

Challenges & Innovations in Technology of Fertilizer Industry: NO_x Abatement Techniques

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ABSTRACT: Attempts to develop new technologies for reduction of nitrous oxide (NO_x) emissions are still carried out all around the world. However, most of them as literature survey suggests is focused on emission control from power plants and mobile vehicles. Fewer investigations are conducted on the NO_x emissions abatement from the chemical industry. While the growing concern to preserve our environment is critical to society and consumers, industries also realize additional benefits of higher production efficiency and lower costs. Current research has focused on identifying the key points of emissions in fertilizer industry by undertaking the life cycle assessment of products. Little work has been done on establishing methodologies that standardize these attempts. The results of research focuses on existing approaches, identifies commonly utilized methodologies and look beyond emissions criteria for sustainable manufacturing. This paper also discusses possible technological approaches to alleviate shortcomings in current process design in fertilizer manufacturing, focusing on NO_x emission abatement, as new techniques for the manufacturing of nitrogen (N) containing fertilizers are available that can lead to drastic reductions of NO_x emission.

KEYWORDS: NO_x emissions, abatement techniques, sustainable development, LCA, new technology.

1 INTRODUCTION

In most regions of the world N is the most important mineral nutrient for crop production and an adequate supply is essential for high yields and quality[1]. The production and application of nitrogen (N) fertilizers causes a lot of greenhouse gases emissions and is based on high energy consumption[2]. With the growing concern about climate change and environmental issues, sustainable manufacturing and efficient resource utilization are gaining popularity with significant potential in theoretical study as well as industrial applications[3]. In the near future, this might lead to a new direction in product production. Not only the price and quality of a product are increasingly important in the consumption chain, but society will increasingly focus on the sustainability of the entire production process[4].

In many studies, it was shown that fertilization is responsible for a high amount of greenhouse gases (GHG) emissions. The fertilizer industry is one of the sectors that contribute to climate change, accounting for roughly 5% of the total GHG emissions worldwide. Therefore reducing these emissions is a primary goal in order to comply with the objectives laid down in the Kyoto protocol to combat climate change.

The aim of our study was to assess the environmental management of fertilizer industry & to analyze the environmental impact of fertilizer products along the production chain. Additionally we studied different components of fertilizer industry and have accounted emissions during production process using life cycle assessment (LCA) as a tool, which also enabled us to suggest alternatives in technology that can be used in process design, in order to verify the environmental preferable one.

2 METHODOLOGY

The present study was conducted in Aonla plant of Indian Farmers Fertiliser Cooperative Limited (IFFCO), having production over 38 million tonnes of fertilizers in 2013-14 and contributed about 18.4% to the total Nitrogen and 23.4% to the total P₂O₅ produced in India. Aonla plant of IFFCO is one of the six natural gas based fertilizer plants set up in the country on the H.J.B. pipe line. This project has been designed to produce 7.26 lakhs tons of Urea per year with plant capacity of 1.148 million metric tons ammonia and 2.000 million metric tons of urea per year. The site is 28 km southwest of Bareilly on Bareilly Aonla Road in the state of Uttar Pradesh, INDIA.

A cradle-to-field life cycle assessment (LCA) for the fertilizer production chain, from extraction of raw materials, via fertilizer production, transportation and storage until final application in the field was taken into consideration [5]. Additionally, a scenario analysis was carried out focusing on nitrous oxide (NOx) emissions, as new techniques for the manufacturing of nitrogen (N) containing fertilizers are available that can lead to drastic reductions of NOx emissions.

2.1 GOAL AND SCOPE OF THE STUDY

The goal of this study was to locate the strong and weak points of fertilizer industry in overall functioning. Study will help to improved IFFCO’s environmental practice and help in whole-system optimisation for GHG emissions reduction and finding the best available techniques for pollution prevention and control in fertilizer industry.

The system boundaries are from ‘cradle to grave’, comprising the following life cycle stages: extraction of fuels and raw materials, processing and transportation of fuels; manufacture and construction of infrastructure; operation of power plants to generate electricity; construction and decommissioning of power plants and waste disposal.

