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Study on Using Scrubbing Tower to Remove SO_2 from Marine Diesel Engine Exhaust

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International Maritime Organization MARPOL73/78 was published to limit sulfur dioxides of marine diesel engine, which regulated that in addition to using fuel of corresponding sulfur to meet emission requirements, marine exhaust scrubbing system can also be used to meet regulations. In order to develop marine exhaust scrubbing system, this paper is based on sodium alkali method to experimentally research the effect of liquid-gas ratio (L/G), scrubbing liquid pH and inlet temperature and exhaust flow rate of scrubbing tower on desulfurization efficiency. The results are as follows: when liquid-gas ratio is of 1.5-2.5 L/m^3, scrubbing liquid pH is higher than 6.7, inlet temperature is lower than 200 °C and exhaust gas flow rate is of 1.5-1.91 m/s, the desulfurization efficiency can be more than 97.15 %. The influence rule of these parameters on desulfurization efficiency can be got and key process parameters in scrubbing tower operation can be obtained, which provides reference for the design and development of desulfurization system in medium scale.

Keywords: Marine diesel engine, Sulfur dioxide, Sodium-alkali method, Desulfurization efficiency.

INTRODUCTION

Sulfur dioxide is a major atmospheric pollutant, which mainly comes from the exhaust produced by combusting fuel of high sulfur content. Generally, large marine diesel engines use heavy fuel oil with average sulfur content of 2.7 %. During the combustion, about 96 % elemental sulfur in fuel is oxidized to SO_2 and only a little part is further oxidized[1] to form SO_3. According to the statistics of International Maritime Organization (IMO), the total annual SO_x emission to the atmosphere is up to 8.5 million tons, which shows an increasing tendency year by year and the land-based emission is about 11 million tons. European clean air plan calculates that along with the decrease of ground-based SO_x emissions, sea-based SO_x emissions of 2025 will be more than global ground-based SO_x emissions[2]. Many countries and international organizations paid attention to the limitation of marine SO_x emission and have developed ship pollutants emission control regulations. Combining ship characteristics to develop exhaust cleaning desulfurization system of high efficiency and low cost becomes home and abroad research hot spot. Through the analysis and contrast of current desulfurization technologies, this paper obtains that sodium-alkali method exhaust desulfurization technology has good application prospect.

Absorption mechanism of SO_2: Sodium hydroxide is using as the absorbent to remove SO_2, in which, exhaust mixes with the scrubbing liquid in the packing layer and SO_2 from the exhaust quickly diffuse to the liquid phase through the gas-liquid interface and then dissolves into the liquid phase to generate H_2SO_3. Sulphurous acid ionizes to react with OH^- of absorbent.

The absorption mechanism of SO_2 is based on the following ion reaction[3]:

$$SO_2\,(g) \rightleftharpoons SO_2\,(aq) \tag{1}$$

$$SO_2\,(aq) + 2H_2O\,(l) \rightleftharpoons HSO_3^-\,(aq) + H_3^+O \tag{2}$$

$$HSO_3^-\,(aq) + H_2O\,(l) \rightleftharpoons SO_3^{2-}\,(aq) + H_3^+O\,(aq) \tag{3}$$

$$OH^-\,(aq) + H_3O^+\,(aq) \rightleftharpoons 2H_2O\,(l) \tag{4}$$

The chemical reaction equation:

$$2NaOH + SO_2 \rightleftharpoons Na_2SO_3 + H_2O\ (pH > 9.0) \tag{5}$$

$$Na_2SO_3 + H_2O \rightleftharpoons 2NaHSO_3\ (5.0 < pH < 9.0) \tag{6}$$

The main side reaction in scrubbing absorption process is oxidation reaction of Na_2SO_3, which generates Na_2SO_4.

EXPERIMENTAL

The experimental system is composed of sample gas simulation system and heating system, scrubbing tower, exhaust analyzer, as shown in Fig. 1.

Simulation sample gas is formulated by mixing pressurized air with pure SO_2. The sample gas heating system is composed of tubular heater and intelligent feedback controller.

