

Kinetics of Oxidation Inhibition of Sodium Sulphite in Wet Flue Gas Desulphurization Process

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The effect of several inhibitors on the oxidation rate of sodium sulphite was determined by both intrinsic and macroscopic experiments using self-designed batch reactor. The results indicated that ethanol is the most suitable inhibitor for wet flue gas desulphurization due to its low cost and non-toxicity. The oxidation kinetics of sodium sulphite inhibited by ethanol was studied using stirred bubbling reactor by varying concentration of sodium sulphite and ethanol, air flow rate and temperature. The reaction orders of all reagents and the apparent activation energy of the reaction were achieved. Finally, a kinetic model was established based on the experimental results, which would be useful for the process optimization of the wet flue gas desulfurization systems.

Key Words: Kinetics, Oxidation Inhibitors, Sodium sulphite, Ethanol, Wet flue gas desulphurization.

INTRODUCTION

The emission of SO₂ caused by fossil fuel combustion is an important factor leading to environmental pollution which has attracted much attention in China¹⁻³. In order to control the sulphur dioxide emission, various flue gas desulphurization (FGD) processes have been developed and applied worldwide. Among them, wet flue gas desulphurization (WFGD) is the main technology in terms of high efficiency for sulphur dioxide removal, simple, low investment and energy consumption^{4,5}.

In wet flue gas desulphurization, sulphite is obtained as a byproduct and it can be easily oxidized to sulphate with a result of the reduction of the desulphurization efficiency and the reliability of the flue gas desulphurization system. Thus, it is necessary to develop effective inhibitor to prevent sulphite's oxidation in aqueous solution and the inhibition process is of commercial importance^{6,7}.

There are two kinds of kinetics, namely intrinsic and macroscopic kinetic, respectively. The former is used to study the mechanisms of chemical reactions, which are usually carried out under homogeneous conditions, while the latter consider not only the chemical reaction, but also mass transfer of reagents between different phases, which are often carried out under heterogeneous conditions. In wet desulphurization, the oxidation of sulphite accompanies mass transfer, which, as mentioned above, is a macroscopic process^{8,9}.

Unfortunately, the existing literature is mainly confined to reveal the inhibitor species, the previous work focused on

the intrinsic or macroscopic kinetics of sulphite oxidation in a single way, the inhibited kinetics are yet to be investigated deeply¹⁰⁻¹⁴. In this paper, effects of several inhibitors were compared by both intrinsic and macroscopic experiments. Ethanol was selected as an effective inhibitor in consideration of low cost and non-toxicity. The inhibited oxidation kinetics of sodium sulphite in presence of ethanol was studied by using a self-designed batch reactor. The reaction order of the reagents, activation energy and rate equation were achieved, which can provide reference for the inhibition technology of sulphite oxidation in wet flue gas desulphurization.

EXPERIMENTAL

The intrinsic reaction was carried out in a sealing reactor with stirring at a constant temperature (Fig. 1). After adding 980 mL high purity water and 0.25 mL inhibitor solution (1 mol/L) into the reactor, the dissolved oxygen electrode was fixed in the reactor and the stirrer was started at a predetermined speed of 120 rpm. 20 mL solution of sodium sulphite (1 mol/L) was added into the reactor rapidly and the reaction began at the same time. The dissolved oxygen in the solution was measured by the dissolved oxygen electrode at a fixed time interval.

The macroscopic reaction and the inhibition reaction of sodium sulphite oxidation in presence of ethanol were carried out in a stirred bubbling reactor, which was installed in a magnetic stirring constant-temperature bath (Fig. 2). After adding 1000 mL 0.1 mol/L sodium sulphite solution prepared by high

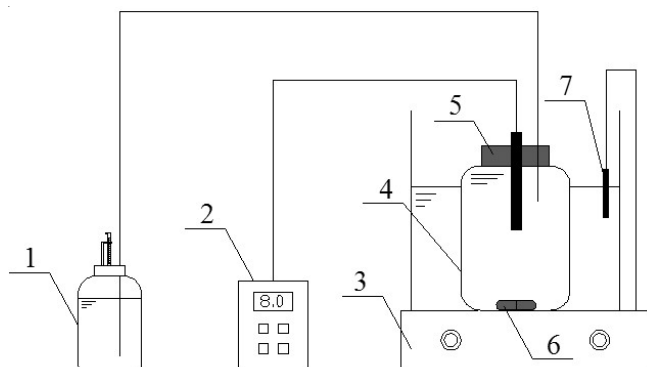


Fig. 1. Intrinsic experimental apparatus of inhibitor screening (1- quantitative liquid filling device; 2- dissolved oxygen meter; 3- magnetic stirring constant-temperature water bath; 4- sealing reactor; 5- rubber stopper; 6- magnetic stirrer; 7- thermocouple)

