional losses and potential import/export have to be allowed for in practice.

Air and/or water for cooling: Will differ from one site to another.

4.1.4 Solvents and additives

The consumption of solvent in the CO_2 removal unit should not normally exceed 0.02-0.04kg.t^{-1} NH_3, or about 2kg.h^{-1} for a BAT capacity plant. Solvent losses are mainly caused by leaks.

The usual treatment additives and regeneration agents are used in the boiler feedwater preparation units. The consumption figures should not differ from those of a standard steam boiler plant at the same location.

4.1.5 Catalysts

Approximate consumption figures, based on average filling volumes and normally recommended operating periods, for a gas based conventional reforming plant, are given in the table below. The consumptions refer to a capacity of 1,500t.d^{-1}.

Catalyst type	Typical replacement, $m^3.y^{-1}$
Hydrodesulphurisation	1
Sulphur removal	5
Primary	5
Secondary reforming	4
High temperature shift	10
Low temperature shift	20
Methanation	2
Synthesis	10

Actual consumptions in existing plants may differ considerably from the guidance figures above.

4.1.6 Energy requirements

The total energy requirement in the reforming BAT processes is 28.8-31.5GJ (LHV).t^{-1} NH_3 for a stand-alone plant with no energy export and no other import than feedstock and fuel. When using process waste heat in a gas heated reformer, the process itself will not produce enough steam to drive all the compressors. A part of the power needed may then be imported from a more efficient power plant outside the process plant. In such cases the total energy consumption may be lowered and approach the present practical minimum of 27 GJ(LHV).t^{-1} NH_3.

In partial oxidation plants the total energy requirement is 36.9(35.1-37.8)GJ(LHV).t^{-1} NH_3. This includes imported power and/or auxiliary steam for driving the machinery.

4.2 Production Output

4.2.1 Ammonia

Ammonia production in the typical size BAT plant is 1,000-1,500t.d^{-1} (300,000-500,000t.y^{-1}). The production not used in downstream plants on site is stored as described in Chapter 3.

Commercial anhydrous ammonia has two grades of purity:-

  – Anhydrous ammonia min. 99.7 wt %, water content (about 0.2% wt)

  – Anhydrous ammonia min. 99.9 wt %

4.2.2 Carbon dioxide

Carbon dioxide is produced according to the stoichiometric conversion and may be recovered for down-stream uses. The carbon dioxide production in steam/air reforming of natural gas is 1.15-1.30kg.kg^{-1} NH_3, dependent on the degree of air reforming. A CO_2/NH_3 mole ratio of 0.5 (weight ratio 1.29), the stoichiometric ratio for urea production, is obtainable in the heat exchange reformer concepts. In partial oxidation of residual oils the CO_2 production is 2-2.6kg.kg^{-1} NH_3, dependent on feedstock C/H ratio.

Carbon dioxide in the combustion gases is not included in the above figures, but is shown in Figure 3.

4.2.3 Sulphur

In BAT partial oxidation most (87-95%) of the sulphur content of the feed to the gasifier is recovered in the Claus unit.

4.2.4 Steam export

Modern steam reforming processes can be designed with no steam export or with some export of low/medium pressure steam if this can be favourably used on site. Steam export is usual in excess air reforming processes where the process air compressor is driven by a gas turbine, and in cases when electric power is used for driving one or more of the main compressors.

Processes with gas heated primary reforming may be designed for zero steam export even with some power import or gas turbine drive.

The partial oxidation process has a steam deficit if all compressors are steam driven.

4.3 Production Emissions and Wastes

4.3.1 Emissions into air from steam reforming plants

From steam reforming plants with a fired primary reformer emissions into air come from the following sources:-

  – Flue-gas from the primary reformer

  – Vent gas from CO_2 removal

  – Breathing gas from oil buffers (seals/compressors)

  – Fugitive emissions (from flanges, stuffing boxes etc.)

  – Purge and flash gases from the synthesis section (usually added to the primary reformer fuel)