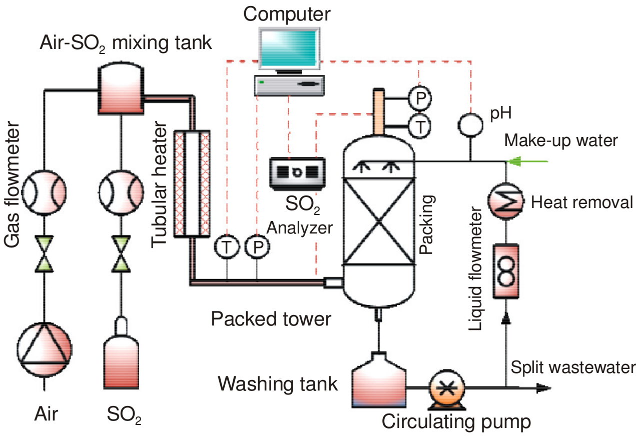

Fig. 1. Flow chart of experiment apparatus

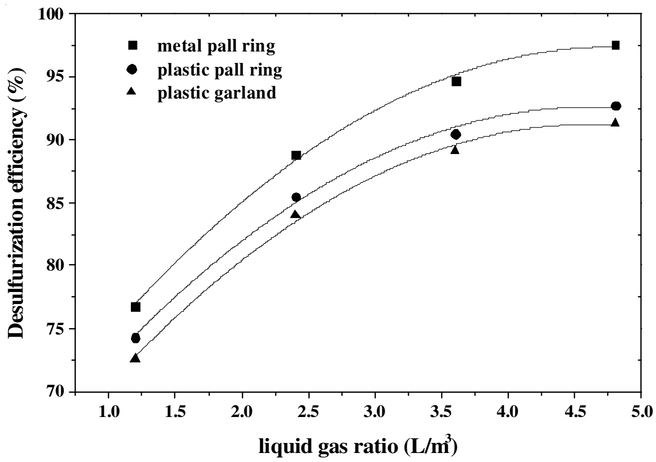

Fig. 2. Influence of packing type on desulfurization efficiency

The scrubbing tower body is made of transparent and high temperature resistant organic glass, in which absorbent is sprayed from the nozzle in the top of tower; the sample gas enters into tower to reversely contact with absorbent through the packing layer. Waste water discharged from the bottom of scrubbing tower, determined by pH value whether to add new absorbent and exhaust gas is analyzed by analyzer to discharge[3].

German Yikang J2KN exhaust gas analyzer is used to measure the inlet and outlet SO_2 concentration. In order to improve the reliability of data, this paper uses the average of multiple sets of data. PHS-25 type acidity meter is used to measure absorbent pH value.

RESULTS AND DISCUSSION

Effect of packing type and height on desulfurization efficiency: Three kinds of packing types are used to research on the influence of different packing types on desulfurization efficiency and Table-1 shows the main performance parameters of these 3 packing types[4].

TABLE-1
MAIN PERFORMANCE PARAMETERS OF PACKING

Parameter	Specific surface area (m^2/m^3)	Void volume (m^3/m^3)	Theory flooding velocity (m/s)
Ø16-metal pall ring	371	0.94	2.355
Ø16-plastic pall ring	188	0.88	3.117
Ø25-plastic garland	269	0.82	2.196

As shown from Fig. 2, when gas flow rate is of 7 m^3/h, operation temperature is room temperature, packing height is 400 mm, the turn of desulfurization efficiency is stainless steel metal ball ring > plastic ball ring > plastic garland; with the increase of liquid gas ratio, the difference between metal ball ring and other two kinds of packing is become bigger.

The specific surface area of Ø25 plastic garland is more than that of Ø16 plastic ball ring and desulfurization of using the former is lower than using latter one. It is for the reason that packing wetting specific surface plays the major role in actual operation. The smaller the packing diameter, the better the packing wetting property is. Owing to the higher maximum surface tension, more wetting specific surface and higher utilization rate of packing surface, the desulfurization efficiency of stainless steel liquid is greater than that of plastic material[5].

Therefore, the packing selection should also consider the wetting property, for the packing with good property plays an important role in reducing equipment size and operation reliability.

As shown in Fig. 3, the packing can improve desulfurization efficiency greatly, with the increase of packing height at a certain liquid gas ratio, desulfurization efficiency increases. The increase of packing height increases the gas-liquid mass transfer area and extends the mass transfer time of gas-liquid and then desulfurization efficiency increases[6]. Only considering from desulfurization efficiency, the increase of packing height is beneficial, but it will lead to the increase of pressure loss, which is detrimental to reduce power consumption. Therefore, it should be overall considered to determine the proper packing height.