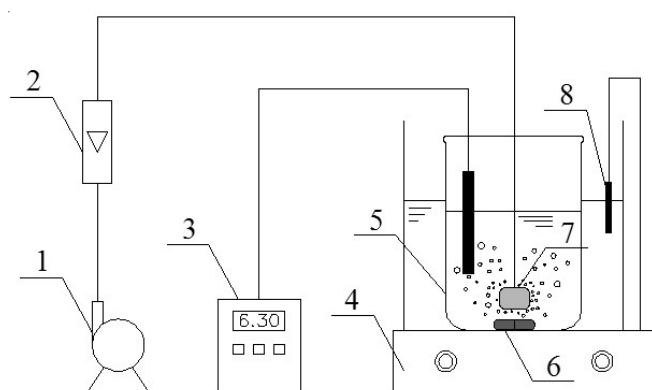


Fig. 2. Macroscopic experimental apparatus of sodium sulphite oxidation (1- air compressor; 2- air flow meter; 3- pH meter; 4- magnetic stirring constant-temperature water bath; 5- stirred bubbling reactor; 6- magnetic stirrer; 7- aeration header; 8-thermocouple)

purity water and a certain amount of inhibitor into the reactor, the stirrer started at a predetermined speed of 120 rpm. The reaction started when the aeration began. The sulphate concentration was measured analytically by means of ion chromatography and the observed oxidation rate can be calculated using the following formula:

$$r = d \frac{C_{\text{SO}_4^{2-}}}{dt} \quad (1)$$

All the chemicals used were of analytical grade in order to reduce the influence of impurities. The software Origin 8.5 was used for regressive analysis of the experimental data.

RESULTS AND DISCUSSION

Selection of inhibitors: As mentioned above, effects of five inhibitors, including ascorbic acid, ethanol, phenol, resorcinol and sodium thiosulphate were compared with the uninhibited one by both intrinsic and macroscopic experiments (Figs. 3 and 4). Five inhibitors all have inhibition effect on the oxidation rate of sodium sulphite in the intrinsic and macroscopic experiments.

Compared with other inhibitors, ethanol had better inhibition effect than sodium thiosulphate and phenol. What's more, ethanol was non-toxic and low-cost in contrast with resorcinol and ascorbic acid. Therefore, ethanol was an

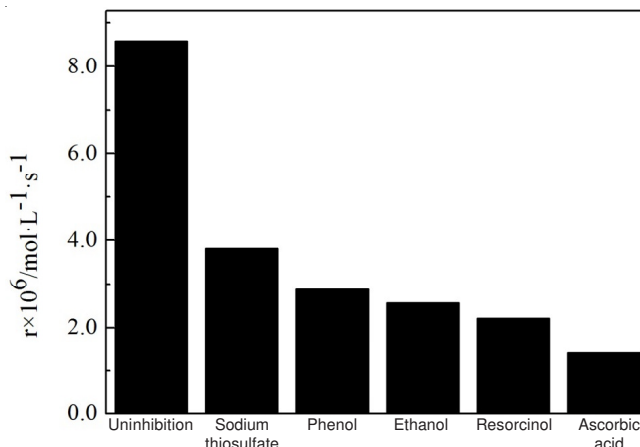


Fig. 3. Screening of inhibitors by macroscopic experiment ($C_{\text{Na}_2\text{SO}_3} = 0.1 \text{ mol/L}$; $C_{\text{inhibitor}} = 1.25 \text{ mmol/L}$; $Q = 0.2 \text{ m}^3/\text{h}$; $T = 293.15 \text{ K}$)

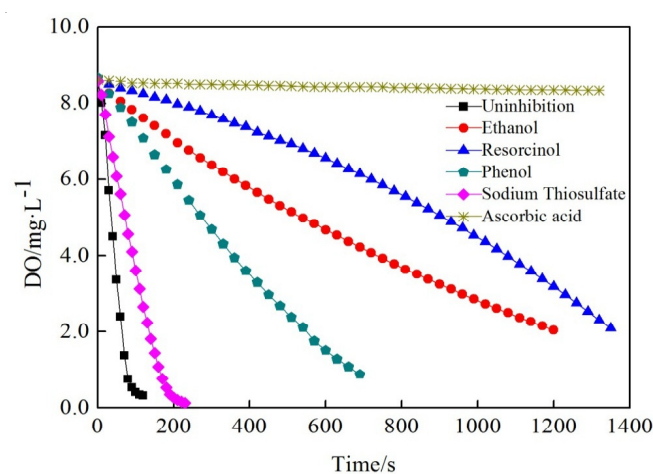


Fig. 4. Screening of inhibitors by intrinsic experiment ($C_{\text{Na}_2\text{SO}_3} = 20 \text{ mmol/L}$; $C_{\text{inhibitor}} = 0.25 \text{ mmol/L}$; $T = 293.15 \text{ K}$)

effective inhibitor which is suitable for applying in wet flue gas desulphurization system.