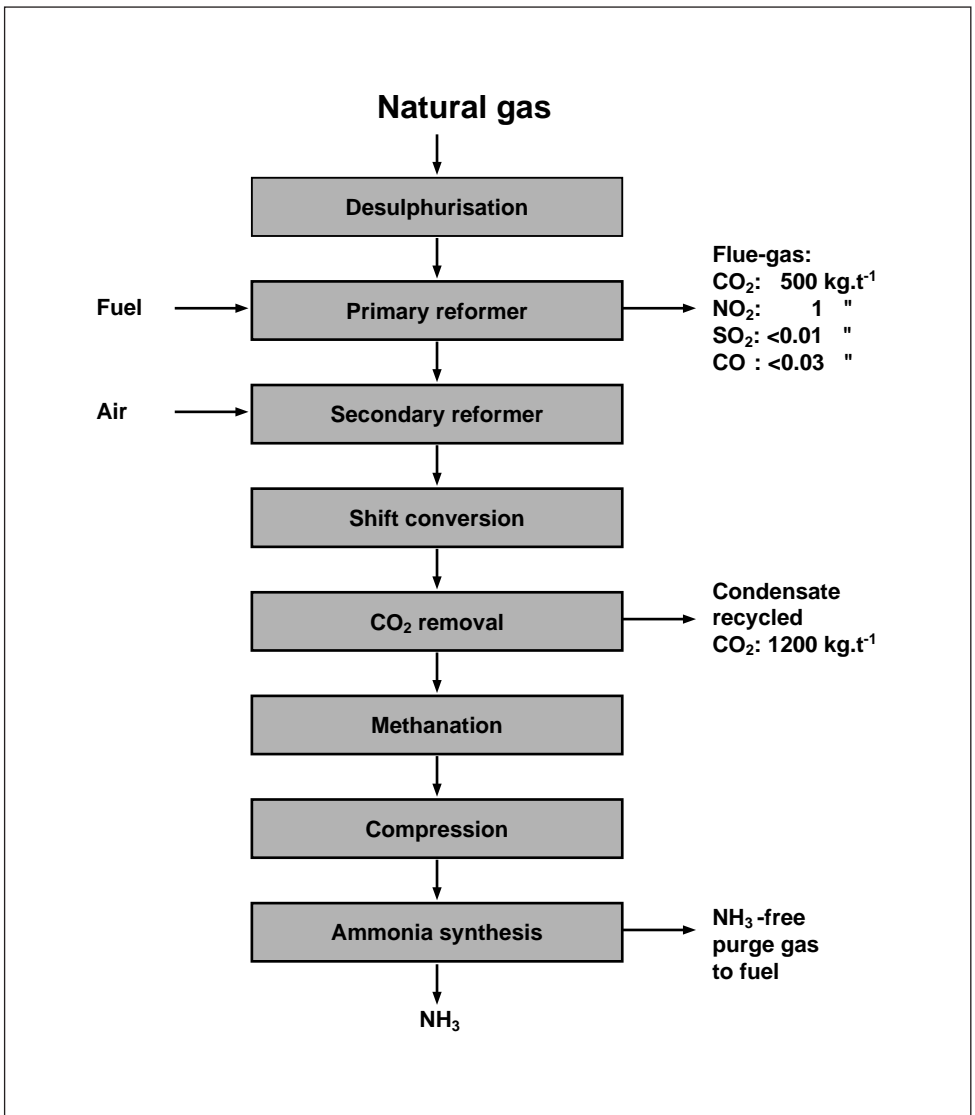 – Non-continuous emissions (venting and flaring)

Figure 3 – Typical emission levels in gas-based steam reforming plants with a gas-fired primary reformer and process condensate recycle.

4.3.1.1 Flue-gas from the primary reformer

The flue-gas volume, at 3% (dry gas base) oxygen, for a gas-based conventional steam reforming plant producing 1,500t.d^{-1}, is approximately 200,000Nm^3.h^{-1}, containing about 8% CO_2 (dry gas base), corresponding to 500kg CO_2.t^{-1} NH_3. The flue-gas volume from excess air reforming may be lower. The other pollutants in the flue-gas are:-

NO_x: 200-400mg.Nm^{-3}, (98-195ppmv), or 0.6-1.3kg.t^{-1} NH_3 expressed as NO_2

SO_2: 0.1-2mg.Nm^{-3}, (<0.01kg.t^{-1}), depending on fuel

CO: <10mg.Nm^{-3}, (<0.03kg.t^{-1})

The NO_x emission depends on several factors and the following features reduce the emission:-

– Low combustion air and fuel gas preheat

– Steam/inert injection

– Low ammonia content in injected purge-gas

– Low excess oxygen

– Low NO_x burners

– Post-combustion measures

The SO_2 emission comes from the sulphur in the fuel gas and can be calculated by a simple mass balance.

4.3.1.2 Vent gases from CO_2 removal

More or less of the CO_2 product may have to be vented, depending on the CO_2 requirements of other production facilities on the site. In some cases, high purity CO_2 is used, while an air-CO_2 mixture from a stripping column is vented.

The CO_2 contains small traces of synthesis gas and absorption solvent vapour.

4.3.1.3 Breathing gas from oil buffers

This contains traces of NH_3, synthesis gas and lube oil.

4.3.1.4 Fugitive emissions

The diffuse emissions from flanges, stuffing boxes etc. should be minimised.

4.3.1.5 Purge and flash gases

The purge and flash gases from the synthesis section are usually washed with water to remove/recover ammonia, and the purge gas may be treated in a recovery unit, before routing the off-gases to the primary reformer fuel gas system. The off-gases are thus combusted and end up as part of the flue-gas. It is important to remove the ammonia as far as possible, as it will contribute considerably to the flue-gas NO_x emission.