A site specific life cycle inventory, LCI, was developed for an existing fertilizer plant using data collected on site visits and via discussion with plant engineers. All energy and material flows as well as emissions associated were identified and quantified in detail. Moreover, the most critical stages from an environmental point of view (hotspots) were identified and alternatives were proposed in order to reduce the impact and improve the environmental and energy profiles which also help to modify and rebuild the existing processes as well to design new methods.

2.2 EMISSIONS FROM FERTILIZER PRODUCTION

Of the major contributors, fertilizer plants contribute the most NOx to the environment resulting from fossil fuel combustion. Emissions to the atmosphere from ammonia plants include sulfur dioxide (SO₂), nitrogen oxides (NOx), carbon monoxide (CO), carbon dioxide (CO₂), hydrogen sulphide(H₂S), volatile organic compounds (VOCs), particulates, methane, hydrogen cyanide and ammonia[6]. The primary sources of pollutants (table 1), with typical reported values, for pollutants in kilograms/ton (kg/t) are as follows:

Table 1:

Flue gas from primary reformer	Carbon dioxide removal
CO ₂ : 500 kg/ton NH ₃	CO ₂ : 1,200 kg/ton
NOx: 0.6–1.3 kg/ton NH ₃ as NO ₂	
SO ₂ : less than 0.1 kg/ton	
CO: less than 0.03 kg/ton	

Emissions of ammonia have been reported in the range of less than 0.04 to 2 kg/t of ammonia produced.

In a urea plant, ammonia and particulate matter are the emissions of concern. Ammonia emissions reported as in recovery absorption vent (0.1–0.5 kg/t), concentration absorption vent (0.1–0.2 kg/t), urea prilling (0.5–2.2 kg/t) and granulation (0.2–0.7 kg/t). The prill tower is a source of urea dust (0.5–2.2 kg/t), as is the granulator (0.1–0.5 kg/t).

2.3 CURRENT EMISSION CONTROL TECHNIQUES

The Indian fertilizer industry also kept pace with the fast developments in fertilizer technology taking place elsewhere in the world. Cleaner technologies, improved design features and innovative measures are adopted to conserve resources and minimize pollution. Retrofitting and revamping of the existing plants, process modifications, recovery of valuable

products, substitution of toxic materials with nontoxic materials, *etc.*, have helped in achieving cleaner production. The best available techniques being used in fertilizer production include:

- Low pressure ammonia synthesis loop for hydrogen recovery
- Membrane based methane recovery from the methanator
- CO₂ removal using physical absorption processes and solvents such as selexol
- Use of high efficiency catalysts like caesium for improving efficiency of SO₂ to SO₃ conversion
- Low NO_x burner & catalytic reduction techniques for reducing NO_x in the tail gas
- CO₂ recovery plant to tap CO₂ from flue gases & to increase urea production
- Hydrolyser stripper for recovery of urea, NH₃ and CO₂ and conserve water through recycling of treated water along with purge gas recovery (PGR) unit
- S-50 converter with new horizontal boiler and steam drum to save energy
- Use of non-chromate based cooling water treatment
- Adoption of dual pressure process (high pressure absorption and medium pressure oxidation) for ammonia production to improve production efficiency
- Multi-stage scrubbing system for reduction of ammonia /particulate matter /fluoride, *etc.* & scrubbing of off-gases with process condensate prior to venting inerts to atmosphere
- Installation of high efficiency cyclones for reduction in dust emission & wet scrubbing of prill tower and granulation plant air to recover urea and NH₃
- Dry de-dusting system along with bag filtration of dust laden air from transfer points, screens, bagging machines, *etc.* coupled with a dissolving system
- Flash melting of solid urea over-size product for recycle to the process

3 RESULTS & DISCUSSION

Several technical solutions for the reduction of NO_x emissions in fertilizer plants have been discussed during the last few years. It is difficult to develop alternative technology for total elimination of NO_x generation [6]. Accordingly, less polluting technologies have emerged for reducing NO_x in exhaust air from the Sulfuric/ Nitric/Ammonia/ Phosphate/ Nitro-Phosphate plants. The results of the study identifies techniques for abatement of NO_x emissions, few out of these techniques are currently being practiced in different fertilizer plants.

