Chemical Engineering Journal 253 (2014) 258–263

Contents lists available at ScienceDirect

Chemical Engineering Journal

journal homepage: www.elsevier.com/locate/cej

Oxidation of ammonium sulfite by oxygen in a microporous tube-in-tube microchannel reactor

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HIGHLIGHTS

- A microporous tube-in-tube microchannel reactor (MTMCR) was used for oxidation.
- Oxidation kinetics of $(NH_4)_2SO_3$ in the MTMCR were studied.
- Oxidation of $(NH_4)_2SO_3$ was significantly enhanced by the MTMCR and Co^{2+} catalyst.
- $(NH_4)_2SO_3$ oxidation rate in the MTMCR reached 80% without cycling sulfite solution.

ARTICLE INFO

Article history:
Received 27 January 2014
Received in revised form 7 May 2014
Accepted 17 May 2014
Available online 27 May 2014

Keywords:
Microporous tube-in-tube microchannel reactor
Oxidation
Ammonium sulfite
Mass transfer

ABSTRACT

The homogeneous catalytic oxidation of ammonium sulfite in a microporous tube-in-tube microchannel reactor (MTMCR) was studied in this paper. It was found that the oxidation rate of ammonium sulfite in the MTMCR is 360 times higher than that in a packing column and could be further boosted about 4–6 times by the Co^{2+} catalyst. The effects of different operating parameters on the oxidation of ammonium sulfite were investigated. Experimental results indicated that the oxidation ratio of ammonium sulfite increased with the increase of the oxygen volumetric flow rate, but decreased with the increase of the liquid volumetric flow rate and sulfite concentration, and a smaller micropore size and annular channel width resulted in a higher oxidation ratio of ammonium sulfite. The oxidation ratio reached 80% under the optimum operating conditions in the catalytic oxidation process. This study reveals that the MTMCR is a potential intensification device for the oxidation process of ammonium sulfite.

1. Introduction

Ammonia desulfurization is an important method of reducing pollution of SO_2 from exhaust gas in industry. The main product of ammonia desulfurization is ammonium sulfite that is usually oxidized to produce ammonium sulfate fertilizer and to avoid re-decomposition of ammonium sulfite to SO_2. Studies on the oxidation process of ammonium sulfite have long been carried out in order to find the most efficient and economical oxidation technology [1,2].

In 1980, Neelakantan and Gehlawat [3] investigated the reaction kinetics of dissolved oxygen and ammonium sulfite and found out that it is a fast reaction. The oxidation reaction takes place in the aqueous phase and is controlled by the absorption process of oxygen. For the oxidation of ammonium sulfite in a stirred cell and packed column reactors, Li and his co-workers [4,5] found that the characteristic time to reach 50% of sulfite oxidation was 15 min with a sulfite concentration of 0.3–0.4 mol L^{-1} and Co^{2+} catalyst concentration of 0.4 mmol L^{-1}, while the characteristic time to reach 50% of sulfite oxidation was greater than 3 h at a higher sulfite concentration of 2.58 mol L^{-1}. Long et al. [6] reported that the highest oxidation rate of ammonium sulfite by oxygen could reach 3×10^{-4} mol L^{-1} s^{-1}. Hu et al. [7] reported that the oxidation rate of ammonium sulfite by a corona plasma-induced oxidation technique was almost two orders of magnitude higher than that obtained in a direct air contact reactor. However, the oxidation rate of ammonium sulfite is still low by those reported methods, and mass transfer intensification technologies are desired to enhance the oxidation efficiency of this process.

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http://dx.doi.org/10.1016/j.cej.2014.05.072
1385-8947/

Nomenclature

C_{10}	Initial concentration of ammonium sulfite (mol L^{-1})
C_{1t}	Concentration of ammonium sulfite at reaction time of t s (mol L^{-1})
C_1	Concentration of ammonium sulfite (mol L^{-1})
C_2	Concentration of oxygen in liquid (mol L^{-1})
C_3	Concentration of ammonium sulfate (mol L^{-1})
C_4	C_o^{2+} concentration (mol L^{-1})
D_h	Micropore size on the inner tube (μm)
E	Activation energy (kJ mol^{-1})
k	Intrinsic reaction rate
k_1	Constant of average oxidation rate
N_i	Flux of ammonium sulfite solution in the MTMCR (mol h^{-1})
n_G	Molar flow rate of gas (mol h^{-1})
n_L	Molar flow rate of liquid (mol h^{-1})
p_2	Partial pressure of oxygen (atm)
Q_G	Gas volumetric flow rate (L h^{-1})
Q_L	Liquid volumetric flow rate (L h^{-1})
R	Universal gas constant (8.314 J mol^{-1} K^{-1})
R_h	Annular channel width between the inner tube and the outer tube (μm)
T	Reaction temperature (K)
t	Resident time of liquid in the MTMCR (s)
v	Average oxidation rate of ammonium sulfite (mol L^{-1} S^{-1})
v'	Intrinsic oxidation rate of ammonium sulfite (mol L^{-1} S^{-1})
V_R	Volume of reactor (L)
X	Oxidation ratio of ammonium sulfite (%)