4.3.1.6 Non-continuous emissions

Emission of NO_x during flaring synthesis gas at start-up or trip situations is estimated to be 10-20kg.h^{-1} as NO_2 [1]. Some plants without a flare, vent to the atmosphere.

4.3.2 Emissions into air from heat exchange reforming

The flue-gas volume (from auxiliary fired equipment) and thus NO_x and CO_2 emissions are considerably reduced, as these processes have much more internal combustion than the fired reformer processes because all the reforming process heat is generated by internal combustion. Total CO_2 emissions are fixed by the energy consumption. For self-sufficient plants the flue-gas volume in heat exchange reforming is about 50% of the figure for conventional steam reforming. In plants with power import the flue-gas volumes are lower. Reduction of NO_x emissions by 80% has been claimed.

4.3.3 Emissions into air from partial oxidation plants

The partial oxidation process has the same emission sources as described for the reforming process except for the primary reformer flue-gas. 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 CO_2 in the flue-gas. Tail gas from sulphur recovery will also contain sulphur oxides. This means that the CO_2 emission from partial oxidation plants (max 1,500mg.Nm^{-3}) is higher than in the reformer flue-gas. Other additional emissions may be H_2S (0.3ppmv), methanol (max. 100ppmv), CO (30ppmv), and dust (traces, max. 50mg.Nm^{-3}). NO_x emission (max. 700mg.Nm^{-3}) depends on the factors listed for the reformer flue-gas and the nitrogen content of the fuel.

Excess nitrogen is usually vented.

4.3.4 Emissions into water

Pollution problems related to water, during normal operation, may occur due to process condensates or due to the scrubbing of waste gases containing ammonia. In partial oxidation, soot and ash removal may cause pollution problems, if not properly handled.

Process condensate is found primarily in the condensation section prior to the CO_2 removal, of the order of 1m^3 per ton NH_3 produced. Without treatment this condensate can contain up to 1kg of ammonia and 1kg methanol per m^3. More than 95% of the dissolved gases can be recovered by stripping with process steam and are recycled to the process. The stripped condensate can be re-used as boiler feedwater make-up after treatment by ion exchange. Total recycle is obtained in this way. In some cases the process condensate is used for feed-gas saturation and thus recycled to the process.

Usually the ammonia absorbed from purge and flash gases is recovered in a closed loop so that no aqueous ammonia emissions occur. Emissions into water from the production plant during normal operation can thus be fully avoided.

Soot from gasification in partial oxidation processes is usually recovered and recycled to the process. Traces of soot and slag are emitted to water.

4.3.5 Solid wastes

The BAT ammonia processes do not normally produce solid wastes. Spent catalysts and mol.sieves have to be removed and valuable metals are recovered from them. In partial oxida-

tion plants sulphur is recovered in the Claus plant and can be used as feedstock in sulphuric acid units. The ash can be upgraded and used as an ore substitute.

4.4 Environmental Data for Ammonia Storage and Transfer

In a refrigerated storage, the cold losses are balanced by recompressing and recondensing the evaporated ammonia. During recompression, some inerts containing also traces of ammonia cannot be condensed but must be flared or scrubbed with water. Small continuous emissions may thus occur, in addition to minor non-continuous emissions during loading operations.

4.5 Environmental Hazards Associated with Emissions and Wastes

The production of ammonia is relatively clean compared to many other chemical processes. During the normal operation of a reforming plant, only the NO_x and CO_2 emissions have to be considered. In partial oxidation plants with oil-fired auxiliary boilers the reduction of SO_2 emissions can be achieved by using low sulphur fuel oil. Generally the emissions from modern ammonia plants have little environmental impact.

4.6 Emission Limits and Guideline Values for Ammonia Production in Some West-European Countries

Two types of emission values are of importance:-

– Legally binding emission limit values for specific pollutants which apply for ammonia production
– Guideline values which are not legally binding but provide the background for requirements laid down in individual permits

Specific legally binding emission limits for ammonia production are only laid down in Germany. In the Netherlands and in Germany limits for emissions from boilers have been laid down which include chemical reactors.

Specific emission guideline values are laid down in the United Kingdom.

With regard to the other countries, no national emission limits or guidelines are fixed for ammonia production plants. Very often the values are the subject of negotiations between the operator and the authority responsible for granting licences. In some countries, these authorities are of local character, so that even within one and the same country, different air pollution requirements may apply for comparable plants. At least in the Benelux countries and Ireland, the licensing authorities take into account emission limits applied in other countries, in particular those laid down in Dutch and German law, in their negotiations with operators. In practice, these values play the role of guideline values.

