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Energy optimization of a network of exchangers-reactors in a nitric acid production plant

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The aim of this work is to improve heat recovery in a nitric acid production plant using process integration. The studied plant produces 1340 tons of 58 % nitric acid per day and the necessary data is taken from its current operating state. Using collected data, the simulation of the process was conducted considering that the reactions continue to occur in pipes, which are regarded as adiabatic plug flow reactors and heat exchange is achieved in counter-current multitubular heat exchangers-reactors. The simulation results allowed to establish the exergy balance of the process and to identify the main zones of energy degradation. The analysis showed that the total exergy losses in the heat recovery exchanger network are about 20 MW and its overall exergetic efficiency is about 93 %. Energy degradation was found to be primarily localized in the water-cooled condenser of the low pressure reaction and in the gas-gas exchangers. Moreover, the application of pinch technology made it possible to estimate the pinch temperature and to determine the minimum consumption of hot and cold utilities. Finally, different solutions were suggested to minimize utility consumption in the studied plant.

1. Introduction

Many industrial processes are basically processes of energy conversion. The considerable energy requirements of an industrial unit make it necessary to pay close attention to energy consumption and to the development of a convenient method for its estimation. Energy use can be determined effectively by considering both the first and the second law of thermodynamics, that is, by applying the concept of exergy. In this concept (Esciubba (2007), Ploumen (2001)), the quality of energy and its degradation in real processes is accounted for. The traditional approaches for energy optimization are useful for improving the efficiency of individual equipments. However, these methods remain insufficient to guide us in the optimization of the total configuration of the system. In fact, various thermodynamic systems show additional irreversibilities when they are interconnected. The reduction of such irreversibilities makes it possible to increase the overall efficiency thanks in particular to a better internal regeneration. Total optimization of such systems has been the object of many studies during the last years (Linnhoff, 1988; Yoda, 1995; Trivedi, 1994). This work lies within the scope of energy

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optimization and aims at the simulation of an industrial nitric acid production unit using a bi-pressure process. The simulation results are used to carry-out exergy balance calculations in order to assess energy degradation in the exchangers' network. Then, by applying the pinch analysis suggestions are made for improving the overall efficiency of the studied unit.

2. Exergy Analysis

Exergy is defined as the maximum work that can be obtained when a system is brought to thermodynamic equilibrium with the environment by means of processes in which this system interacts only with this environment (Esciubba, 2007).
Since the purpose of a heat exchanger is to transfer some of the exergy of the hot flow to the cold one, its exergy efficiency is defined as the ratio of the exergy received by the cold stream to that given by the hot stream:

$$\eta_{ex} = \frac{(Ex_{cold,out} - Ex_{cold,in})}{(Ex_{hot,in} - Ex_{hot,out})} \quad (1)$$

Exergy can be calculated with the help of flow sheeting. For the present work, Aspen Plus software was used to this purpose. This permitted the determination of thermodynamic properties such as enthalpy, entropy, fugacity, activity as well as the characteristics of streams (temperature, pressure, composition, etc.). The exergy calculator performs tasks in order to get the exergy of a material stream.

3. Description of the Nitric Acid Unit

The nitric acid process begins with the oxidation of ammonia to produce nitrogen oxides. This step is followed by gas phase oxidation of nitric oxides by oxygen, and subsequent absorption and reaction of the higher nitrogen oxides into water to produce nitric acid. In this work the focus is on bi- pressure processes. A typical process flow diagram is presented in Figure 1. Catalytic oxidation of ammonia is commercially one of the most important reactions in heterogeneous catalysis. Oele (1957) has shown that the overall oxidation rate is controlled by the transfer of NH_3 from the bulk gas phase to the platinum surface. This has been later supported by the rate of chemical reaction model proposed by Fila and Bernauer (Fila (1994)). The gases leave the ammonia converter at about 1138 K whereas the NO_x absorber operates in the range of 325-315 K. Therefore, the gases need to be cooled in such a way that the heat to be exchanged is used advantageously for steam generation and for preheating various streams. These features need to be included in the heat exchanger network. The present model for heat exchanger network, addresses all these aspects along with the chemical reaction taking place within exchangers A, B, C, E and F. Condensers (D and G) are generally heat exchangers of large surface area. The process gas enters from those heat exchangers which contain NO_x gases, N_2, unreacted O_2 and water vapor as a product of ammonia oxidation reaction.

