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Chemical Engineering and Processing 44 (2005) 1075–1081

Chemical Engineering and Processing

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Experimental study and modelling of mass transfer during simultaneous absorption of SO_2 and NO_2 with chemical reaction

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Received 26 November 2004; received in revised form 7 February 2005; accepted 1 March 2005
Available online 10 May 2005

Abstract

The aim of this paper is to model the simultaneous absorption mass transfer of NO_2 and SO_2 with chemical reactions. The absorption has been studied at low temperature (25 °C) in a gas–liquid stirred tank reactor, open for the gas flow and closed for the liquid phase. The kinetics of the reactions between sulphite and nitrite ions, obtained respectively from the absorption of SO_2 and NO_2, depend mainly on the pH of the solution. With a weakly acid solution ($4 < \mathrm{pH} < 5$), at low temperature, after the simultaneous absorption and interaction between the ions generated, it is possible to transform NO_2 and SO_2 into two products: N_2O and hydroxylamine disulfonic acid (HADS). In the first time, the mass transfer during the absorption of the two gases, without chemical reaction was characterized separately. Then the mass transfer during the simultaneous absorption with chemical reaction was quantified. The experimental conditions have been fixed at pH 4 and 5 for different gas flow rates. The mass transfer for NO_2 was clearly improved by the interaction between nitrite and sulphite ions. The modelling of mass transfer in the liquid phase of the reactor allowed to specify the hydration kinetics of nitrogen dioxide.

Keywords: Mass transfer; Modelling; NO_2; SO_2; Simultaneous absorption

1. Introduction

The combustion of fossil fuels (coal, fuel-oils, gas, etc.), household waste incineration and road traffic produce acidic gases such as SO_2 and NO_X. In order to respect the new Europeans regulations [1] concerning the gaseous wastes, the combustion gas should be treated before being ejected into the atmosphere. The elimination of nitrogen oxides has been frequently investigated in the literature [2,3]. Several processes have been developed at different level temperature: very high (900–1200 °C) or high (280–400 °C). At high temperature [4], nitrogen oxides can be reduced, without catalyst, by injection of ammonia or urea. It is also possible to inject other chemical reagents as: Na_2CO_3 [5], $CO(NH_2)_2$ and $Ca(OH)_2$ [6], and NH_3 and CH_3OH [7]. The use of a catalyst allows to decrease the treatment temperature [8]. Another option is to carry out absorption of nitrogen oxides, at room temperature, into a slightly acidic urea solution [9,10]. But for this kind of treatment, nitrogen oxides should be previously oxidated into nitrogen dioxide because the solubility of NO in water is weaker than that of NO_2. In the following work, we have studied only the absorption of NO_2 and SO_2 in water at a fixed pH.

For desulfuration and denitrification processes, Chang et al. [11] proposed a theoretical diagram of the probable interactions between sulphite and nitrite ions. From this diagram, the authors show that it is possible to produce gaseous nitrogen and sulphuric acid. In order to evaluate all the different chemical reactions proposed by Chang et al. [11], we have developed a study in a precedent work [12] in an isothermal (25 °C) closed-batch and stirred tank reactor without oxygen. The results of our experiments show that for $0.77 \leq \mathrm{pH} \leq 5$, the reaction was described by a three steps model (see Fig. 1). For $0.77 \leq \mathrm{pH} \leq 1$, the nitrite ions were totally transformed into gaseous nitrous oxide (N_2O) and completely converted into hydroxylamine disulfonic acid (HADS) when

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doi:10.1016/j.cep.2005.03.001

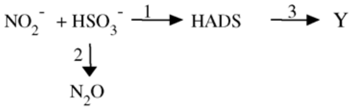

Fig. 1. Interactions between nitrite and sulphite ions in acid solution.

$4 \leq pH \leq 5$. In the intermediary conditions for $1 < pH < 4$, a competition between three reactions was observed: production of N_2O, production of HADS and acidic hydrolysis of HADS (giving an unidentified product Y). Moreover, we have found that for a neutral or basic pH, no interaction occurs. In the range of pH studied, the reactions between sulphites and nitrites ions never lead to N_2 formation. However, we have shown that at low temperature in a weakly acidic solution ($4 \leq pH \leq 5$), it is possible to convert NO_2 and SO_2 after absorption into hydroxylamine disulfonic acid (Eq. (1)).