Indirectly, the emission limits laid down for combustion installations play an important role because the energy consumption of an ammonia plant is relatively high. The emissions from a fired reformer or auxiliary boilers should conform with emission limits and guideline values adopted by the Council of EC in Directive 88/609/EEC or applied by the state.

More detailed information is given in Reference [1].

5. EMISSION MONITORING

As outlined in Chapter 4, the emissions of pollutants to be expected from ammonia production are mainly:-

- CO_2, NO_x, SO_2, and CO in the flue-gas from steam reforming processes with a fired primary reformer and/or auxiliary boilers
- SO_2 from the sulphur removal and recovery systems in partial oxidation processes
- CO_2 and traces of removal solvents and synthesis gas in vent streams from the CO_2 removal system
- Small non-continuous and fugitive emissions
- NH_3 and methanol in process condensates (if not recycled)

The following emissions into air should be monitored as part of a proper supervision:-

- NO_x in flue-gases
- SO_2 in flue-gases (may be calculated by mass balance instead of monitoring emission, if S input is known)
- SO_2 and H_2S from sulphur removal/recovery systems in partial oxidation processes

The other emissions into air need not be monitored. CO_2 emission can be calculated from fuel specification and energy consumption, CO emission is fixed by the operating conditions and usually stable and low. Non-continuous and fugitive emissions are difficult to measure.

The frequency of monitoring depends on local circumstances and the operating stability of the actual plant. Under normal operating conditions, measurements once a month are usually sufficient.

Methods for discontinuous and continuous measurements of NO_x, SO_2 and H_2S are available and are to a large extent standardised at national level (Norme Belge/Belgische norm, British Standard, AFNOR, Verein Deutscher Ingenieure, Nederlands Normalisatie Instituut). Chemiluminescence or photometry are the most widely used methods for NO_x. SO_2 is determined by Infra Red (IR) absorption techniques. Traces of H_2S are measured by lead acetate.

Emissions into water from new plants are virtually zero as process condensates are recycled and monitoring is not normally required. In existing plants without recycle of process condensate, the ammonia and methanol content should be monitored.

A description of available methods for monitoring emissions is given in Appendix 1.

6. MAJOR HAZARDS

Historical data show that the major accidents in ammonia plants are explosions and fires. In addition there is also the potential for toxic hazard due to the handling and storage of liquid ammonia.

The following credible major hazards events are identified in an ammonia production plant:-

– Fire/explosion hazard due to leaks from the hydrocarbon feed system

– Fire/explosion hazard due to leaks of synthesis gas in the CO removal/synthesis gas compression areas (75% hydrogen)

– Toxic hazard from the release of liquid ammonia from the synthesis loop

In ammonia storage the release of liquid ammonia (by sabotage) is a credible major hazard event.

Confined explosions in ammonia plants appear to be limited to explosions equivalent to a few hundred kg TNT. Such explosions are normally not fatal for humans at 50-60m distance, and thus in most cases not severe for people outside the plant fence. The same is true for fire balls equivalent to 500kg hydrogen. Fires and explosions are usually not a hazard or only a minor hazard to the local population although potentially most severe for the plant operators. Appropriate precautions to protect both the operators and the local population are taken in the design and operation of the plants.

The toxic hazard of a potential large release of liquid ammonia (ie. from a storage tank) may be much more serious for the local population. An emergency plan for this event, covering the operators and the local population must be maintained.

7. OCCUPATIONAL HEALTH & SAFETY

The occupational health and safety issues associated with ammonia production and storage are:-

– Fire/explosion injuries

– Poisoning

– Suffocation

Fires or explosions from the involuntary ignition of leaks are credible, especially when these occur in the feed-gas and synthesis gas systems (hydrocarbons, hydrogen).

The most important toxic components are CO from potential leaks in the synthesis gas generation and shift areas and NH_3 from leaks in the ammonia synthesis and ammonia handling areas. In partial oxidation plants H_2S and SO_2 are present in the sulphur removal/recovery sections. Traces of carbonyls (iron and nickel) may form during operation.

Suffocation due to lack of oxygen may occur at points where the breathing air has been diluted with inert gases. In ammonia plants CO_2 and N_2 are potentially suffocating gases.

ACGIH [4] occupational exposure limits for ammonia and other components associated with ammonia production are given in the table below. All the figures are ppmv:-

Component	TLV-TWA (8hr)	TLV-STEL (15min)
NH_3	25	35
NO_2	3	5
SO_2	2	5
H_2S	10	15
CO	50	400
CO_2	5,000	30,000

The figures are subject to updating and may vary between European countries.

Full health and safety information is given in Safety Data Sheets which must be available and updated. General product information on ammonia is given in Appendix 2.

