Energy 36 (2011) 3733–3744

Contents lists available at ScienceDirect

Energy

journal homepage: www.elsevier.com/locate/energy

Application of the exergy method to the environmental impact estimation: The nitric acid production as a case study

Zornitza Kirova-Yordanova*

University "Prof. Assen Zlatarov", Department of Inorganic Technology, 8010 Bourgas, Bulgaria

ARTICLE INFO

Article history:
Received 28 March 2010
Received in revised form
9 December 2010
Accepted 17 December 2010
Available online 11 February 2011

Keywords:
Exergy
Cumulative exergy consumption
Environment
Emissions
Nitric acid
Tail gas

ABSTRACT

In this work the exergy method is used to compare various methods for removal of NO_x from waste (tail) gas released into the atmosphere from nitric acid production plants with respect to their overall environmental impact. Three basic methods for NO_x abatement are analysed: selective catalytic reduction (SCR), non-selective catalytic reduction (NSCR) and extended absorption. The positive and negative effects and the net effect from the NO_x abatement are calculated. The following exergy-based indicators are used for comparing the energy efficiency and the environmental impact of different treatment processes as a result from pollutants removal: reduction of the exergy of the emissions from the whole process route (ammonia and nitric acid production units); exergy of the additional emissions, arising as a result of the treatment process; total net reduction of the exergy consumption, Cumulative Energy Consumption (CEnC) and Cumulative Exergy Consumption (CExC) of natural resources as a result of the waste flows treatment.

1. Introduction

Nitric acid is one of the basic industrial chemicals with annual world production of about 50 million metric ton/year (100% basis). Around 80% of nitric acid is produced as "weak acid" (50–69%) and is used in fertilizers production. The major products of nitric acid-based fertilizers industry are ammonium nitrate (AN), calcium-ammonium nitrate (CAN), urea-ammonium nitrate solutions (UAN) and some kinds of complex NP and NPK fertilizers (nitrophosphates).

The weak nitric acid production is based on three main chemical processes: catalytic oxidation of ammonia in air to nitric oxide, homogeneous oxidation of NO to NO_2 and absorption of NO_2 in water. Due to the specificity of these chemical reactions, two main features exist in nitric acid plants: environmental problems, ensuing from N_2O and NO_x presence in the waste gas (referred as "tail gas") and high energy recovery, making nitric acid production process a very interesting subject of Second-Law-based analysis and optimization investigations.

After the original work of Riekert [1], a comprehensive exergy analysis of a relatively old kind of nitric acid production plant is presented in the book of Szargut, Morris and Steward [2]. Sama et al. [3], Gaggioli et al. [4] use the exergy method to optimize the energy recovery and energy integration of a modern nitric acid plant.

In a previous work of the author [5], the results from an exergy analysis of two modern dual pressure plants are presented, complemented by the cumulative exergy consumption (CExC) analysis. A comparison is made with reference data from available publications. In the same paper, as well as in some subsequent publications of the author [6], the exergy method and the concept of cumulative exergy are used to estimate the efficiency of energy recovery and energy integration in nitric acid plants.

However, the tail gas treatment processes used in nitric acid production plants have still not been studied from a thermodynamic point of view.

A Second-Law-based analysis of waste flows treatment processes raises some problems, being the first of them the estimation of the overall effect from a treatment process.

As the overall effect is the difference between positive and negative effects, it could be positive or negative.

The positive effect is the reduction of the emitted pollutants. If the pollutants are recycled back to the production process, the positive effects would include also the reduction of the feedstock and energy consumption and the respective reduction of the emissions from the intermediates and energy production.

The treatment processes, as a rule, require some additional chemicals and energy (heat, power) consumption. In consequence,

* Tel.: +359 56 858274, +359 0899 195613 (mobile); fax +359 56 880249.
E-mail addresses: zkirova@btu.bg, zornitzakirova@yahoo.co.uk.

0360-5442/$ – see front matter © 2010 Elsevier Ltd. All rights reserved.
doi:10.1016/j.energy.2010.12.039

Nomenclature

BAT	Best available techniques
CDP	Cumulative degree of perfection
CEnC	Cumulative energy consumption
CExC	Cumulative exergy consumption
D	Exergy losses
E	Exergy
EA	Extended absorption
GHG	Greenhouse gases
HP	High pressure
LP	Low pressure
MP	Middle pressure
NSCR	Non-selective catalytic reduction
SCR	Selective catalytic reduction

some additional emissions are produced, mainly GHGs (CO_2). The additional consumption of the natural resources and the additional emissions constitute the negative effects of a treatment process.

Thus, the analyzed system should include not only the treatment process itself and not only the production process from which the waste flows are emitted, but the thorough technological chain, from feedstocks through intermediates and utilities to the final product.

