# Rigorous modelling of $NO_x$ absorption in tray and packed columns

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## Abstract

The absorption of $NO_x$ into pure water or nitric acid is usually a kinetically controlled operation in which complex reactions in both gas and liquid phases are combined with multicomponent mass transfer. To be able to describe this process adequately, a rigorous general rate-based model for the reactive absorption in tray and packed columns has been developed based on earlier works (see, e.g. [Kenig et al., 2001. Chemical Engineering Science 56, 343–350; Kenig et al., 2003. Chemical Engineering and Technology 6, 631–646]). Heat and multicomponent mass transfer in the film phases, chemical reactions and thermodynamic non-idealities are taken into account. Furthermore, the influence of column internals and hydraulics is considered via relevant correlations. For tray columns, a special consideration of the empty sections above the gas–liquid layer on a tray is included. The model is implemented into the simulation environment Aspen Custom Modeler$^{TM}$ and validated by comparison with experimental data for a pilot scale packed column and an industrial sieve tray column equipped with cooling coils. The simulation results obtained for both column types agree well with the experimental measurements. In addition, the influence of cooling on the process behaviour is studied.
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## 1. Introduction

Absorption of nitrous gases represents a widespread and important operation in the chemical process industries. It is mainly used in the production of nitric acid and in the purification of exhaust gas streams, e.g. in the fertiliser industry. One the other hand, it is a highly complex process due to the interaction of several components (e.g. NO, $NO_2$, $N_2O_4$, $HNO_3$), both in the liquid and gas phases, parallel and consecutive chemical reactions and simultaneous absorption and desorption.

The design of columns for $NO_x$ absorption is mostly based on experience and/or on usage of simplified models which cannot reproduce the process behaviour with sufficient accuracy. As a consequence, possible design errors can lead to serious problems (e.g. exceeding emission limits for nitrogen oxides). A rigorous and reliable process description would help to avoid these difficulties.

Modelling and simulation of gas–liquid reactor units have been usually based on the equilibrium stage concept in which a unit is subdivided into several axial segments (stages). The column profiles are determined assuming the equilibrium state between the streams leaving each stage and by using the HETP-values (Height Equivalent to a Theoretical Plate) (Taylor and Krishna, 1993). However, the application of the equilibrium stage concept is difficult for processes driven by rate controlled phenomena. This is just the case with reactive absorption operations, in which reaction kinetics and mass and heat transfer resistances represent the key issues (Schneider et al., 1999).

The rate-based approach is a more consistent modelling method to consider reaction and transport kinetics. Here, gas and liquid phases are balanced separately, whereas the mass and heat fluxes across the interface are taken into account directly (Taylor and Krishna, 1993). In addition, mutual influence of chemical reactions and mass

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transfer can be properly taken into account (Kenig et al., 2001).

Absorption of $NO_x$ is one of the most complex gas–liquid reaction operations. This is the reason why various simplifications reducing the accuracy and predictivity of the rate-based approach have been made, e.g. consideration of mass transport of the key components $NO_2$ and $N_2O_4$ only (Emig et al., 1979; Greve and Bode, 1994; Wiegand et al., 1990), assumption of equal component diffusivities (Emig et al., 1979; Ramanand and Phaneswara Rao, 1996; Suchak et al., 1991), application of enhancement factors (de Paiva and Kachan, 2004), or neglecting the reactions in the gas film (Patwardhan et al., 2002; Suchak et al., 1991).

The present work is free of such simplifications. We developed a general rate-based model which is valid for both packed and tray columns and applicable for a broad spectrum of $NO_x$ absorption operations. The model is an extension of previous models (see Kenig et al., 1997, 2001, 2003; Schneider et al., 1999) developed for the description of reactive absorption in packed columns. The model involves the film model equations combined with relevant reaction and diffusion kinetics for all reactions and components, in both the gas and liquid phases, and it is extended to include an additional element—the so-called gas area—which considers the influence of the gas-phase reactions on the composition in the empty section above the gas–liquid layer on a tray. Further, the model includes the description of cooling effects through cooling coils installed in tray columns.

The model is realised with the help of the simulation environment Aspen Custom Modeller$^{TM}$ and successfully validated with $NO_x$ absorption experimental data for columns of both packed and tray type.