Ammonia plants have high technological standards and need professional management, operating and maintenance working routines and personnel. Precautions taken to prevent accidents and injuries during operation are incorporated in the operating and safety procedures for the plant.

8. SUMMARY OF BAT EMISSION LEVELS

8.1 Achievable Emission Levels for New Plants

The following emission levels can be achieved for new ammonia plants. These levels relate to steady-state production, not accounting for peaks which can occur during the unsteady transient conditions of start-up and shut-down and during emergencies.

8.1.1 Emissions into air

	ppmv	mg.Nm^{-3}	kg.t^{-1} of product
NO_x (as NO_2 at 3% O_2)	75	150	0.45

SO_2 (partial oxidation plants): as for combustion plants.

8.1.2 Emissions into water

NH_3 or NH_4 (as N)   0.1kg.t^{-1} of product

8.1.3 Waste material

Spent catalysts etc.   <0.2kg.t^{-1} of product

Reclaiming of raw materials from spent catalyst by specialised companies prior to their disposal is common practice in the ammonia industry.

In new reforming plants the total energy consumption should not exceed 29.3GJ(LHV).t^{-1} and process condensate recycle should be a pre-requisite.

8.2 Achievable Emission Levels for Existing Plants

The following emission levels can be achieved for existing ammonia plants. As for new plants, these levels do not account for peak values during unsteady or transient conditions. Contributions from ammonia-containing purge gases can be excluded from these figures in special cases, when authorised locally.

8.2.1 Emissions into air

	ppmv	mg.Nm^{-3}	kg.t^{-1} of product
NO_x (as NO_2 at 3% O_2)	150	200-400	0.9

SO_2 (partial oxidation plants): as for combustion plants.

8.2.2 Emissions into water

NH_3 or NH_4 (as N)   0.1kg.t^{-1} of product

8.2.3 Waste material

Spent catalysts etc.   <0.2kg.t^{-1} of product

8.3 Cost of Pollution Control Measures

The costs of pollution control measures in the fertilizer industry are difficult to generalise as they depend on a number of factors such as:-

– The emission target or standard to be met

– The type of process, the degree of integration with other processes on site, production volumes, type of raw materials being used etc.

– Whether the plant is new so that the design can be optimised with respect to pollution abatement, or whether the plant is an existing one requiring revamping or end-of-pipe pollution abatement equipment

Generally, it is more economic to incorporate the pollution abatement system at the process design stage rather than revamping or "adding-on" equipment at a later stage.

Process condensate recycle can be included to bring existing plants to BAT standards for emissions into water and a rough investment of the order of 2.9 to 3.3million EUR can be anticipated (1,500t.d^{-1}).

9. REFERENCES

[1] Commission of the European Communities Integrated Pollution Prevention and Control "Best Available Technique Reference Document on Ammonia Production, March 1997.

[2] Appl, M: Ammonia, Methanol, Hydrogen, Carbonmonoxide. Modern Production Technologies. British Sulphur Publishing, 1997. ISBN 1-873387-26-1.

[3] Appl. M: Ammonia. Principles and Industrial Practice. Published by Wiley-VCH. Weinheim, Germany, 1998 ISBN 3-527-29593-3.

[4] Threshold Limit Values for Chemical Substances and Physical Agents and Biological Exposure Indices, 1993-1994. American Conference of Governmental Industrial Hygienists (ACGIH). Cincinnati, OH: ACGIH. – ISBN 1-882417-03-8.

GLOSSARY

The following abbreviations occur frequently throughout the series of Booklets but without necessarily appearing in each Booklet:-

ACGIH	American Conference of Governmental Industrial Hygienists
AFNOR	Association Française de Normalisation (France)
AN	Ammonium Nitrate
AQS	Air Quality Standard
AS	Ammonium Sulphate
BAT	Best Available Techniques
BATNEEC	Best Available Technology Not Entailing Excessive Cost
BOD	Biological Oxygen Demand
BPL	Basic Phosphate of Lime (Bone Phosphate of Lime)
BS	British Standard
CAN	Calcium Ammonium Nitrate
CEFIC	Conseil Europeen de l'Industrie Chimique (European Chemical Industry Council)
COD	Chemical Oxygen Demand
DAP	Di-Ammonium Phosphate
DIN	Deutsches Institut für Normung (Germany)
EEC	European Economic Community
EFMA	European Fertilizer Manufacturers Association
ELV	Emission Limit Value
ESA	European Sulphuric Acid Association
EU	European Union (Formerly, European Community, EC)
IFA	International Fertilizer Industry Association
IMDG	International Maritime Dangerous Goods (Code)
IPC	Integrated Pollution Control
IPPC	Integrated Pollution Prevention and Control
ISO	International Standards Organisation (International Organisation for Standardisation)
MAP	Mono-Ammonium Phosphate
MOP	Muriate of Potash (Potassium Chloride)
NK	Compound fertilizer containing Nitrogen and Potash
NP	Compound fertilizer containing Nitrogen and Phosphate
NPK	Compound fertilizer containing Nitrogen, Phosphate and Potash
NS	Fertilizer containing Nitrogen and Sulphur
OEL	Occupational Exposure Limit
SSP	Single Super-Phosphate
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TSP	Triple Super-Phosphate
TWA	Time Weighted Average
UAN	Urea Ammonium Nitrate (Solution)

CHEMICAL SYMBOLS

The following chemical symbols may be used where appropriate in the text.