Effect of Na_2SO_3 concentration: The oxidation rates of sulphite with different sodium sulphite concentration were shown in Fig. 5, which was found to be 0.98 order with respect to sodium sulphite and with a correlation of 0.99. As reported by Wang¹⁵, the reaction was 1.0 order with respect to the sodium sulphite when the oxidation reaction was taken in presence of phenol as an inhibitor, which was similar to our results. It can be concluded that high concentration of sodium sulphite would promote the oxidation itself.

Effect of $\text{C}_2\text{H}_5\text{OH}$ concentration: Fig. 6 showed that the oxidation rate of sulphite decreased rapidly with the ethanol concentration raising to 2.5 mmol/L, then the oxidation rate decreased slowly as the ethanol concentration got higher. The oxidation inhibition efficiency could reach 92.9 % when the ethanol concentration was 5 mmol/L, which is more efficient than that reported by Chang and Brna¹⁶ for limestone slurry flue gas desulphurization progress. The reaction order was found to be -0.94 order with respect to ethanol.

Effect of air flow rate: The result in Fig. 7 showed that the oxidation rate of total sulphite increased quickly with the air flow up to 0.3 m^3/h , above which it increased slowly. This tendency was similar to that reported by Wang and Zhao⁸. The

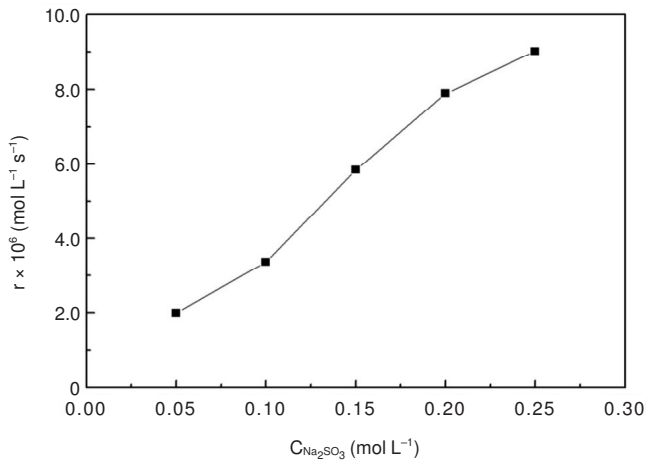


Fig. 5. Effect of sodium sulphite concentration on the oxidation rate ($C_{C_2H_5OH} = 1.25$ mmol/L; $Q = 0.2$ m³/h; $T = 293.15$ K)

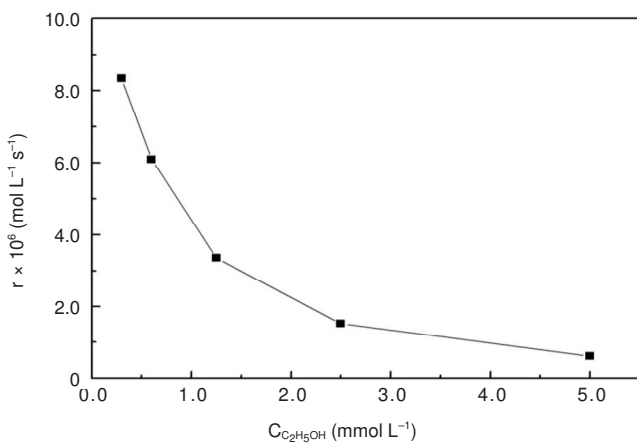


Fig. 6. Effect of ethanol concentration on the oxidation rate ($C_{Na_2SO_3} = 0.1$ mol/L; $Q = 0.2$ m³/h; $T = 293.15$ K)

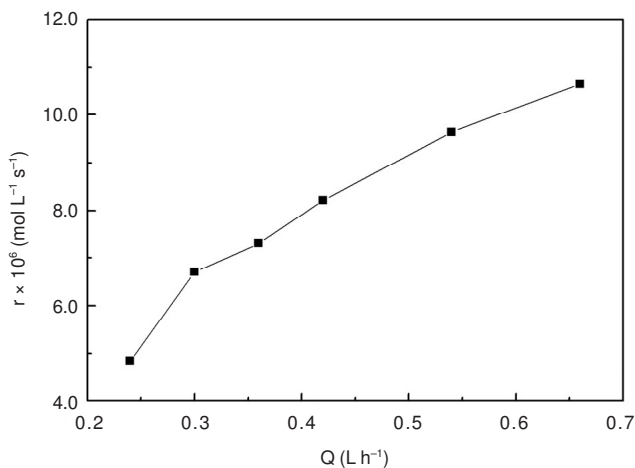


Fig. 7. Effect of air flow rate on the oxidation rate ($C_{Na_2SO_3} = 0.1$ mol/L; $C_{C_2H_5OH} = 1.25$ mmol/L; $T = 293.15$ K)

reason may be that the bubbled air dispersed uniformly in a quiet bubbling area under 0.3 m³/h, causing that the mass transfer rate of oxygen increased quickly as the air flow rate increased. When the air flow rate increased to 0.3 m³/h, some air forth collided and agglomerated, resulting in a little change of gas-liquid contact area thus the mass transfer rate of oxygen increased slowly.