3.1 NO_x EMISSION ABATEMENT TECHNOLOGIES

NO_x control techniques operate either through suppression of NO_x formation or through physical or chemical removal of NO_x from stack gases. The types of control technology which are currently available is divided into two (1) Primary measures or combustion control, also called clean techniques and (2) Secondary measures or post combustion control, also called clean up techniques or flue gas treatment[7]. Depending upon the stages in the process, the approaches of lowering NO_x & N₂O from fertilizer plants can be classified into three groups:

- Primary: preventing NO_x from being formed in the ammonia burner
- Secondary: removal of N₂O from NO_x gases between the ammonia converter and the absorption column.
- Tertiary: removal of NO_x from the tail gas downstream

3.1.1 TECHNOLOGIES FOR PRIMARY ABATEMENT

The catalytic oxidation of ammonia over platinum-rhodium gauzes takes place through several reaction paths depending on the temperature. Under current industrial operating conditions, the process yields up to 97% NO, the desired product in nitric acid production. Although the process is well established, optimising the NO selectivity by improving the catalyst, reactor design and operating conditions are considered as part of primary abatement along with changes in the geometry and configurations of gauzes as well as the development of oxide-based catalysts [8].

3.1.2 TECHNOLOGIES FOR SECONDARY ABATEMENT

THERMAL DECOMPOSITION:

Norsk Hydro developed a reactor technology based on the thermal gas phase decomposition occurring down-stream from the reactor chamber[9]. The technology has been implemented in an acid plant in Porsgumn, Norway.

CATALYTIC DECOMPOSITION:

The catalytic reduction of N₂O include the decomposition of N₂O into N₂ and O₂ over various types of noble metal, metal oxide and mixed oxide catalysts. However, an ideal catalyst is one that satisfy the N₂O reduction target of >90% under severe oxidising environments at high temperature and pressure and with a minimal loss of NO.

Norsk Hydro patented a series of catalysts comprising Co_{3-x}M_xO₄ where M=Fe or Al and x= 0 to 2 supported on CeO₂. The presence of a small amount of ZrO₂ was reported to prevent the degradation of catalyst activity[10]. This catalyst is claimed to be non-NO destructive and thermally stable, which can be applied over a wide temperature and gas composition range, in the presence of oxygen and water vapour.

A Ce-Co catalyst was commercialised by Yara International as Yara 58-Y1. It contains >80% cerium oxide, <1% cobalt (II, III) oxide and <1% aluminium cobalt tetraoxide [11]. This catalyst is claimed to be able to achieve upto 90% N₂O conversion and has been installed in 11 Yara plants and 11 locations under the clean development mechanism (CDM) or joint implementation (JI) countries as defined by the Kyoto Protocol[12].

Hermsdorfer Institut Für Technische Keramik (HITK) has produced and patented a ceramic based catalyst consisting of metal oxides such as Cr, Mn, Fe, Co, Ni, Cu and La on a porous ceramic support[13], which claims 100% N₂O conversion at temperature above 800°C.

3.1.3 TECHNOLOGIES FOR TERTIARY ABATEMENT

The tail-gas, leaving the absorber column, contains N₂O, NO_x, O₂ and H₂O at temperatures from 523-773K at pressures of 3-13 bar[14].

Uhde has developed a system for the removal of N₂O and NO_x from the tail gas of nitric acid plants under the trade name EnviNO_x[®][15]. The system features a tail gas reactor consisting of two beds of iron-zeolite catalyst with intermediate ammonia injection installed directly upstream of the tail gas turbine. The EnviNO_x[®] catalysts are manufactured by Süd-Chemie with brand names EnviCat[®]-N₂O and EnviCat[®]-NO_x. The system was first implemented in 2003 in a 1000 Mt/day dual-pressure nitric acid plant by AMI in Linz (Austria)[15] and still operates at an efficiency of 98%[16].

The Energy Research Center of the Netherlands (ECN) has developed a combined catalytic technology for the removal of NO_x and N₂O based on selective catalytic reduction (SCR) using propane as a reducing agent. Iron and cobalt-containing zeolites are placed in series in a single reactor operated at pressure upto 10 bar. The conversions of N₂O and NO_x ~ 90% was achieved[17].