C	Carbon
$CaCO_3$	Calcium Carbonate
Cd	Cadmium
CH_3OH	Methanol
CH_4	Methane
CO	Carbon Monoxide
CO_2	Carbon Dioxide
F	Fluorine
F^-	Fluoride
H (H_2)	Hydrogen
H_2O	Water
H_2S	Hydrogen Sulphide
H_2SiF_6	Hydrofluorosilicic Acid (Hexafluorosilicic Acid)
H_2SO_4	Sulphuric Acid
H_3PO_4	Phosphoric Acid
HNO_3	Nitric Acid
K	Potassium
KCl	Potassium Chloride (Muriate of Potash) ("Potash")
K_2O	Potassium Oxide
N (N_2)	Nitrogen
N_2O	Dinitrogen Monoxide (Nitrous Oxide)
NH_3	Ammonia
NH_4-N	Ammoniacal Nitrogen
NH_4NO_3	Ammonium Nitrate
NO	Nitrogen Monoxide (Nitric Oxide or Nitrogen Oxide)
NO_2	Nitrogen Dioxide
NO_3-N	Nitric Nitrogen
NO_x	Oxides of Nitrogen (Excluding Nitrous Oxide)
O (O_2)	Oxygen
P	Phosphorus
P_2O_5	Phosphorus Pentoxide
S	Sulphur
SO_2	Sulphur Dioxide
SO_3	Sulphur Trioxide

UNITS

Units have been standardised as far as possible and these are abbreviated as follows:-

bar	Unit of pressure (equivalent to one atmosphere)
GJ	Giga Joule
kg	Kilogramme
$kg.h^{-1}$	Kilogrammes per hour
kWh	Kilowatt hour (1,000kWh = 3.6GJ)
l	Litre (liquid volume)
m	Metre
LHV	Lower Heating Value *
m^3	Cubic Metre (liquid or solid volume)
mg	Milligramme
$mg.l^{-1}$	Milligrammes per litre
MJ	Mega Joule
μm	Micrometre
Nm^3	Normal cubic metre (gas volume)
ppb	Parts per billion
ppm	Parts per million
ppmv	Parts per million by volume
t	Tonnes (Metric Tons)
$t.d^{-1}$	Tonnes per day
$t.y^{-1}$	Tonnes per year
°C	Degree Celsius
K	Degree Kelvin

*Net caloric value or LHV H_i: The amount of heat evolved by the complete combustion of a unit volume of gas V (T_v: P_v) with air at a constant pressure of 101.325kPa and a constant temperature T_H when the combustion products have once more cooled to the starting conditions and whereby the water produced by the combustion is assumed to remain as vapour.

The internationally applicable starting conditions are:-
an absolute pressure of 101.325kPa
a temperature T_H of 298.15K (25°C)

The definition of net calorific value is covered by an international standard,
ISO 6976-1983 (E).

APPENDIX 1 EMISSION MONITORING IN AMMONIA PLANTS

1. Introduction

Monitoring of emissions plays an important part in environmental management. It can be beneficial in some instances to perform continuous monitoring. This can lead to rapid detection and recognition of irregular conditions and can give the operating staff the possibility to correct and restore the optimum standard operating conditions as quickly as possible. Emission monitoring by regular spot checking in other cases will suffice to survey the status and performance of equipment and to record the emission level.

In general, the frequency of monitoring depends on the type of process and the process equipment installed, the stability of the process and the reliability of the analytical method. The frequency will need to be balanced with a reasonable cost of monitoring.

An extractive gas sampling system for continuous gas monitoring will typically comprise:-

– A coarse filter (heated if necessary) which may be in the stack or duct or outside

– A heated line to convey the sample gas from the stack but this may not be necessary if probe dilution is used

– A cooler may be used to reduce moisture

– A further drier installed before the analyser

– A pump, situated before or after the analyser, as appropriate, to pull the gas from the stack or duct

– A fine filter may be put immediately before the analyser

National standards for gas sampling exist and the appropriate method should be adopted.

Iso-Kinetic sampling will be necessary when particulates are present.

Manual methods may be necessary or accepted by the authorities in certain cases and for situations where no continuous method is available.

Vent streams are not normally measured by on-line methods and when measurements are required as base line checks, manual methods may be more appropriate.