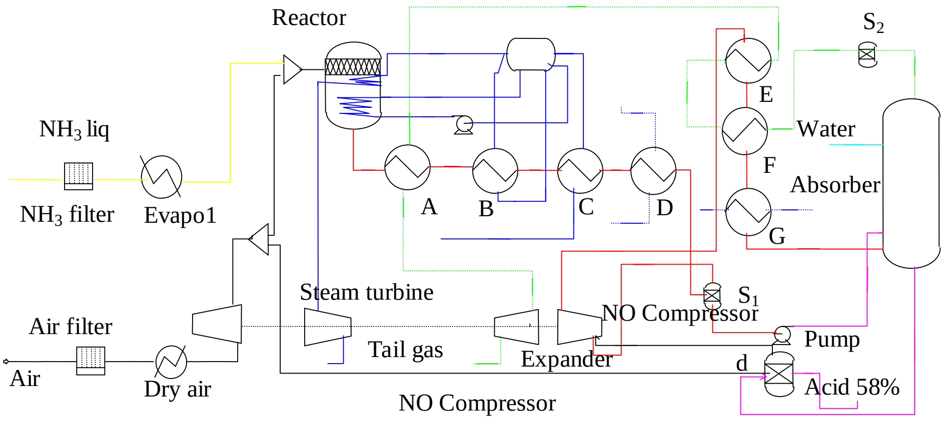

Figure 1: Process low diagram: A,B,C,E and F: heat exchangers, D&G cooler/condenser, d: bleacher, S1:nitric acid separator, S2:gas separator.

4. Process Simulation

In what follows, Aspen Plus software is used to simulate the process of nitric acid production. The simulation results provide the necessary data for exergy balance calculations and pinch analysis. For the simulation, the pipes are regarded as reactors with adiabatic plug flow. The exchangers are considered as multitubular plug flow reactors with cooling in the counter-current mode. For each exchanger, we must provide dimensions, the existing reactions and the overall heat transfer coefficient. The thermodynamic model used in the liquid phase is based on the NRTL equation but takes into account interactions of the electrolytic type. Thermodynamic calculations in the gas phase were carried out using the Redlich-Kwong equation of state (Aspen Plus User Guide, 2000). The reactions presented in Table 1 are used in the simulation of the absorption column (Dalaouti, 2005; Hüpen, 2005).

Table 1: Used reactions

Reaction	**Kinetic /Equilibrium constant**
$2NO+O_2 \leftrightarrow 2NO_2$	$\log_{10}(k_1)=\frac{652,1}{T}-0,7356$ [15]
$2NO_2 \leftrightarrow N_2O_4$	$\log_{10}(K_2)=\frac{2993}{T}-9,226$ [15]
$3NO_2 + H_2O \rightarrow 2HNO_3 + NO$	$\log_{10}(K_4)=\frac{2003,8}{T}-10,763$ [16]

5. Exergy Balance Results

To make exergy balance calculations, we must compute the exergy of all input and output streams (material, heat and work) for each equipment. The exergy losses and the exergetic efficiencies for the exchangers of the studied network are given in Table 2.

Table 2: Exergy losses (Exp) and exergetic efficiencies (η_{Ex}*) for the heat exchangers network.*

	Exchanger type	**Ex$_p$ (kW)**	**Ex$_p$ (%)**	**$\eta_{\xi E}$(%)**
2A	Exchanger gas/gas H.T (1110E)	8904.096	45.43	50
B	Exchanger vaporizer (1117E)	233.696	1.19	87
C	Economizer (1108E)	570.25O	2.91	84
D	Condenser of water reaction L.P (1109E)	4426.667	22.58	18
E	Exchanger gas/gas L.T (1116E)	4830.096	24.64	14
F	Gas preheater of tail (1113E)	407.467	2.08	40
G	Condenser of water reaction H.P (1111E)	228.263	1.17	46
Total exergy loss (kW)	**19 600.535**			
Overall exergy efficiency (%)	**48.43**			