In order to estimate the overall effects from the treatment processes in this work a building block model and a top-down approach are used [7,8].

This approach not only analyzes the emissions from the studied process but also the emissions from all the preceding processes in which intermediates are produced, as well as the emissions from the utilities (power plant and/or separate steam boiler) in the production site. As the emissions from these processes are rather different, the total mass rate of the emissions (incl. pollutants and GHGs) is not representative; also the application of some weight coefficients is not well-grounded.

Therefore, the second problem is how to express the positive and negative effects from a treatment process by some thermodynamic-based quantities.

As exergy is by definition connected with the environment, it could be an appropriate measure of the environmental impact of some human activities, especially process and power industry, transport, etc., which use fuels, ores, minerals, water, air, etc. from the nature and release gaseous and liquid emissions and solid wastes into the environment. The relationships between exergy and environment concern both the consumption of natural resources and the impact of emissions and wastes on the environment. The Cumulative Exergy concept [2] has been used for many years as an useful approach for evaluation of the overall consumption of all kinds of natural resources at every step of a production process.

However, whether exergy could be used as a measure of the impact of the emissions and wastes on the environment, is still an open problem. There are many difficulties, ensuing from the fact, that the thermodynamic environment is not identical to the real environment, which is much more complex and multiform. Many authors propose various approaches, concerning different aspects of the environment and exergy nexus: Ayres [9], Rosen [10], Valero and Botero [11], Cornelissen [12], Gong and Wall [13], etc.

The total chemical exergy of the emissions and GHGs would be a more acceptable criterion, because the potential of the emissions to damage the environment, depends mainly on their chemical composition and especially, on the concentrations and properties of the pollutants [14]. However, in most cases there is no direct correlation between the chemical exergy of the pollutants and their impact on the various components of the environment.

Therefore, the most useful information could be obtained by comparing the exergy consumption and the cumulative exergy consumption in the analyzed processes for emissions abatement, including all the preceding processes in which intermediates and utilities are produced. In a recent paper [8] this approach was applied to the ammonium nitrate production process and was used to compare different processes for waste flows treatment and pollutions abatement.

The aim of this work is to use the exergy method and the cumulative exergy concept in order to estimate and compare the overall net effects of three basic methods for NO_x emission removal from the nitric acid production process: extended absorption, selective catalytic reduction (SCR) and non-selective catalytic reduction (NSCR). Exergy balances of the tail gas treatment subsystems are calculated and the results are compared. A set of various Second-Law based indices is defined and used to estimate the thermodynamic cost and benefits of the tail gas treatment, including the natural resources consumption and the pollutants and GHGs emissions from the whole technological chain of the nitric acid production.

The structure of the building block model of the analyzed system includes production of ammonia as an intermediate, and also a steam and power plant (Fig. 1). The accumulated reduction and rise of the emissions are calculated by tracing out from the nitric acid plant back down to the ammonia unit and also to the steam and power plant.

2. Nitric acid process background

Catalytic oxidation of ammonia in air to nitric oxide (NO) and water is carried out on Pt/Rh alloy catalyst gauzes at 800–950 °C :

$$NH_3 + 5/4O_2 = NO + 6/4H_2O_{(g)} + 226.3\ \text{kJ} \tag{1}$$

However, only 93–98% of ammonia is converted to NO by the main reaction (1); the balance is converted to nitrogen and nitrous oxide (N_2O) by two undesired side reactions:

$$NH_3 + O_2 = N_2O + 6/4H_2O_{(g)} + 276.2\ \text{kJ} \tag{1a}$$

$$NH_3 + 3/4O_2 = N_2 + 6/4H_2O_{(g)} + 317.3\ \text{kJ} \tag{1b}$$

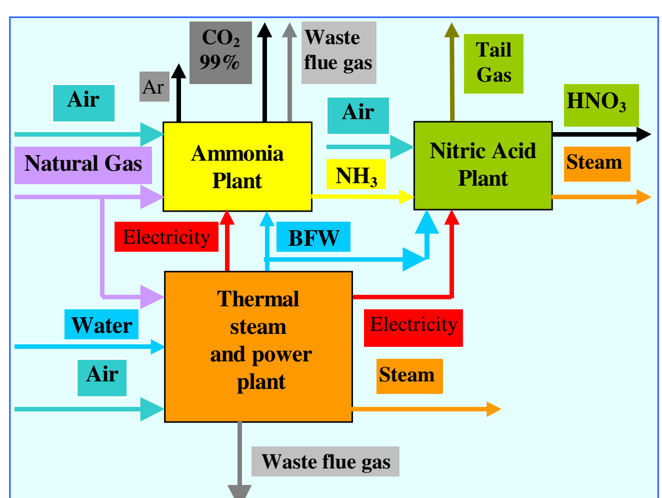

Fig. 1. Block flow diagram of a weak nitric acid production site.