Typical methods for monitoring emissions into water rely on flow-proportioned sample collection or high frequency spot sampling together with analysis and continuous flow measurement.

The use of trained staff is essential.

Methods available for monitoring the emissions given in Chapter 8 of this Booklet are briefly described overleaf.

2. Emissions into Air

2.1. Flue-gas CO_2, NO_x, SO_2, CO on-line analysis

Commonly used methods:-

CO_2 – Infra Red Spectrometry (Non-Dispersive Infra Red (NDIR))

NO_x – Chemiluminescence

SO_2 – Infra Red Spectrometry (NDIR)

CO – Infra Red Spectrometry (NDIR) or Electrochemical

Extractive sampling with appropriate sample conditioning is used.

NOTE: It may be possible to determine CO_2 by fuel specification and energy consumption figures and the CO may be sufficiently low and stable to avoid the need for continuous monitoring. The SO_2 may also be calculated on the basis of measuring the input of sulphur to the system. In such cases a monthly check may be acceptable – refer to the manual methods section.

2.2 Sulphur Removal/Recovery SO_2 and H_2S

Commonly used methods:-

SO_2 – Infra Red Spectrometry (NDIR)

Extractive sampling with appropriate sample conditioning is required.

H_2S – Routine manual sampling and analysis using instrumental methods such as electrochemical cells or gas chromatography with flame photometric detection are required for accurate measurements

## 2.3 On-Line Methods

2.3.1 Infra red spectrometry

In the simplest form of IR spectrometry, the equipment consists of an optical filter, the sample cell and a detector. When the wavelength of the radiation is not selected using a prism or diffraction grating, the instrument is known as a non-dispersive infra red gas analyser (NDIR). In a single-beam instrument a filter selects the part of the spectral range most characteristic of the substance. In a twin-beam instrument, (the most commonly used for on-line analysis) the radiation from the source is split and a comparison is made of the two beams after one has passed through a reference cell and the other through the sample gas.

The two beams are brought together onto a half-silvered mirror or rotating chopper which alternately allows each beam to reach a detector cell which compares the heat received, by capacitance or resistance measurements. The twin-beam method is preferred in an on-line system as it overcomes some of the problems associated with drift due to small changes in detector sensitivity and in the optical and spectral properties of the optical filter. However, regular zeroing and calibration are needed to correct zero and range drift.

2.3.2 Chemiluminescence

These instruments use the property of fluorescence which can take place with some chemical reactions. By selecting two gases to react under carefully controlled conditions, the chemiluminescence can be measured to determine the concentration of reacting gases.

NO_x measurement makes use of the reaction:-

$$NO + O_3 \longrightarrow NO_2 + O_2 + kv$$
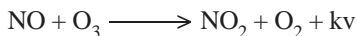
The sample gas is passed through a catalytic converter to change any nitrogen dioxide to nitric oxide and is then reduced in pressure and reacted with ozone. The chemiluminescence (kv) is measured by a photomultiplier tube after passing through an appropriate band pass filter.

2.3.3 Range of methods available

Method	Potential Interferences	Comments
Sulphur Dioxide		
Extractive NDIR	H_2O, CO_2, CO, NO, NO_2 SO_3 and particulates.	The extraction system should be designed to allow the elimination of H_2O, SO_3 and particulates.
In-situ NDIR	As for extractive NDIR	High moisture, particulates and etching of the lens give problems. Calibration may be difficult.
Extractive UV second derivative measurement		Eliminate the effects of other UV absorbing compounds.
Extractive NDUV	CO_2, CO, NO_2, SO_3, hydrocarbons and particulates	The extractive system should be designed to allow the elimination of H_2O, SO_3 and particulates.
In-situ UV-visible	H_2O	
Extractive fluorescence	NO_2	
Extractive flame photometry	H_2O, SO_3	
Extractive electrochemical	H_2O, NH_3, H_2S	Sample requires conditioning to remove particulates and moisture to stop condensation and dissociation of salts.

Method	Potential Interferences	Comments
Oxides of Nitrogen		
Chemiluminescence	CO_2, H_2O and NH_3	
In-situ NDIR	H_2O and particulates	Interferences can be reduced by precise selection of the wavelength.
Carbon Monoxide/Carbon Dioxide		
Extractive NDIR	H_2O and particulates	Straightforward conditioning
In-situ IR (fibre optics)	Other IR absorbing components, H_2O, particulates, fibre optic losses	Reduced accuracy due to interferences.

