Experimental Research on SO_x from Ship Emissions by Lye Absorption

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Abstract: To protect environment, and to comply with the IMO's (International Maritime Organization) newest regulations about ship's SO_x emission. This thesis illustrates a closed recycling absorb system based on NaOH solution recycling particularly for SO_x onboard. The goal is to use NaOH solution to absorb SO_x, and reduce the damage the ships made towards environment. The thesis analyzes the main features that could influence the absorption of SO_x on board, and the precipitations during the experiment. To reveal that NaOH solution is very highly effective and economic in absorption of SO_x on ships by this experiment, and to set a theoretical basic fundamental for future application of alkali solution recycling absorption system for SO_x.

Key words: Environment protection, marine diesel engine, emission control, SO_x, economy.

1. Introduction

The main content of SO_x emission onboard is SO₂, it is the main pollution gas of atmosphere. SO₂ [1] can stipulate mucous in aspiration system, it will make people breath less air and cause coughing when reaching certain concentration. It also can cause dyspnea, chest distress, even death if the concentration continues rising. SO₂ [2] can form acid rain and photochemical smog, cause damage to creatures and plants alike.

Diesel engines on ship use fuel which contents 3% of sulfur, the SO₂ proportion is low in exhaust gas. But due to vast amount of ships and long distance traveling, the fuel consumption is huge, thus the SO₂ emission of ships [3] is huge. According to a survey submitted to IMO by Norway, the distribution of SO_x by ships has reached 7% of the world's SO_x emission [4]. The SO_x emission from diesel engines on ships severely pollutes atmosphere, it even becomes the major pollution source in some ports and heavy traffic zones.

The fifty-eighth session of Marine Environment

Protection Committee held 6 to 10 October 2008 (MEPC 58/23) had approved the amendment for further restriction of ship's emission. The amendment came into force at 1st July 2010. The allowable amount of fuel sulfur was reduced to 1.0% in July 2010 and is to be further lowered to 0.1% in January 2015 in ECA (Emission Control Area), or else the shipping company would implement emission trading with same amount [5]. Outside of ECA's, the current global limit of 4.5% sulfur-in-fuel will be reduced to 3.5% in 2012, then 0.5% in 2020 or 2025 depending on a review in 2018 to determine the availability of fuel to enable implementation of this standard. US and EU [6] have regulated the fuel sulfur for ships cannot exceed 0.1% for all the ship's to dock in its area. Thus the emission of SO_x is facing huge pressure, it is necessary to reduce SO_x on board.

2. Current Condition

There are pre-processing and post-processing to desulfurize ship's emission: pre-processing is low the concentration of the sulfur in fuel before it enters engine, post-procession is process the SO_x in exhaust gas. But pre-process involves fuel distillation

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technology which is complicated and costly. Besides, a series problem will occur if engine runs in low sulfur fuel. Thus pre-process is not widely adopted.

Most research facilities are focusing on post-process for emission desulfurization. The research progress for ship's SO_x emission reduction world widely is still in test. Wartsila, Alfa Laval Aalborg, Belco, Clean Marine, Couple, MAN, MES are doing R&D for this field. The research on this field in china is rather rarer, mainly Dalian Maritime University [7], Wuhan Textile University [8], and Shanghai Maritime University [9] etc. have done it. The emphases of their research are mainly about open desulfurization based on seawater [10, 11] or desulfurization system based on plasma [12] but never closed recycling desulfurization for ships.

This thesis adopts NaOH solution, with closed recycling system to absorb the SO₂ in exhaust gas of ships, analyzes the influence of changing for start temperature, gas inlet rate, NaOH solution concentration, diameter of the reactor, height of solution, also analyzes the economy for desulfurization with closed recycling alkali system, so as to set a basic theory for future application of alkali solution recycling absorption system for Sox.

3. Experiment Theory

The main component for Ship's SO_x in the exhaust gas is SO₂, so this experiment will use SO₂ as research target.