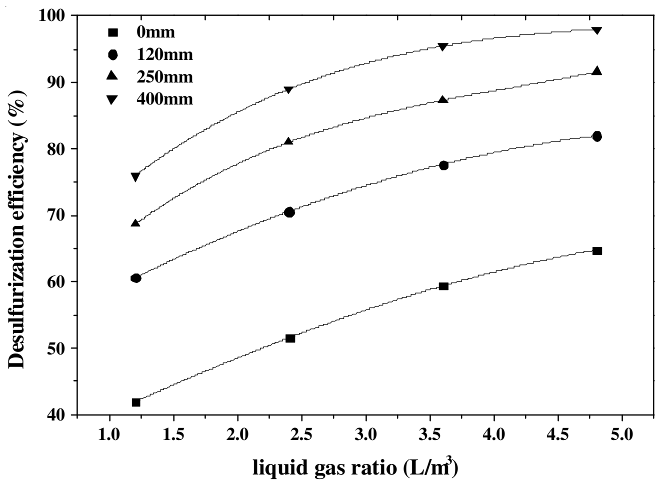

Fig. 3. Influence of packing height on desulfurization efficiency

Influence of liquid-gas ratio on desulfurization efficiency: Fig. 4 showed that the desulfurization efficiency increases with the increase of liquid-gas ratio and it changes greatly when liquid-gas ration is smaller; when liquid-gas ratio is more than 2.5, desulfurization efficiency change tends to be smooth. It is because that NaOH consumption increases with the increase of liquid-gas ratio and pH decreases slowly from the top to bottom of tower, which can maintain higher pH value. The increase of absorbent is beneficial to accelerate the mass

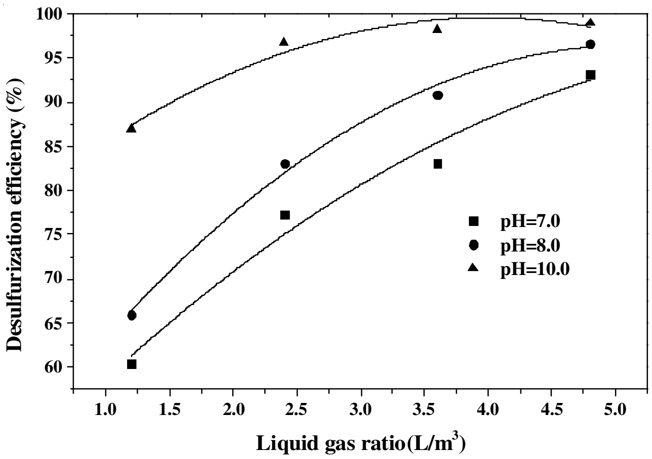

Fig. 4. Influence of liquid-gas ratio on desulfurization efficiency

transfer of liquid-gas contact in packing layer, which is beneficial to improve desulfurization efficiency[7]. When liquid-gas ratio increases further, the promotion effect decreases gradually, so the increases of desulfurization efficiency tends to be smooth.

In the actual operation of desulfurization system, there is an optimal liquid-gas ratio, making the desulfurization system maintained at a higher level. Meanwhile, it will decrease invest and operation cost of desulfurization efficiency. In this paper, the experimental results show that liquid-gas liquid-gas ratio of 2.0-3.5 L/m^3 is appropriate[8].

Influence of pH of washing liquid on desulfurization efficiency: In the condition, (flow rate is 7 m^3/h, normal temperature, concentration of SO_2 is 740 ppm, Bauer metal ring packing, packing height is 400 mm) (Fig. 5). With the washing liquid pH value increases, the desulfurization efficiency increased and the variation tendency is apparent when the liquid-gas is relatively low[9].

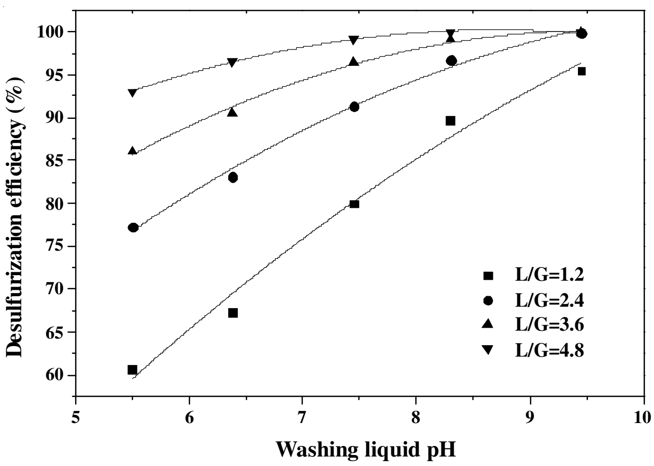

Fig. 5. Influence of pH value of washing liquid on desulfurization efficiency

When the pH value is high, SO_2 is absorbed and reacted into sulfite. The resistance of liquid phase mass transfer is small and the absorption rate will be high[10]. So the desulfurization efficiency can be higher than 95 %.