In 2006, ECN tested a trimetallic zeolite-based ECN catalyst at nitric acid plant in Ijmuiden, the Netherlands. This catalyst requires no addition of a reducing agent. It can be operated at temperatures of 475-525°C and at pressures of 1-12 bar, with N₂O conversion efficiency of 70-95%.

N.E. Chemcat has developed a catalyst named DASH-30D D812. The catalyst consists of palladium supported on alumina silica and magnesium oxide and has been installed in many plants like Caprolactam production plant in Thailand and nitric acid plant of Kaifeng Jinkai Chemical Ind. Co., Ltd, China[18] and is found to have an efficiency of 80-90%.

3.1.4 NO_x CONTROL TECHNOLOGIES FOR COMBUSTION PROCESSES

In combustion processes, NO_x is formed due to the oxidation of fuels like coal, residual oils and natural gas which produce NO_x in significant amounts.

The most common NO_x control technology for the combustion process is *Low-NO_x burners (LNB)*, used separately or in combination with post-combustion control technologies like catalytic reduction and involves the modification of the process into a two stage combustion process: a fuel-rich zone where primary combustion takes place and a fuel-lean zone for secondary combustion at lower temperature. LNB technology affords up to 60% reduction for the combustion process[19].

Selective Non-Catalytic Reduction (SNCR) and Selective Catalytic Reduction (SCR) are based on the chemical reduction of NO_x molecules into molecular nitrogen (N₂) and water vapour (H₂O) by a nitrogen-based reducing agent such as ammonia or urea. In these processes the reducing agent is injected into the post-combustion flue gas stream and heat from the boiler provides the energy for the reduction reaction, except that SCR has a solid catalyst bed installed downstream of the combustion chamber. NO_x reductions upto 90% can be achieved by optimising the reactor design and operation such as ammonia dosage and mixing[20]

Another technique offered is the hybrid SNCR/SCR concept, which uses the excess ammonia (ammonia 'slip') of the SNCR to promote additional NO_x reduction in a downstream SCR catalyst and to compensate for the reduction of flue gas temperatures, a Regenerative Selective Catalytic Reduction (RSCR™) System is used which allows the efficient use of an SCR downstream of a particulate control device. The primary application of an RSCR system is the reduction of NO_x emissions taking place on a conventional SCR catalyst using anhydrous or aqueous ammonia, where the flue gas is typically at 300-400°F[21]. Additionally, some oxidation of CO to CO₂ in the flue gas occurs.

The RSCR also combines a regenerative thermal oxidizer (RTO) (e.g., retention chamber burner) with SCR technology, having an ability to control flue gas temperatures, allowing high NO_x reduction under varying temperature conditions[22]. The RSCR is able to reduce NO_x by 60 to 75% and CO by about 50%.

Another technologies such as Over-fire Air (OFA) and Reburn can also prove to be efficient in reducing NO_x emissions upto 5-55% or even higher.

Reburn, destroys or chemically reduces NO_x shortly after it is formed rather than minimizing its formation, simply by introducing the reburn fuel (natural gas) into the boiler above the main burner region. A portion of the heat input from the primary fuel is replaced by the reburn fuel. Subsequently, this 'fuel-rich' environment reacts with and destroys the NO_x formed in the main burners. One important feature of reburn is its compatibility with a particular type of boiler – 'Cyclone' – for which the previously mentioned technologies are not well suited. Reburn performance has been shown to range from 30 to 60% reduction in NO_x emissions.

Over-fire air(OFA) offers NO_x reductions upto 30 to 65% by minimizing the formation of NO_x during combustion and by controlling the quantities and the way in which fuel and air are introduced and mixed in the boiler (usually referred to as 'fuel or air staging'). These technologies are prevalent in the electric power industry and in ICI boilers at present.

4 CONCLUSIONS

All industries are moving towards more efficient and low or zero emission processes due to economic benefit, regulation and concern for the environment. New materials and process technologies are playing an important role in emission treatment and by-product utilisation. This research has focussed on technologies that offer the highest efficiencies and lowest emissions including physical and chemical mechanisms in industrial production. Results show that different technologies offers innovative options for mitigating emissions at production level, some are even 90% efficient and should be promoted in order to deal with the increasing NO_x emissions in all countries.

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