Pump SO₂ into a certain concentration solution of NaOH, analyzes the absorption effect under different conditions (concentration of NaOH solution, SO₂ inlet, temperature, diameter and height of the reactor). This experiment content a steel cylinder 4 as the container of SO₂; reactor 5; relief valve 1; pressure gauge 2; flow meter 3; high-accuracy electronic balance scale 7; gear pump 8; collector 9 etc. The experiment duration was 30 minutes, record data every 2 minutes, and analyze sample. The experiment equipment is shown in Fig. 1. SO₂ stores in steel cylinder, adjusting its outlet pressure by relief valve to 0.11 Mpa which was similar to the

pressure [13] of exhaust gas of ship's engine. Then the gas will go through the barometer and a diffuser to Fine bubble before access to NaOH solution, so the absorb effect would be maximized. There are two gear pumps drive the whole recycle system, the high-accuracy electronic balance would measure the mass change for SO₂ and the reactor. Its chemical equation [14] is shown in Eq. (1):

4. Experiment Result and Analysis

4.1 Influence of Startup Temperature for Absorptivity

In order to find out the influence of startup temperature for SO₂ absorptivity, the experiment adopted 25 °C, 40 °C, and 55 °C as startup temperature. All the following conditions were constant as SO₂ inlet flow was 0.5 L/min, NaOH solution concentration was 4 mol/L, NaOH solution height was 240 mm, reactor diameter was 125 mm, diffuser diameter was 104 mm, duration was 30 minutes, record data every 2 minutes and sample than calculate average value. The result is shown in Fig. 2.

Fig. 1 SO₂ assimilation equipment.

1-relief valve; 2-pressure gauge(outlet pressure); 3-flowmeter; 4-SO₂ bottle; 5-reactor of NaOH solution; 6-diffuser; 7-high-accuracy electronic balance scale; 8- gear pump; 9-collector;10-flow control valve;11-bypass valve.

Fig. 2 The influence of startup temperature for SO₂ assimilation rate.

According to Fig. 2, the absorptivity reaches 89.42% when the startup temperature is 25°C. As the Startup temperature raised, the absorptivity is decreasing. The absorptivity declined to 81.80% when the startup temperature raised to 40 °C. The absorptivity reduced to 77.83% when startup temperature reaches 55 °C. The cause of this is that the reaction between NaOH and SO₂ is a neutralization reaction which generates heat. High temperature is not fit for reaction. Thus it's recommended to minimize the temperature of NaOH solution in reality application.

4.2 Influence of Concentration of NaOH Solution for Absorptivity.

Prepare NaOH solution with concentration of 2 mol/L, 4 mol/L, 8 mol/L, the experiment condition stays constant as temperature was 25 °C, SO₂ inlet flow was 0.5 L/min, NaOH solution heights was 240 mm. The result is shown in Fig.3.

According to Fig. 3, when the concentration of NaOH solution was 2 mol/L, 4 mol/L and 8 mol/L, the absorptivity reached 88.48%, 89.42% and 91.51%. It shows that SO₂ absorptivity is proportional to the concentration of NaOH solution. The absorptivity increased 0.94% when the concentration of NaOH solution raised from 2 mol/L to 4 mol/L, and it increased 2.09% when the concentration of NaOH solution raised from 4 mol/L to 8 mol/L. the absorptivity of SO₂ increases palpably with the rising of NaOH solution concentration. The higher the concentration of NaOH solution, the better it absorbs SO₂. But actually the absorptivity is already above 90% when the concentration reaches 6mol/L, so economically, it is not recommended to use solution that has higher concentration than 6 mol/L.

4.3 The Influence of SO₂Inlet Rate for Absorptivity

To analyze influence of the SO₂ inlet rate for absorptivity, the experiment adopted three inlet rate as 0.5 L/min, 1.0 L/min and 1.5 L/min. The other experiment condition stays constant as temperature

was 25 °C, NaOH concentration is 8 mol/L, NaOH solution heights was 240 mm. The result is shown in Fig. 4.