Microreactor is an efficient mass transfer intensification device, which has been extensively studied in many processes, such as absorption, hydrogenation, catalytic reaction, reaction precipitation, mixing, nanomaterials preparation, etc. [8–13]. It has a microstructure with a high specific surface area, and mass transfer, heat transfer and mixing in the microreactor can be enhanced notably [14–23]. A microporous tube-in-tube microchannel reactor (MTMCR) is one microreactor with high-throughput, and high micro-mixing and mass transfer efficiency [24–26]. It has been used for CO_2 capture and the results indicate that the volumetric mass transfer coefficient in the MTMCR is 1–2 times higher than that in the conventional gas–liquid contactors [27].

In this study, an MTMCR was adopted for sulfite oxidation by the absorption of oxygen into ammonium sulfite solution. Experimental and reaction kinetics studies were carried out to investigate the intensification efficiency of this process by the MTMCR. The effects of the operating parameters on the oxidation ratio of ammonium sulfite were explored.

2. Experimental section

2.1. Materials and setup

Ammonium sulfite ($(NH_4)_2SO_3{\cdot}H_2O$, purity of 96%) was purchased from Shanghai Jiacheng Chemical Materials Co. Ltd., China. Ammonium sulfate and heptahydrate cobalt sulfate (analytical grade) were obtained from Beijing Sinopharm Chemical Reagent Co. Ltd., China. Standard $Na_2S_2O_3$ solution was purchased from the National Institute of Metrology, China, and deionized water was supplied by a water purification system (Shanghai Hogon Scientific Instrument Co. Ltd., China).

Fig. 1 shows the photographs of the MTMCR, which consists mainly of the concentric dual tubes (the inner tube and the outer tube). The microporous section with a length of 1 cm and an average pore size of 10–200 μm sits at one end of the inner tube, and there are one liquid inlet and four sampling nozzles (not used in this study) on the outer tube. The annular channel between the inner and outer tubes serves as the chamber for mixing and reaction. The specifications of the MTMCR used in this study are given in Table 1.

2.2. Experimental procedures

The schematic diagram of the experimental setup for the oxidation of ammonium sulfite in the MTMCR is shown in Fig. 2. The ammonium sulfite solution was insulated in a liquid tank by N_2 to avoid the oxidation of ammonium sulfite by air. The temperature of the reaction system was controlled at 303–333 K by a water-bath.

The mixed gas stream of O_2 and N_2 was introduced into the inner tube from the gas inlet of the MTMCR under an inlet pressure of 0.2 MPa and flowed radially through the micropores into the annular channel between the inner and outer tubes, while the ammonium sulfite solution containing Co^{2+} catalyst was pumped into the MTMCR from a liquid tank under an inlet pressure of 0.102–0.106 MPa and flowed axially in the channel. The gas and liquid streams contacted cross-currently in the channel to realize the absorption of O_2 into the ammonium sulfite solution and the oxidation of ammonium sulfite before flowing out of the MTMCR. Finally, the gas–liquid mixture stream flowed into the liquid collector from the mixture outlet. Liquid samples were collected at the sample exit to analyze ammonium sulfite concentration.

The oxidation rate of ammonium sulfite in the MTMCR is dominated by the mass transfer of oxygen because the oxidation is a fast reaction. In this study, the concentration of ammonium sulfite was determined by the iodometry, and the oxidation ratio of ammonium sulfite was calculated by the following formula:

$$X = \frac{C_{10} - C_{1t}}{C_{10}} \tag{1}$$

2.3. Oxidation rate of ammonium sulfite in the MTMCR

The oxidation reaction of sulfite can be written as:

$$SO_3^{2-} + \frac{1}{2}O_2 \overset{C_o^{2+}}{\rightarrow} SO_4^{2+} \tag{2}$$

The average oxidation rate of sulfite in the MTMCR is determined by the initial concentration of SO_3^{2-} in the solution and partial pressure of O_2, and can be written as:

$$v = k_1 C_{10}^{n_1} p_2^{n_2} = \frac{\int_0^t v' dt}{t} = \frac{k \int_0^t C_1^a C_2^b dt}{t} \tag{3}$$

where k_1 is the average oxidation rate constant. n_1 and n_2 are orders of the concentration of ammonium sulfite and the partial pressure of oxygen, respectively. k is the intrinsic reaction rate constant of Reaction (2), a and b are orders of the concentration of ammonium sulfite and oxygen in liquid, respectively. To obtain the values of k, n_1 and n_2, Eq. (3) is converted into the following form:

$$\ln v = \ln k_1 + n_1 \ln C_{10} + n_2 \ln p_2 \tag{4}$$

In Eq. (3), k_1 and k are determined by temperature and can be obtained by Arrhenius equation: