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Process intensification in manufacture of nitric acid: NO_x absorption using enriched and pure oxygen

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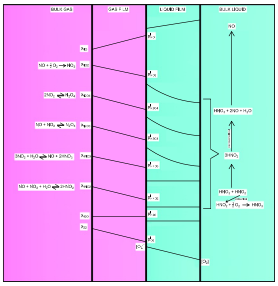
HIGHLIGHTS

- Mathematical model has been developed for nitric acid manufacture.
- Kinetics of oxidation and decomposition of nitrous acid included in the model.
- The role of enriched oxygen on the oxidation of NO and HNO_2.
- A novel method has been proposed for the liquid phase oxidation of HNO_2.
- The novel method stops NO desorption and saves volume for gas phase oxidation.

GRAPHICAL ABSTRACT

The process of absorption of NO_x gases in water/nitric acid is most complex case of heterogeneous reaction involving many steps. The figure shows the reactions occurring in the gas phase which include the irreversible oxidation of nitric oxide (NO) to nitrogen dioxide (NO_2). The remaining four reactions are reversible and instantaneous equilibria get established between NO_2, N_2O_4, NO, N_2O_3, H_2O, HNO_2 and HNO_3. All these components transfer through the gas film with a driving force of bulk partial pressure (p^0) and interface partial pressure (p^i). From the interface, NO_2, N_2O_3 and N_2O_4 transfer through the liquid film and are accompanied by chemical reaction to produce nitric acid (HNO_3) and nitrous acid (HNO_2). Further physical mass transfer of HNO_3, HNO_2, H_2O and O_2 occur through the gas and liquid films. The HNO_2 in the liquid phase decomposes to HNO_3 and NO, the latter desorbs to the gas phase through the liquid and gas films. The present paper for the first time, considers the kinetics of decomposition and oxidation of nitrous acid. It also proposes a novel method of complete liquid phase oxidation. The role of enrichment of oxygen has also been examined. The recommendations of the present paper are expected to result in substantial reduction in column dimensions and hence capital as well as operating costs.



SCHEMATIC REPRESENTATION OF CONCENTRATION PROFILE FOR NOx GAS ABSORPTION IN WATER.

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ABSTRACT

Absorption column occupies a dominant place in the manufacturing of nitric acid. A mathematical model has been developed for the absorption of NO_x gases using air and enriched oxygen in packed columns. For the first time, this paper considers the kinetics of nitrous acid decomposition and oxidation in the liquid phase. Till date, the published literature considers the instantaneous decomposition of nitrous acid in the liquid phase. The same case has also been considered in this paper as the base case. In addition, three more cases have been considered: (1) decomposition and oxidation kinetics of nitrous acid with a typical concentration of oxygen which is usually employed in nitric acid plants (2) complete decomposition and oxidation with enriched oxygen (3) complete conversion of nitrous to nitric acid by liquid phase nitrous

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Nomenclature

$\underline{a}$	interfacial area ($m^2\,m^{-3}$)
a_p	dry packing area ($m^2\,m^{-3}$)
[A]	concentration of species A, in the solution ($kmol\,m^{-3}$)
[A*]	concentration of the gas species A, at the gas–liquid interface ($kmol\,m^{-3}$)
[B_o]	concentration of species B in the bulk phase ($kmol\,m^{-3}$)
dh	differential height of column (m)
d_p	nominal packing size (m)
D_C	column diameter (m)
D_x	diffusion coefficient of species x ($m^2\,s^{-1}$)
f	friction factor (–)
G	flow rate of inert ($kmol\,s^{-1}$)
G^*	mass flow-rate of gas ($kg\,m^2\,s^{-1}$)
$H_x\sqrt{kD_x}$	absorption factor for fast pseudo-first order reaction of component x ($kmol\,m^{-2}$) ($kN\,m^{-2})^{-1}$ s
H_x	Henry's constant/solubility in the solution of component x ($kmol\,m^{-3}$) ($kN\,m^{-2})^{-1}$
i^-	anion contribution of electrolyte
i_g	solute gas contribution
I	ionic strength ($kg\,ion\,m^{-3}$)
k_1	rate constant for NO oxidation (($kN\,m^{-2})^{-2}\,s^{-1}$)
k_d	decomposition rate constant ($m^3\,kmol^{-1}\,s^{-1}$)
k_G	gas side mass transfer coefficient ($kmol\,m^{-2}$ s ($kN\,m^{-2}$))
k_i	rate constant of species i (NO_2, N_2O_3, N_2O_4)
k_L	liquid side mass transfer coefficient ($m\,s^{-1}$)
k_s	salting out parameter ($m^3\,(kg\,ion)^{-1}$)
K	equilibrium constant for reaction
m	order of reaction w.r.t species A (–)
$\sqrt{M}$	$\frac{\sqrt{\left(\frac{2}{m+1}D_A k_{mn}[A^*]^{m-1}[B_o]^n\right)}}{k_L}$
n	order of reaction w.r.t species B (–)
p_x	partial pressure of species x in bulk gas ($kN\,m^{-2}$)
p_x^b	heterogeneous partial pressure of species x ($kN\,m^{-2}$)
p_x^i	interphase partial pressure of species x ($kN\,m^{-2}$)
R	universal gas constant ($kJ\,kmol^{-1}\,K^{-1}$)
$R\underline{a}_{x,G}$	rate of absorption of species x ($kmol\,m^{-3}$ s)
$R\underline{a}_{x,L}$	rate of absorption of species x ($kmol\,m^{-3}$ s)
$R\underline{a}_{NO,o}$	oxidation rate of NO ($kmol\,m^{-3}$ s)
$R_{d,HNO_2,L}$	decomposition rate of HNO_2 ($kmol\,m^{-2}$ s)
$R_{o,HNO_2,L}$	oxidation rate of HNO_2 ($kmol\,m^{-2}$ s)
Re_L	Reynold's number for the liquid flow (–)
S	cross-sectional area (m^2)
T	temperature (K)
V_G	superficial gas velocity ($m\,s^{-1}$)
V_L	superficial liquid velocity ($m\,s^{-1}$)
X_i	molar flow-rate of species i in liquid ($kmol\,s^{-1}$)
$Y^*_{H_2O}$	moles of water in form of oxy-acids and free water in gas phase per mole of inert (–)
Y^*_N	moles of reactive nitrogen in gas phase per mole of inert (–)
Y^*_{NO}	moles of divalent nitrogen in gas phase per mole of inert (–)