According to Fig. 4, the absorptivity raised when SO₂ inlet rate increased. The absorptivity was 89.43% when SO₂ inlet rate was 0.5 L/min, the absorptivity 92.14% when SO₂ inlet rate was 92.14%. The absorptivity was 92.27% when SO₂ inlet rate was 1.5 L/min. as it shows, the absorptivity increased 2.73% when the SO₂ inlet rate raised from 0.5 L/min to 1.0 L/min. But the absorptivity only increased 0.13% when SO₂ inlet rate raised from 1.0 L/min to 1.5 L/min. so it is recommended that SO₂ inlet rate is not very big when applied in practical absorption.

4.4 The Influence of Reactor Diameter for Absorptivity

To analyze the influence of reactor diameter for absorptivity, the experiment has adopted reactors with diameters as 120 mm, 180 mm and 240 mm. The other experiment condition stays constant as temperature was 25 °C, NaOH concentration is 4 mol/L, NaOH solution height was 240 mm, SO₂ inlet rate 0.5 L/min, diffuser diameter 104mm. The result is shown in Fig. 5.

According to Fig. 5, the absorptivity raised at first than fall with the rise of the reactor diameter. The absorptivity increased from 89.42% to 91.67% when

Fig. 3 The influence of NaOH concentration for SO₂ absorptivity.

Fig. 4 The influence of SO₂ inlet rate for absorptivity.

Fig. 5 Influence of reactor diameter for absorptivity.

Fig. 6 Sodium sulfite precipitation.

Table 1 Cost calculation for recycling alkali solution SO_x absorb system.

Oil consumption(kg/h)	$0.17 \times 8,500 = 1,445$
SO ₂ output (kg/h)	$2.7\% \times 1,445 \times 2 = 78.03$
Necessary NaOH amount need (kg/h)	$78.03 \times 80 / 64 = 97.5$
NaOH price (\$/T)	256
Cost of process exhaust gas of 2.7% HFO(\$/T)	$256 \times 0.0975 / 1.445 = 17.3$
BW380 price(\$/T)	337.00
BW0.1%S (\$/T)	600.50
Different of cost per ton(\$/T)	263.5

Oil price source: *Bunker world*.

reactor diameter raised from 120 mm to 180 mm. As the reactor diameter reaches 240 mm, the absorptivity reduced to 90.91%. The influence of reactor diameter is greater than NaOH solution height. But the absorptivity maximized when the ratio of reactor diameter over diffuser diameter reaches 1.8.

4.5 The Analysis of Precipitations during Experiment

The precipitation progress happened in experiment varies by the SO₂ inlet rate. Less precipitations appeared when SO₂ inlet rate and NaOH solution concentration were both low, and vice versa. When

SO₂ inlet rate was 1.5 L/min and the NaOH solution is 8mol/L, the solution turns white after 10 minutes, then turns turbid later on. There were white precipitations on the diffuser, as is shown in Fig. 6.

This is sodium sulfite according to analysis. The distribution of precipitation is uneven on the diffuser. The cause is that the resultant-sodium sulfite can be dissolved when the experiment begins because it is not abundant in the water. Sodium sulfite begins to precipitate after reaching saturated concentration. Sodium sulfite mainly gathers at the surface of diffuser especially where the SO₂ inlet is big by the efforts of tensions between molecules.

5. Analysis of Economy

The analysis of economy for ship's closed recycling SO_x absorb system with sodium hydroxide solution contains: equipment cost and operation cost.

Equipment cost [15]: The equipment cost is rather expensive. It will need 1-4 years to repay the cost as the price for whole set is 1.5million.

Operation cost: Set an occasion as a 10 MW unit running with MCR is at 85% and consumes 2.7% HFO. The specific fuel consumption rate for this is 170 g/kW·h. see Table 1.

According to Table 1: It needs 17.3\$/t to process 2.7% HFO for diesel engines with 10 MW power. While the different of cost between 2.7% HFO and 0.1% HFO is 263.5 dollars.

6. Conclusions

This thesis studies on ship's SO_x absorption with NaOH solution. The usage of NaOH solution for SO₂absorption is effective and economical according to experiment. The adoption of closed recycling system prevents the damage to sea environment. The reduction of cost varied by duration the ship's sailing in the emission control area. According to the calculation with the current oil price, 363.46\$ could be saved per hour for a ship with 10 MW power in emission control area, which is rather economical.

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