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Effluent stream treatment in a nitrogenous fertilizer factory: An exergy analysis for process integration

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ABSTRACT

The industrial processes used for the production of nitrogenous fertilizers are the main generators of reactive nitrogen compounds, chemicals and effluents that ultimately impact the biosphere. Exergy analysis has been performed to a nitrogen fertilizer factory in the State of Bahia, Brazil, where the Anaerobic Ammonium Oxidation (Anammox) and other physical–chemical processes are used to partially or totally handle the feed streams normally sent to a stripping tower.

The results showed that the combined use of physical–chemical and biological process can improve the overall exergetic efficiency and avoid the emission of reactive compounds to the atmosphere allowing the recovery of the condensate lost as effluent, so that it can be reincorporated in the production of steam network, increasing energy efficiency and environmental performance of the process.

Keywords: Nitrogen; Ammonia; Fertilizer plant; Exergy analysis

1. Introduction

Since the industrial revolution, anthropogenic processes have changed the environment on a global basis. Rockström et al. (2009) showed that three processes at global level have violated the boundaries that define a safe operating space for humanity in relation to the earth's system: climate change, rate of biodiversity loss and interference with the nitrogen cycle due to the removal of atmospheric N_2 to generate reactive nitrogen species for human use (ammonia, urea, nitrates, etc.). Extensive agriculture is the main vector of environmental contamination by these species (Galloway et al., 2004), contaminating rivers, coastal and terrestrial systems, stimulating the production of gases by microorganisms that also have an impact on global warming. For instance N_2O is over 296 times more impacting per unit of weight than CO_2 (Crutzen et al., 2007).

The manufacturing processes of fertilizers fix around 120 million tons of atmospheric N_2 into reactive forms per year, and this amount is larger than all natural processes combined (Galloway et al., 2004). The contribution of the industrial unit studied in this paper, a nitrogenous fertilizer factory in the State of Bahia, Brazil accounts for around 0.40% of this total. This implies the estimate of 250 fertilizer plants of the same size in the world. To solve this excessive anthropogenic input of reactive nitrogen, Rockström et al. (2009) have suggested reducing of the current amount of N_2 fixation by about 75% to return to a safe limit for humanity. This means a production of about 30 million tons per year of reactive N_2 compounds. This analysis does not consider the process operations where

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Nomenclature

$\frac{dE_{cv,sys}}{dt}$	rate of exergy change in the system (kW)
$\dot{Q}_j$	rate of heat transfer in the system (kW)
T_0	reference ambient temperature for exergy (considered here 298 K)
T_j	temperature of the "j" process (K)
$\dot{W}_{cv}$	rate of energy transfer by work in the system (kW)
p_0	reference pressure (1 bar)
$\frac{dV_{cv}}{dt}$	volume change of the system (L)
$\dot{m}_i e_{fi}$	rate of exergy change related to the inlet mass flow (kW)
$\dot{m}_e e_{fe}$	rate of exergy change related to the outlet mass flow (kW)
$\dot{E}_{Ch}$	rate of chemical exergy change (kW)
$\dot{E}_D$	rate of destruction of exergy due to the irreversibilities inside the control volume (kW)
T	temperature (K)
h	specific enthalpy (kJ/kg)
s	specific entropy (kJ/kg K)
g	gravitational acceleration (9.8 m/s^2)
z	height (m)

flue gases or liquids emit considerable amounts of reactive nitrogen species into the environment. Reducing the current fixation of nitrogen by man by 25% is unrealistic in the short term, but a reduction in industrial emissions may be more feasible and will improve energy efficiency as well as the environmental performance of such processes.

Fertilizer plants generate multiple effluents from the process of getting products such as ammonia, nitric acid, hydrogen, carbon dioxide and urea, with significant loads of reactive nitrogen, usually present as ammonium. In this case study, most of these effluents are sent to a stripping tower (Fig. 1), which operates with multiple inputs, primarily *process condensate effluent stream*, *CO_2 station effluent stream* and other minor sources. Other minor sources are discontinuous streams containing ammonia and methanol. The *CO_2 station* means the CO_2 compressor facilities, outside the battery limits.