$$NO_2^- + 2HSO_3^- + H^+ \Leftrightarrow HON(SO_3)_2^{2-} + H_2O \qquad (1)$$

We have characterized the kinetics of this reaction as first order:

$$r = k_1[NO^{2-}][HSO_3^-][H^+] \qquad (2)$$

For a given temperature and pH, the integration of the nitrite ions mass balance in a batch reactor, leads to the relation:

$$A = k_1 t \qquad (3)$$

with

$$A = \frac{1}{(H^+)([HSO_3^-]_0 - 2[NO_2^-]_0)} \ln \times \left[\frac{([HSO_3^-]_0 - 2[NO_2^-]_0 + 2[NO_2^-]_t)[NO_2^-]_0}{[HSO_3^-]_0[NO_2^-]_t} \right] \qquad (4)$$

The indices zero correspond to the initial concentration values. For $4 \leq pH \leq 5$, the variation of A, as a function of time t (see Fig. 2) is linear, which confirms the validity of the kinetic law Eq. (3). The kinetic constant at 25 °C is $3.92 \times 10^3\ L^2\ mol^{-2}\ s^{-1}$. This value is partially confirmed by the constant obtained by Oblath et al. [13], $k_1 = 3.80 \times 10^3\ L^2\ mol^{-2}\ s^{-1}$ in the following conditions: $[HSO_3^-] = 1.7 \times 10^{-3}\ mol\ L^{-1}$, $[NO_2^-] = 8.4 \times 10^{-4}\ mol\ L^{-1}$, pH 2.79 and $T = 20\ °C$.

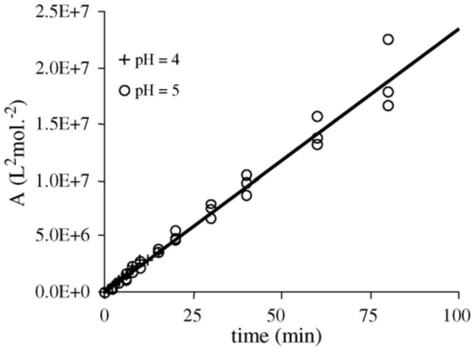

Fig. 2. Variations of "A" (Eq. (4)) as a function of time for pH 4 and 5.

The aim of the present work is to study the mass transfer characteristics during the simultaneous absorption of NO_2 and SO_2 in presence of a chemical reaction in the liquid phase at low temperature. We have chosen a low temperature for process economy reasons and the acidic conditions to produce some environmentally safe products. The mass transfer characteristics have been investigated by monitoring the chemical species in the gaseous phase (infrared gas analyzer), and more especially in the liquid phase (capillary ion analyzer). These investigations allow us to study the influence of the presence of chemical reaction in the liquid phase on the absorption rate. Finally, from our experiments, we have developed a model based on the mass transfer to verify the chemical reaction order.

2. Experimental set-up

The absorption with and without reactions were studied in a closed system where the aqueous phase is agitated by a turbine (self inducing type of device) to improve the gas–liquid transfer, with an agitation speed fixed at 1000 rpm. The experimental system (see Fig. 3) is constituted by a double jacket glass vessel reactor, the capacity of which is $1800\ cm^3$. The temperature regulation (fixed at 25 °C) is provided by a water circulation in the double jacket of the vessel, equipped with baffles. This reactor is completed by a recirculation system (capacity: $200\ cm^3$) which is performed by a peristaltic pump. The recirculation system allows to adjust the pH at 4 and 5 and to withdraw liquid samples for analysis. The reactions were studied without oxygen in the gas and liquid phases. To eliminate oxygen, an inert gas (N_2) is introduced into the

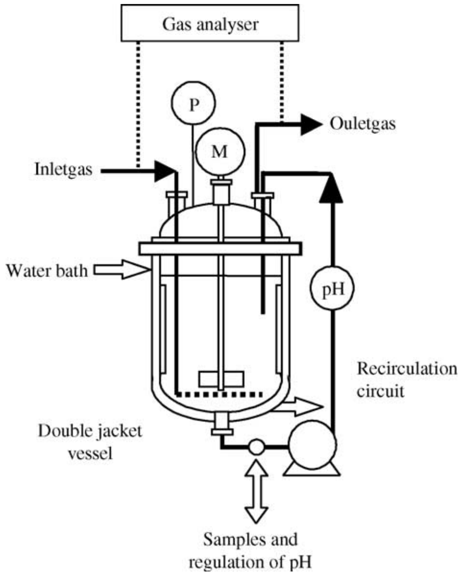

Fig. 3. Experimental device.