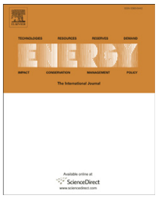
ARTICLE IN PRESS

Energy xxx (2016) 1–20

Contents lists available at ScienceDirect

Energy

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



On the efficiency, exergy costs and CO_2 emission cost allocation for an integrated syngas and ammonia production plant

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A R T I C L E I N F O

Article history:
Received 23 October 2015
Received in revised form
5 May 2016
Accepted 21 May 2016
Available online xxx

Keywords:
Ammonia production
Renewability
Exergy cost
CO_2 emissions
Exergy efficiency

A B S T R A C T

This paper presents an exergy and environmental assessment of a 1000 metric t/day ammonia production plant based on the steam methane reforming (SMR) process, including the syngas production, purification (CO_2 capture) and compression units, as well as the ammonia synthesis and purge gas treatment. An integrated heat recovery system produces power and steam at three pressure levels, besides exporting hot water, CO_2 and fuel gas, with no additional heat or power consumption being required. Two configurations for ammonia refrigeration process (−20 °C) are compared in terms of power consumption. Exergy cost data for upstream processing stages of natural gas is used to calculate the extended exergy cost of the products of the plant, namely ammonia, CO_2 and fuel gas. Moreover, an appropriated methodology is employed to properly allocate the renewable and non-renewable exergy costs, as well as the CO_2 emissions of the reforming, shift and furnace stack among the products of the plant. By considering that the cost reduction of the combustion gases is a linear function of the exergy flow rate reduction in each component of the heat recovery system, an improved allocation of the CO_2 emission cost along the convection train is performed. A breakdown of the total exergy destruction rate of the plant (136.5 MW) shows that about 59% corresponds to the reforming process followed far behind by the ammonia synthesis and condensation (18.3%) and the gas purification units (13.2%). The overall exergy efficiency of the ammonia plant is calculated as 66.36%, which is enhanced by recovering the hydrogen-rich and fuel gases in the purge gas treatment process. The total and non-renewable exergy costs and CO_2 emission cost of the ammonia produced are calculated as 1.7950 kJ/kJ and 0.0881 kg_{CO2}/MJ, respectively. In addition, a rational exergy cost of 1.6370 kJ/kJ and CO_2 emission cost of 0.0821 kg_{CO2}/MJ are allocated to the CO_2 gas, which can be supplied as feedstock to an associated chemical plant (urea, methanol, polymers, etc.).

1. Introduction

Some fundamental mineral nutrients limiting the vegetal growing, e.g. carbon and oxygen, can be easily obtained by the plants through the soil and the surrounding air. Others, like nitrogen, must be first fixed into plant-accessible forms, e.g. synthetic nitrogen fertilizers (SNF)[1] [1], which currently are thought to be responsible for at least 50% of crops yield [2]. In fact, alongside the population growth, the world nitrogen fertilizers demand (as N) is expected to increase more than 5.8 million of metric tons between 2014 and 2018 [3], with the largest annual growth rate in the Americas expected in Latin America (3.27%), especially in Brazil [4]. However, regardless of the large production volumes, the national fertilizer industry has not enough capacity for supplying the total demand and, thus, more than 60% of the national SNF consumption must be imported [5]. The fact that the growth in demand for fertilizers has surpassed Brazilian production capacity makes the country vulnerable to variations in prices in the international markets, natural gas prices, shipping costs and logistical problems at Brazilian ports [6]. Technological and economic lags are partly, but not exclusively, due to existent plants still based on low efficiency technologies. Aiming to reduce foreign dependence to only 13% in 2020 [7], further investments in the construction of new plants or revamping old ones are envisaged [5,7–9]. Besides, considering that steam methane reforming (SMR) is the most cost-

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[1] The products classified in the category of SNF include ammonia, urea, ammonium nitrate and some others straight (calcium nitrate, ammonium sulfate, etc.) and complex (ammonium phosphates, nitro-phosphates, etc.) fertilizers.

http://dx.doi.org/10.1016/j.energy.2016.05.096

Please cite this article in press as: Flórez-Orrego D, de Oliveira Junior S, On the efficiency, exergy costs and CO_2 emission cost allocation for an integrated syngas and ammonia production plant, Energy (2016), http://dx.doi.org/10.1016/j.energy.2016.05.096

efficient technology for ammonia synthesis due to the relative gas availability, higher H_2/CO ratios and lower energy use [10]; recent natural gas discoveries in the Pre-salt region may also help to stabilize SNF production, to decrease the external dependence and the internal price fluctuation. Yet, the technological and logistical adaptations to extract that natural gas are still expensive [11]. Aside from those economic aspects, the environmental performance of chemical processes also became a growing awareness in industry in the last decades and SNF plants have continuously deserved more legal surveillance [12]. However, in spite of the existing regulatory policies, unclearly defined limits render the impact quantification difficult and in some cases the mitigation unprofitable (e.g. in post-combustion CCS for flue stacks) [8]. For instance, if ammonia is used for urea manufacture, then a fraction of the process by-products such as CO_2 gas from desorber vent are no more emitted to the atmosphere, but recovered and recycled as feedstock, whereas liquid process condensates are typically purified and recycled, decreasing both the energy consumption and wastes, which should be accounted for in the whole environmental analysis.