## 2. Process description

A typical simplified flow diagram of $NO_x$ absorption process is shown in Fig. 1, with three columns connected counter-currently. The inlet of the raw gas consisting of nitrogen oxides and air is at the bottom of the first column. The solvent is fed at the top of the third column. The nitrogen oxides are absorbed by the solvent flowing
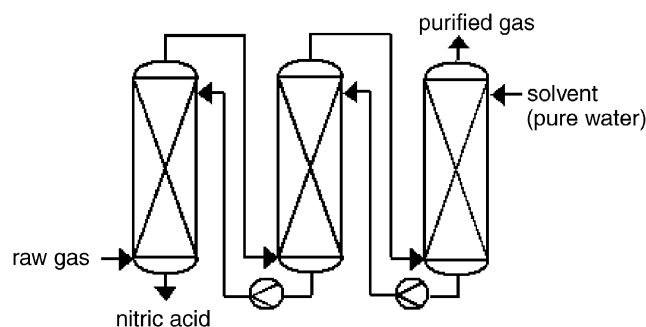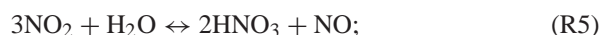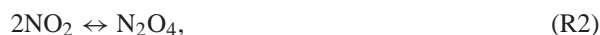


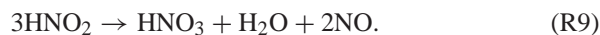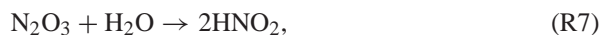Fig. 1. Simplified flow diagram of a $NO_x$ absorption process.

counter-currently to the gas and form nitric acid which is drawn off at the bottom of the first column. These columns can be either of a packed or of a tray type. Tray columns are often additionally equipped with cooling coils on trays in order to achieve higher absorption rates via cooling.

The reaction network of the $NO_x$ system is extremely complicated. Altogether, there are more than 40 reactions known. For the simulation of the process, a relevant set of reactions was taken from Suchak et al. (1991). It contains five gas-phase and four liquid-phase reactions presented below:

- gas-phase reactions

$$2NO + O_2 \rightarrow 2NO_2, \tag{R1}$$

$$2NO_2 \leftrightarrow N_2O_4, \tag{R2}$$

$$NO + NO_2 \leftrightarrow N_2O_3, \tag{R3}$$

$$NO + NO_2 + H_2O \leftrightarrow 2HNO_2, \tag{R4}$$

$$3NO_2 + H_2O \leftrightarrow 2HNO_3 + NO; \tag{R5}$$

- liquid-phase reactions

$$2NO_2 + H_2O \rightarrow HNO_2 + HNO_3, \tag{R6}$$

$$N_2O_3 + H_2O \rightarrow 2HNO_2, \tag{R7}$$

$$N_2O_4 + H_2O \rightarrow HNO_2 + HNO_3, \tag{R8}$$

$$3HNO_2 \rightarrow HNO_3 + H_2O + 2NO. \tag{R9}$$

For the process performance, the oxidation of nitrogen monoxide to nitrogen dioxide (R1) is especially significant, because of the low solubility of nitrogen monoxide in water. Compared to nitrogen monoxide, the solubility of nitrogen dioxide is one order of magnitude higher. Reaction (R1) is a kinetically controlled reaction and it is assumed to be irreversible for temperatures below $350\,°C$. In reactions (R2)–(R5), nitrogen dioxides instantaneously react to intermediate products (e.g. $N_2O_3$ or $HNO_2$) whose solubility increases with increasing molecular weight.

The liquid-phase reactions are kinetically controlled and assumed to be irreversible at nitric acid concentrations below 35 wt% (Joshi et al., 1985). Via reactions (R6)–(R8) the dissolved nitrogen oxides are transformed into nitric and nitrous acids. NO produced in reaction (R9) is desorbed due to its low solubility.

The instantaneous gas-phase reactions (R2)–(R5) are taken into consideration by means of the mass action law

$$K_r^G = \frac{\prod_p (y_p^G P)^{v_{p,r}}}{\prod_e (y_e^G P)^{v_{e,r}}}. \tag{1}$$

The chemical equilibrium constants $K_r$ are given in Table 1.

The reaction rates of the irreversible, kinetically controlled reactions are defined by the following