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Modeling, simulation and optimization: Mono pressure nitric acid process

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Abstract

The present work focuses on a strategy for optimizing mono pressure weak nitric acid plants. The optimization strategy addresses important processes which include oxidation of ammonia to nitric oxide, heat recovery from product stream of ammonia oxidation reactor and absorption accompanied by complex chemical reactions of multi-component nitrogen oxide gases into water. In design and optimization of nitric acid process, it is essential to understand the rate controlling step for ammonia oxidation process, strategy to be adopted for heat exchanger network design, rates of mass transfer and chemical reaction for nitrogen oxide absorption and the combined effects of several equilibria. The work addresses these issues taking through the complexities in the above mentioned processes.

The parametric sensitivity of few parameters such as ammonia to air ratio, excess oxygen/air, selectivity, power recovery based on the performance efficiency of compressor and expander, inlet and outlet nitrogen oxide composition in condenser and absorption column have been a part of our investigation either explicitly or implicitly. Further, for the absorption column, the effects of geometrical parameters, excess air, extent of absorption, product acid concentration, temperature and pressure have been analyzed for the purpose of optimization of nitric acid plant. All parameters having major influence on annualized cost of product acid have been analyzed and presented.

Keywords: Nitric acid manufacture; Optimization strategy; Ammonia oxidation; Platinum losses; Multi-component absorption; NO*x* absorption; HNO_3 tray profiles

1. Introduction

In making nitric acid, as in most other products, there is no single "right way". It would be difficult to cite a process so common to industrial chemical scenario and yet posing so severe a challenge to our comprehension of its fundamental mechanism as that of absorption of nitrogen oxides in water to produce nitric acid. The manufacture of nitric acid process comprises of oxidation of ammonia to produce nitrogen oxides, followed by gas phase oxidation of nitric oxide 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 mono high pressure processes. A typical process flow diagram is presented in Fig. 1 [1].

In a mono high pressure process, the absorption column plays a dual role: (a) HNO_3 manufacture and concurrently (b) NO*x* abatement. Hence, the understanding of the mechanism of NO*x* absorption holds the key to nitric acid manufacture. Considerable research efforts have been expended [2–7] to bring out the following aspects of NO*x* absorption: (i) NO*x* gases consists of several components NO, NO_2, N_2O_3, N_2O_4, HNO_2, HNO_3, etc. and the liquid phase contains two oxyacids (i.e. nitric acid and nitrous acid), (ii) several reversible and irreversible reactions occur both in gas and liquid phases, (iii) absorption of multiple gases is accompanied by chemical reaction, (iv) desorption of gases occur preceded by chemical reaction, (v) heterogeneous equilibria prevail between the gas and the liquid phase components, (vi) heat effects of the absorptions and the chemical reactions. All these aspects make the process of NO*x* absorption probably the most complex with respect to other absorption operations.

In addition to these attempts made in the past [8–10], the following important features have been considered in the present model for absorber. (i) The rates of absorption of NO_2, N_2O_3 and N_2O_4 in nitric acid are different from those in water. The rates decrease with an increase in concentration of nitric acid. (ii) Carberry [11] in his work has shown that, for a given set of partial pressures of NO, NO_2 and N_2O_4, there exists a certain limiting concentration of nitric acid beyond which no absorption of either N_2O_4 or NO_2 occurs. This heterogeneous equilibrium substantially reduces the rates of absorption of NO_2, N_2O_3 and