Over the last few years, SNF technology has undergone radical developments in terms of both design and equipment. The efforts have mainly focused on reducing power and feedstock consumption [13], improving the heat recovery network [14–20], minimizing stack losses, cutting energy consumption for CO_2 removal [21–23] and designing better and more active catalysts (Ru-based) [13,24–27]. Exergy and environmental analyses on SMR process, ammonium nitrate and nitric acid plants have also been performed [28–31]. More recent studies carried out the thermo-environomic analysis of ammonia production [32]. Notwithstanding the level of energy integration and recent developments in modern ammonia plants, the specific exergy consumption has not been reduced radically so far. In fact, it is noteworthy that the minimum theoretical exergy consumption in ammonia plants is still much lower (18–21 GJ/t_{NH3}) [33] than the best figures reported in the literature (28–31 GJ/t_{NH3}), which vary widely with local conditions and project-specific requirements [13,31]. Thus, according to The European Roadmap of Process Intensification (PI - PETCHEM), the potential benefits in the ammonia production sector are significant: 5% higher overall energy efficiency for the short/midterm (10–20 years) and 20% higher (30–40 years) for the long term [34]. Clearly, better developments will be subjected to economic aspects, but increasing the efficiency of domestic production's share could be the first step towards the reduction of the large non-renewable exergy consumption and environmental impact that SNF industry is responsible for. Accordingly, in this work, exergy is used to analyze an integrated syngas and ammonia production plant in order to quantify the exergy efficiency and destruction in each unit. Even though energy-based Life Cycle Analyses has been previously reported for the Brazilian SNF scenario [35], neither unit exergy costs nor specific CO_2 emission cost allocation have been performed. Thus, by using an appropriated methodology, the renewable and non-renewable unit exergy costs and the CO_2 emissions, arisen from the combustion furnace, as well as from the reforming and shift reactions in the SMR facilities, are allocated among all the products of the plant. Also, due to the interplay among the various processing units with the heat recovery network and the utilities plants, major attention is given to the exergy cost and CO_2 emission cost allocation in the convection train of the reformer.

2. Methodology

In this work, the exergy method is used for defining indicators to assess the performance of the processes present in an integrated syngas and ammonia production plant. In the following sections, the main definitions, as well as the exergy cost allocation methodology and the efficiency calculation criteria are presented.

2.1. Exergy calculation

In the last decades, several tools based on the First and Second Laws of Thermodynamics have been developed for defining indicators to assess the performance of chemical and industrial processes. The combination of these two laws led to the concept of *exergy*. Exergy is defined as the maximum available work that can be obtained from a thermodynamic system through its interaction with the environment by means of reversible processes until the equilibrium state (mechanical, thermal and chemical) with the environment components is attained [36]. In this work, the reference ambient parameters (pressure, temperature and composition) considered for calculating exergy correspond to those reported by Ref. [36] as 1 atm and 25 °C. Total exergy accounts for potential (P), kinetic (K), thermo-mechanical or physical (PH) and chemical (CH) exergy components, each one calculated by using Eqs. (1)–(4), respectively:

$$B^K = 1/2mv^2 \tag{1}$$

$$B^P = mgz \tag{2}$$

$$B^{PH} = H - H_O - T_O(S - S_O) \tag{3}$$

$$B^{CH} = n_{mix}\bar{b}^{CH} = n_{mix}\left[\sum_i y_i b_i^{CH} + R_u T_O \sum_i y_i \ln \gamma_i y_i\right] \tag{4}$$

The terms y_i and γ_i in Eq. (4) are the mole fraction and the activity coefficient of component *i* in the mixture, respectively, and b_i^{CH} is the standard chemical exergy of component *i*. Equation (4) is especially useful when calculating the chemical exergy of gaseous fuels whose composition can be readily determined and thermochemical data for the components are thoroughly reported. However, solid and liquid industrial fuels and other substances are often solutions of numerous chemical compounds of, usually, unknown nature. Therefore, by assuming that the ratio of chemical exergy to the lower heating value ($\varphi = b^{CH}/LHV$) is the same for pure chemical substances having the same ratios of chemicals constituents (H/C, O/C, N/C), Szargut and Styrylska derived correlations expressing the dependence of φ on those atomic ratios [36].

Since the integrated syngas and ammonia production plants are complex multi-component/multi-phase systems, Aspen HYSYS® simulation software is used to determine the thermodynamic and transport properties of each flow by using Peng-Robinson and Soave-Redlich-Kwong equations of state, as well as proprietary Acid Gas® fluid package. Additionally, as the previous tool only provides the result of mass, energy and entropy balances, thus molar physical and chemical exergies of each stream must be calculated by programming *scripts* as *user defined functions* in Aspen Hysys® environment [37].

2.2. Exergy cost balances

As long as exergy stands for the useful energy required for an economic activity to be accomplished, it is reasonable to evaluate the cost of the energy on the basis of its exergy content [38]. Besides, as exergy can be considered as measure of the departure of the environmental conditions, it also serves as an indicator of environmental impact, taking into account both the efficiency of supply chain (from primary exergy inputs) and the efficiency of the production processes (e.g. syngas and ammonia plants) [39]. In this

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