Only considering the effect of desulfurization, the higher of the pH value of scrubbing liquid, the better it will be. But considering the cost, high pH value will inevitably lead to the increase of NaOH consumption and rising cost. So liquid pH value in the range of 10-10.8 is more reasonable.

Influence of SO_2 concentration on desulfurization efficiency: The big differences of the sulfur content in heavy fuel oil which is supplied by admiralty fuel oil market all over the world result in the concentration of SO_2 in the exhaust gas of diesel engine is not stable. So the study on the influence of SO_2 concentration on removal efficiency is of great significance. The results are shown in Fig. 6.

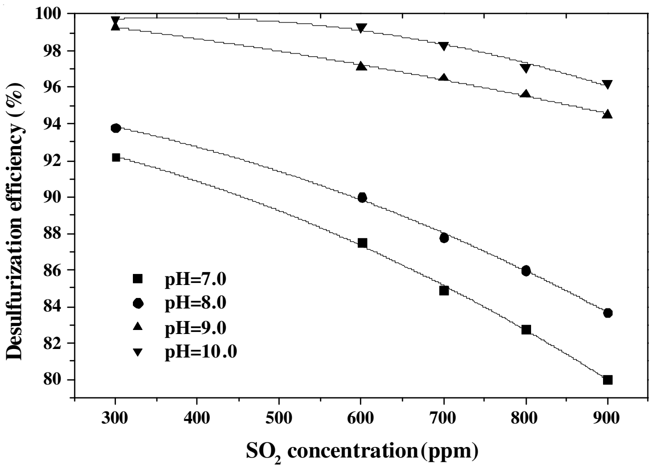

Fig. 6. Influence of concentration of SO_2 on desulfurization efficiency

From Fig. 6, we can see that under the conditions of different pH value, desulfurization efficiency decreased while SO_2 concentration increased. As other operating conditions are the same, when the concentration of SO_2 is higher, the scrubbing liquid from unit SO_2 is less, which is equivalent to reducing the liquid-gas ratio, so the desulfurization efficiency decreased. In practical application, we can determine the SO_2 concentration of system design according to sulfur content level of the admiralty fuel oil market, which can make the desulfurization washing meet International Maritime Organization emission regulations[11].

Influence of concentration of CO_2 on desulfurization efficiency: The CO_2 concentration in the exhaust gas from ship's diesel engine is about 5 %, the SO_2 concentration of it is about 80-100 times. Carbon dioxide belongs to the acid gas, it can be absorbed in the process of desulfurization by washing. So the study on the influence of CO_2 concentration in flue gas on desulfurization efficiency is necessary.

Fig. 7 showed that the influence of CO_2 concentration in the exhaust gas on desulfurization efficiency is small. Although the system desulfurization efficiency decreased, the decreased amplitude is very small. This is because both SO_2 and CO_2 are acid gas, the pH value will decrease after absorbing the two gases. But the acid that is formed by dissolving SO_2 is far stronger than that of CO_2. In the low pH value, the formed acid by dissolving CO_2 will have a trend of decomposing. At the same time, even though the CO_2 is absorbed in the absorption solution whose pH value is higher, its products, Na_2CO_3 or $NaHCO_3$, has the ability to absorb SO_2. Therefore, in practical engineering design, we can ignore the effects of CO_2 on the process of absorbing SO_2.