Effect of temperature: The effect of temperature on oxidation rate was shown in Fig. 8. It indicated that the reaction rate would increase greatly with the rise of temperature. The logarithm of reaction rate was plotted with $1/T$ (Fig. 9), indicating that the effect of temperature on the oxidation rate complies with Arrhenius law in the range from 293.15 to 333.15 K. The apparent activation energy was calculated to be 19.74 KJ/mol.

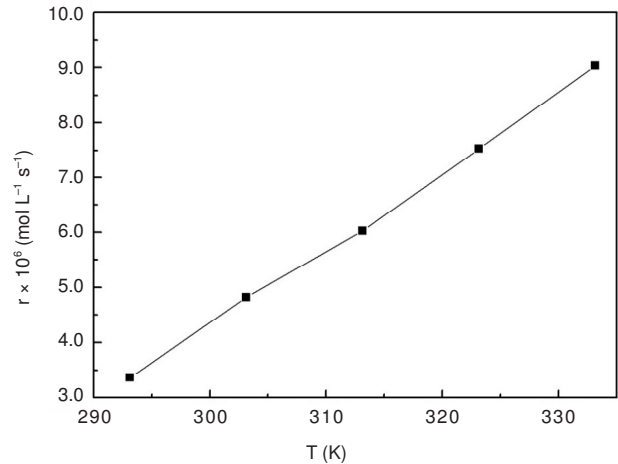


Fig. 8. Effect of temperature on the oxidation rate ($C_{Na_2SO_3} = 0.1$ mol/L; $C_{C_2H_5OH} = 1.25$ mmol/L; $Q = 0.2$ m³/h)

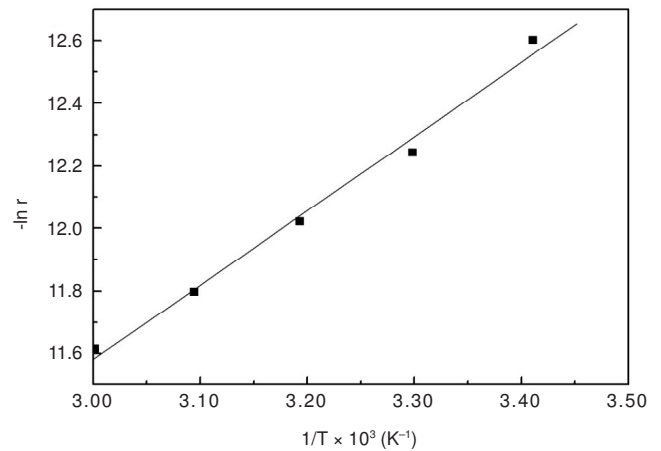


Fig. 9. Apparent activation energy of the sodium sulphite oxidation inhibition by ethanol

Kinetic model: Based on the experimental results above, the kinetics of oxidation inhibition of sodium sulphite could be expressed as:

$$r = 2.78 \times 10^{-6} \exp\left(\frac{-19736}{RT}\right) C_{Na_2SO_3}^{0.98} \cdot C_{C_2H_5OH}^{-0.94} \quad (\ln Q + 2.34) \quad (2)$$

The kinetic model would be useful for the process optimization of the wet flue gas desulphurization systems and the oxidation inhibition results on other types of desulphurization scrubber can be obtained by adjusting the air flow item of the equation.

Conclusion

Effect of five inhibitors on the oxidation rate of sodium sulphite were compared by both intrinsic and macroscopic experiments in self-designed batch reactors. The results showed that ethanol is the most suitable one for wet flue gas desulphurization systems.

Oxidation inhibition of sodium sulphite in wet flue gas desulphurization process depended on the concentration of sodium sulphite and ethanol, air flow rate and temperature. The reaction was found to be 0.98 order with respect to sodium sulphite and -0.94 order with respect to ethanol. Ethanol had good inhibition effect on sodium sulphite oxidation, which could reach an inhibition efficiency of 92.9 % at 5.0 mmol/L. The apparent activation energy for the overall oxidation was calculated to be 19.74 KJ/mol.

A kinetic model had been established on the basis of analysis of the experimental results. The developed kinetic model, including all the operating parameters, provided a satisfactory simulation of the experimental results. The model would be beneficial for designing or optimizing the oxidation process in wet flue gas desulphurization systems.

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