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Nomenclature

$\hat{a}$	wire area per gauze cross sectional area ($m^2\,m^{-2}$)
$\underline{a}$	surface area per unit volume ($m^2\,m^{-3}$)
C_i	concentration for species *i* ($kmol\,m^{-3}$)
D	diameter (m)
e	efficiency
f	friction factor
F_i	molar flow rate for species *i* ($kmol\,s^{-1}$)
g	acceleration due to gravity ($m\,s^{-2}$)
G	inert molar flow rate ($kmol\,s^{-1}$)
H	height of column (m)
k	mass transfer coefficient ($m\,s^{-1}$)
k_b	backward rate constant for reaction Eq. (5) ($kmol\,kN^{-1}\,s^{-1}$)
k_f	forward rate constant for reaction Eq. (5) ($kmol\,kN^{-1}\,s^{-1}$)
k_1	forward rate constant for nitric oxide oxidation (kPa^{-1})
K_{eq}	equilibrium constant for reaction Eq. (5)
K_H	heterogeneous equilibrium constant (kPa^{-2})
K_n	equilibrium constants for reactions tabulated in Table 1 (*n* = 2–5) ($kPa^{-2}\,s^{-1}$)
K_6	parameter defined by Eq. (2.22) ($kPa^{-1/2}$)
L	molar flow rate of water ($kmol\,s^{-1}$)
M_i	molecular weight of species *i* ($kg\,kmol^{-1}$)
N	number of catalyst screens
p_i	partial pressure of species *i* (kPa)
P	operating pressure (kPa)
$\mathbf{P}$	power (kW)
P_f	power factor
Q	flow rate ($m^3\,s^{-1}$)
r_{NH_3}	rate of mass transfer of ammonia on catalyst surface ($kmol\,m^{-3}\,s^{-1}$)
r_{PtO_2}	rate of platinum oxidation ($kmol\,m^{-3}\,s^{-1}$)
R	gas constant ($kJ\,kmol^{-1}\,K^{-1}$)
Ra_i	volumetric rates of mass transfer for species *i* ($kmol\,m^{-3}\,s^{-1}$)
Re	reynold's number
S	cross sectional area (m^2)
t	thickness (m)
T	temperature of operation (K)
u	fluid approach velocity ($m\,s^{-1}$)
V	volume (m^3)
w	weight percentage of nitric acid
x	conversion of ammonia to nitric oxide
X_N^*	moles of reactive nitrogen per mole of water
Y_i	moles of species *i* per mole of inert
$Y_{H_2O}^*$	moles of water per mole of inert
Y_N^*	moles of reactive nitrogen per mole of inert
Y_{NO}^*	moles of divalent nitrogen per mole of inert
z	length (m)

Greek letters

ΔP	pressure drop (kPa)
ε	volume fraction
ρ	density ($kg\,m^{-3}$)
τ	tortuosity factor

Subscripts

G	gas phase
i	inlet
L	liquid phase
n	stage number
o	outlet
s	screen
S	side stream

Superscripts

b	heterogeneous equilibria value
o	bulk
s	surface

N_2O_4, and the extent of reduction increases with an increase in the nitric acid concentration and finally approaching the equilibrium value. (iii) Substantial quantity of nitric acid is formed in the gas phase, at high temperature and pressure. (iv) The heat effects due to absorption and oxidation. (v) 1/3 mole of NO desorbs for every mole of NO*x* absorbed. This shows that the rate of oxidation and absorption/desorption are linked. (vi) Absorption rate of NO is negligible, however in the presence of NO_2, the NO forms N_2O_3 and subsequently HNO_2 because of the presence of H_2O vapor in the gas phase. The rates of N_2O_3 and HNO_2 absorption are very high as compared with even NO_2. Therefore the presence of NO_2 enhances the rate of absorption of NO. (vii) Maximum permissible concentration of nitric acid decreases with an increase in the mole fraction of nitric oxide. As the absorption continues, mole fraction of NO increases due to the absorption of N_2O_4, N_2O_3 and HNO_3. Therefore, multistage absorption is needed to get the desired concentration of nitric acid where, each stage comprises of an absorption section and an oxidation section. The plate spacing depends upon the gas phase composition and the desired extent of oxidation, also the extent of absorption on a stage is a variable. (viii) The effect of temperature is multifold. The rate of NO oxidation decreases whereas the rate of absorption increases with an increase in temperature. The equilibria (for the formation of N_2O_4 and N_2O_3) are favored at low temperature. Moreover, for a given NO*x* composition in the gas space, the maximum permissible nitric acid concentration increases with fall in temperature. (ix) Total pressure influences both the rates: NO oxidation and the NO*x* absorption.

In addition to the process of NO*x* absorption, ammonia oxidation and platinum losses from the catalyst screens also play a major role in optimization process. The heat recovery and power recovery are important aspects that need attention while developing a strategy for optimizing the process parameters for nitric acid process. The objective of the present work is to provide a strategy for improvement of production capacity and product quality in an operating plant, along with proposing an optimization strategy. The need was felt to develop models for all the units