The obtained results indicate that the total exergy losses in the heat exchangers' network are of about 20 MW. They also indicate that:

The low pressure water reaction condenser (D, 1109E) is responsible for 4.4 MW of lost exergy which represents almost 22.6 % of the total losses. These losses are essentially due, on one hand, to the chemical reactions taking place in the gas phase between NO and O_2 as well as the dimerisation in gaseous phase of NO_2 which gives N_2O_4 and, on the other hand, to the absorption in the liquid phase of NO_2 and N_2O_4 by the water leading to the formation of dilute nitric acid. For this device, thermal exergy losses are also important. Increasing the flow of cooling water is a solution that needs to be considered for improving the efficiency of this device. The low temperature gas/gas exchanger (E, 1116E) is responsible for an exergy loss of 4.8 MW, i.e. more than 24 % of the total losses. This important energy degradation is attributed mainly to the temperature difference between the streams going through this apparatus combined to the irreversibility of the reaction.

An exergy loss of 8.9 MW is associated with the high temperature gas/gas exchanger (A, 1110E) which represents more than 45 % of the total losses, and has an exergy efficiency of (50 %). This important power degradation is attributed mainly to the big temperature difference between the streams and to the irreversibility of the reaction of oxidation of NO to NO_2, which takes place in this apparatus. For this device, thermal exergy loss is also the most important (5.9 MW).

Hence, these three exchangers (A, D and E) combined are responsible of about 92.6 % of the total losses and efforts for improving the overall efficiency of the network must be oriented towards them.

6. Pinch Analysis

Based on the simulation results cold and hot utility consumptions are equal to 44.5 and 6.3 MW, respectively. In this process, the hot utilities are used for evaporating and overheating ammonia and for air pre-heating. It arises from the analysis of these results that the consumption of the cold utilities is much more significant compared to that of the hot utilities. Under the actual condition the heat exchanger network operate with a ΔT_{min} of 562.4 K.

Using an optimal ΔT_{min} of 438 K, the process require only cooling (38.2 MW) and the pinch temperature correspond to 904 K. This order of magnitude has been reported in the literature for this type of process. Indeed, Farvart and Staine, 1994, by studying a simplified manufacturing unit of nitric acid, defer an optimal ΔT_{min} of 577 K and a pinch temperature of 961 K.

To reach this condition the following solutions are suggested:

(i) Replace the hot utility used for the evaporation and superheating of ammonia leaving the first evaporator.

(ii) Replace the total hot utility used for the evaporation and superheating of ammonia (alternative solution).

(iii) Replace the hot utility used for the pre-heating of air.

Hence, the quantity of heat, which was evacuated to the environment, will be used for the heating of ammonia and air. One thus saves the quantity of vapor used for the vaporization and superheating of ammonia by getting the necessary heat duty from rich gas which needs to be cooled. At the same time, the pre-heating of air can be realized using produced gas. For all the suggested solutions, the existing exchangers can be kept and no major modifications in the network are needed. In fact, the rating of these exchangers for the new applications showed that they can satisfy the temperature targets of the process fluids. The geometries and current TEMA types of the exchangers as well as the characteristics and the physical properties of the fluids were accounted for in the rating operation.

7. Conclusions

In this work, exergy balance calculations and pinch analysis were conducted on a nitric acid production unit. The necessary data was obtained by process simulation. It was found that the total exergy losses in the heat recovery exchanger train amount to 20 MW with an overall exergetic efficiency of 93 %. The water-cooled condenser and the gas-gas exchangers are responsible for more than 92 % of exergy losses in the exchangers. Network pinch analysis showed that the actual value of the pinch is high and that considerable savings can be achieved by bringing it closer to the optimum. Finally, different solutions were suggested for reducing utility consumption by increasing the amount of heat transferred between process streams.

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