2.4 Manual Methods

2.4.1 Sulphur dioxide

Standard methods rely on the solubility and acidic nature of the gas. An oxidising agent is generally used to convert the SO_2 to SO_3. National standard methods include the use of hydrogen peroxide solution as the oxidising agent with titration against standard alkali or gravimetric analysis using barium chloride and hydrochloric acid to precipitate the sulphate. An alternative to this uses a sample collected in hydrogen peroxide solution and titration against barium perchlorate with thorin as indicator. A method which draws the filtered gas through a standard solution of iodine in potassium iodide is also used. The unreacted iodine is determined by titration with sodium thiosulphate and the SO_2 calculated from the amount of iodine used to oxidise the SO_2.

All the methods have errors associated with the interferences and the user should be knowledgeable about the method and its suitability.

2.4.2 Oxides of nitrogen

The instrumental methods given in 2.3 are preferred.

2.4.3 Carbon monoxide/carbon dioxide

These gases are generally measured by solution absorption into liquid reagents specific for each gas.

3. Emissions into Water

Whilst emissions into water are likely to be intermittent and of a low level, it is probable that any site operating an ammonia plant will have at least one overall consent for emissions into water and a requirement for plant monitoring. Typical monitoring methods may rely on flow proportioned sample collection or high frequency spot sampling and flow measurement. In either case the samples obtained may be analysed as follows:-

3.1 Ammonia/Ammoniacal N

The spectrophotometric method for ammonia relies on the reaction in which monochloramine is reacted with phenol to form an indophenol blue compound. This method is particularly suitable for the determination of ammonia in cooling waters derived from saline sources (dock, estuarine or sea water) and may be used in continuous flow colorimetry.

Ion selective electrodes can also be used and are suitable for saline applications as well as pure water.

Note that free ammonia exists in equilibrium with NH_4^+ as follows:-

$$NH_4^+ + H_2O \longleftrightarrow NH_3 + H_3O^+$$
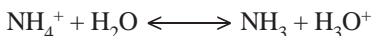
and that the equilibrium depends on pH. The above method determines the NH_4^+ ammonia. Free ammonia is particularly toxic to fish and should an incident occur, it may be more important to relate the NH_4^+ result to free ammonia. Any suitable pH determination may be used and the free ammonia estimated as given in "Hampson B L, J Cons Int Explor, Mer, 1977,37. 11" and "Whitfield M, J Mar Biol. Ass UK, 1974,54, 562".

Manual laboratory based methods may be used for spot checks using Kjeldahl methods for the determination of organic and ammoniacal nitrogen in a mineralised sample.

3.2 Methanol

The spectrophotometric method for methanol relies on the oxidation reactions of potassium permanganate under acid conditions to give formaldehyde. The formaldehyde is reacted with acetylacetone in the presence of excess ammonium salt, to form diacetyldihydrotoluidine. The method may be used in continuous flow colorimetry or gas chromatography.

APPENDIX 2 GENERAL PRODUCT INFORMATION ON AMMONIA

1. Identification

Name   : Ammonia
Commonly used synonyms   : Liquid Ammonia
C.A.S. Registry number   : 7664-41-7
EINECS Number   : 231-635-3
EINECS Name   : Anhydrous Ammonia
Molecular formula   : NH_3

2. Hazards to Man and the Environment

To man

Ammonia is toxic by inhalation and pulmonary oedema may occur up to 48 hours after severe exposure and could be fatal.

Vapours cause irritation and watering of eyes and in the presence of moisture, irritation of the skin.

Liquid ammonia splashes may produce severe burns to the skin and permanent damage to the eyes.

In enclosed spaces (eg vessels, closed workshops) ammonia vapour may be flammable/explosive.

To the environment

Ammonia is toxic to aquatic life.

3. Physical and Chemical Properties

Appearance   : Colourless liquefied gas
Odour   : Pungent, suffocating
pH water solution (1%)   : 11.7
Melting point (triple point)   : –77.7°C
Boiling point   : –33.4°C at 101.3kPa
Explosive limits   : 16-27% NH_3 by vol. in air at 0°C
Auto-ignition temperature   : 651°C
Vapour pressure   : 1013kPa at 25°C
Relative vapour density   : 0.6 (air =1)
Solubility in water   : 529g.l^{-1} at 20°C
Solubility in organic solvents   : Soluble in alcohol, acetone, chloroform
Liquid density   : 0.6386g.cm^{-3} (at 0°C, 101.3kPa)
Gas density   : 0.7714g.l^{-1} (at 0°C, 101.3kPa)

**Best Available Techniques Booklets
were first issued by EFMA in 1995
Second revised edition 2000**

1. Production of Ammonia

2. Production of Nitric Acid

3. Production of Sulphuric Acid
   (in collaboration with ESA)

4. Production of Phosphoric Acid

5. Production of Urea and Urea-Ammonium Nitrate

6. Production of Ammonium Nitrate and Calcium Ammonium Nitrate

7. Production of NPK Compound Fertilizers by Nitrophosphate Route

8. Production of NPK Compound Fertilizers by Mixed Acid Route