Greek symbols

$\in$	voidage (–)
μ_L	viscosity of liquid (Pa s)
μ_w	viscosity of water (Pa s)
ρ_G	gas density ($kg\,m^{-3}$)
ρ_L	liquid density ($kg\,m^{-3}$)
$\boldsymbol{\epsilon}_G$	fractional gas hold up (–)
$\boldsymbol{\epsilon}_L$	fractional liquid hold up (–)

acid oxidation. Enriched oxygen results in substantial reduction in column volume and/or the operating pressure. The enriched oxygen enhances the rate of nitrous acid oxidation (to nitric acid) and hence the nitrous acid available for decomposition reduces throughout the column. This implies that lesser quantity of nitric oxide gets desorbed to the gas phase. This feature has crucial implication because the need for gas phase oxidation of NO reduces and hence the absorption column becomes compact due to reduction in oxidation volume. Thus, the enriched oxygen plays a significant role in process intensification and equipment miniaturization. Additionally, the liquid phase oxidation of nitrous acid carried out in a suitable oxidizer was found to give substantial additional reduction in the column volume.

For packed column absorber, the effects of design parameters viz. column diameter, heights of packed and empty sections, and operating parameters such as pressure and temperature have been examined.

1. Introduction

In the manufacturing of nitric acid; an important step is the absorption of NO_x gases. In comparison to additional absorption operations NO_x gas absorption is perhaps the most complex. The basis for the complexity is: (i) NO, NO_2, N_2O_4, N_2O_3, etc. comprises the NO_x gas mixture and two oxyacids, nitric acid and nitrous acid are formed by the subsequent absorption of NO_x gas in water. (ii) The occurrence of numerous reversible and irreversible reactions is seen in both the gas and liquid phase. (iii) Chemical reaction is preceded by simultaneous absorption of numerous gases and followed by simultaneous desorption of several gases. For case in point, the NO_2, N_2O_3 and N_2O_4 absorption is accompanied by chemical reaction; whereas NO, NO_2 and HNO_2 desorption are preceded by chemical reaction. (iv) Heterogeneous equilibria exists between the gas phase and liquid phase components. The above aspects of NO_x absorption are reviewed by Sherwood et al. [1] and Joshi et al. [2].

It is essential to know the combined effects of numerous equilibria, mass transfer rates and chemical reaction; for the process design of NO_x absorption towers. Additionally, NO_x absorption is linked to substantial heat effects. Hence, variations in temperature must be taken into consideration in the process design. Noteworthy, attempts have been made in this direction. For illustration, diverse features of the process design of packed columns, plate columns; and packed bubble columns used for the manufacturing of nitric acid is reported in the literature by Koval and Peters [3], Andrew and Hanson [4], Koukolik and Marek [5], Carleton and Valentin [6], Hoftizer and Kwanten [7], Makhotkin and Shamsutdinov [8], Holma and Sohlo [9], Emig et al. [10], Counce and Perona [11–13], Joshi et al. [2], Miller [14], Gutierrez-Canas et al. [15], Wiegand et al. [16]. These efforts will be reinforced if