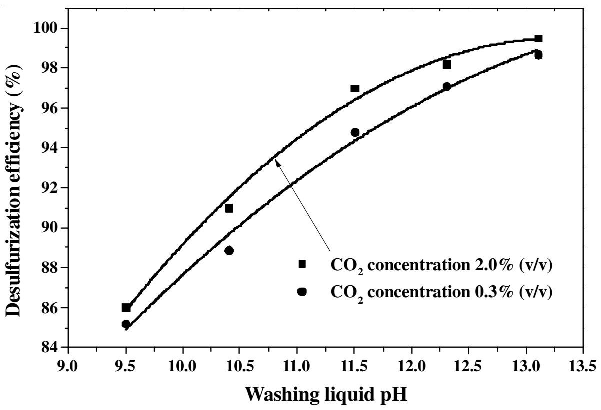

Fig. 7. Influence of CO_2 concentration on desulfurization efficiency

Influence of gas temperature on desulfurization efficiency: From the theory of gas-liquid absorption, we can know that the temperature of exhaust gas greatly influence the temperature of absorption and reaction, thus influence the desulfurization efficiency of the scrubbing tower (Fig. 8).

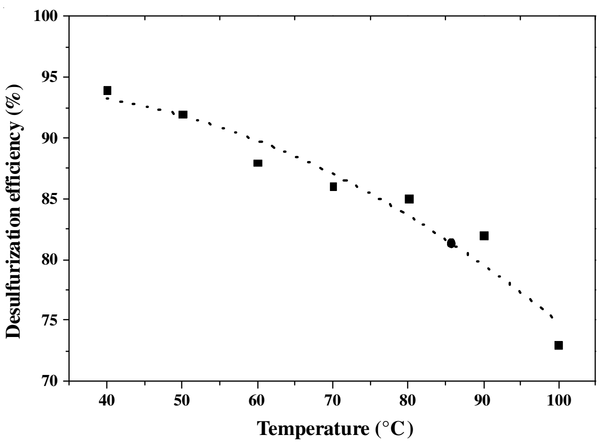

Fig. 8. Influence of flue gas temperature on desulfurization efficiency

So we should do the experimental study and theoretical analysis of the factors to ensure the temperature of exhaust gas.

Fig. 9 showed that when other conditions are the same, the temperature of exhaust gas will lead to the increase of reaction temperature and SO_2 partial pressure, which leads to the decrease of propulsion of chemical absorption and the desulfurization efficiency. The exhaust gas is produced by fuel. According to the actual test results, the average temperature of exhaust gas is about 200 °C, the temperature after spraying is around 50-60 °C. In the wet desulfurization device, we need to cool down the temperature of exhaust gas, but the temperature should not be too low. When it is below the dew point, desulfurization device will be corroded and gas diffusion will be difficult. It is observed that the appropriate temperature of absorption and reaction is 40-50 °C in the system of sodium, sulfur and acid[12].

Conclusion

• The sodium-alkali method is used to reduce the SO_2 in the waste gas. The higher the pH value of absorption liquid, liquid gas ratio and the height of packing are, the higher desulfurization efficiency is. The desulfurization characteristic

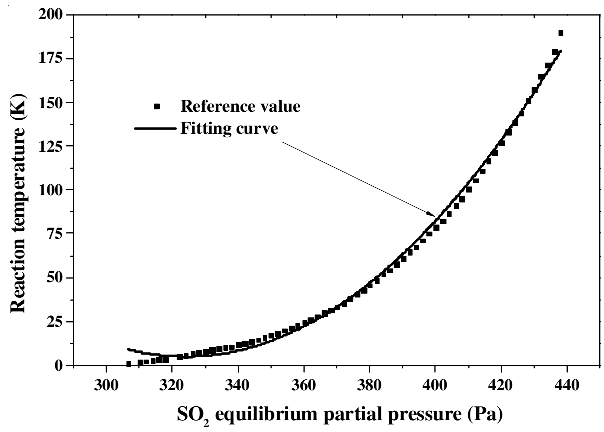

Fig. 9. Relationship between reaction temperature and SO_2 equilibrium partial pressure

of metal Bauer ring packing is better than plastic Bauer ring in the same condition. When the concentration of SO_2 in the exhaust gas increases, desulfurization efficiency will reduce.

• We can use the metal Bauer ring packing in the process of testing. When the packing height is 400 mm, liquid gas ratio is 4.8 L/m^3, the pH of scrubbing liquid is 10 and the SO_2 content in the exhaust gas is 740 ppm (1500 mg/Nm^3), the desulfurization efficiency can reach 98.2 %.

• The experiment has proved that the CO_2 concentration has little effect on the desulfurization efficiency, so when we design the system, one can ignore its effect on desulfurization efficiency.

• The temperature of exhaust gas has key influence on the desulfurization efficiency of the scrubbing tower. It reacts directly in the temperature of gas-liquid mass transfer. The high temperature is not conducive to the absorption process, then the inlet temperature is low.

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