This combined stream is treated with low pressure steam (0.35 MPa) volatilizing and sending compounds such as ammonia and methanol into the atmosphere, about 500 and 100 ton/year, respectively. In the stripping process a new effluent is generated still containing reactive nitrogen and methanol. The latter is finally sent to a treatment plant to be disposed of in the environment at concentrations that are within the prevailing environmental limits. This practice has been applied to date, but the use of stripping towers is considered an outdated technology, an "end of pipe" treatment without attacking the problem at the source, and without thinking about the reuse of these reactive nitrogen species and water which is being wasted. Applying the concepts of clean technologies will lead to the segregation, reduction, treatment and reuse of the wastewater with considerable environmental and economic gains.

Bioprocesses for treating wastewater with high nitrogen loading have been developed and used industrially, such as: SHARON, Anammox, InNitri, BABE, MAUREEN, Oland, and CANON (Abma et al., 2006, 2007; Ahn, 2006; Third et al., 2001).

The Anammox process (Anaerobic Ammonium Oxidation) was chosen for this study due to the advantages it presents when compared to other technologies such as: (a) higher treatment capacity (more than 6-fold in comparison to other technologies, 6–12 kg of nitrogen/m^3/day); (b) no need for external carbon source; (c) very low sludge production; (d) lower power consumption (around 1 kWh/m^3 effluent) and is a consolidated technology, commercially available, with several plants in operation worldwide (http://en.paques.nl/pageid=66/ANAMMOX%C2%AE.html, 03-26-2013).

This process consists of the oxidation of ammonia and nitrite in nearly equal proportions generating gaseous nitrogen and nitrate formation with low biomass production (Eq. (1)), using microorganisms of the group *planctomyocetes* (Strous et al., 1998; Ahn, 2006).

$$1\,NH_4^+ + 1.32\,NO_2^- + 0.66\,HCO_3^- + 0.13\,H^+ \rightarrow 1.02\,N_2 + 0.26\,NO_3^- + 0.66\,CH_2O_{0.5}N_{0.15} + 2.03\,H_2O \quad (1)$$

Exergy balances are useful to calculate the exergy destruction of the system components and identify the thermodynamic inefficiencies, and therefore can help in choosing the best available technology (Wall and Gong, 2001; Tsatsaronis and Cziesla, 2004). Changes of exergy are not necessarily equal to the gross exergy transferred, as this may be destroyed due to irreversibilities in the system during operation (Moran and Shapiro, 2006).

The purpose of this study was to evaluate the use of Anammox technology combined with some physicochemical processes through mass, energy and exergy balances in the system that involves the stripping tower in a nitrogenous fertilizer factory located in Camaçarí, in the State of Bahia, Brazil, to achieve environmental gains. Two potential solutions were analyzed, one of which eliminates the use of the current stripping tower, preventing atmospheric emissions and minimizing the generation of reactive nitrogen effluents.

2. Materials and methods

2.1. Characterization of the streams

Physicochemical characterization of the streams entering and leaving the stripping tower were made in the laboratories of the industry in Camaçari, Bahia, Brazil, determining the pH, flow rate, temperature, concentration of ammonia (mg/L) and methanol (mg/L).

2.2. Cases for analysis

Three cases were analyzed:

Case 1: Actual operation: treatment of the streams *process condensate effluent* and *CO_2 station effluent* by the use of a stripping tower. This generates two streams (Fig. 1): a gas that goes into the atmosphere containing ammonia and methanol and a liquid with methanol and ammonia that goes (after mixing with other streams) to the effluent treatment plant of the petrochemical complex of Camaçari. The process consumes energy in the form of saturated steam at 0.35 MPa. To carry out a comparative analysis in terms of exergy balance, the effluent generated by the stripping tower was hypothetically used to