Removal of tar from coke oven flue gas by emulsion liquid membrane

Junjie Zhang¹, Pengxiong Dong¹, Chunying Li², Hongxia Li¹*

¹Collage of Chemical Engineering, Collage of Life Science, College of Psychology, North China University of Science and Tecnology, 21Bohai Road, Caofeidian Xingcheng, Thangshan 063210, Hebei, China.
²Shenyang Environmental Monitoring Center, Shenyang, 110015, P. R. China
*Corresponding author’s e-mail: lhx2453@126.com

Abstract. The new method for removal tar from coke oven flue gas by emulsion liquid membrane was developed. The W/O emulsion was prepared by using kerosene as organic solvent, L-113B as surfactant, water as internal phase and external phase, respectively. The optimum operating conditions were obtained: The optimum experimental conditions of the ELM process for initial tar concentration of 62.5 mg/L are: absorption time: 40 min; concentration of L-113B: 4% (v/v); emulsification speed: 4000 r/min; volume ratio of emulsion to external water phase: 1:4; gas flow rate: 100 mL/min; stirring speed: 630 r/min; volume ratio of oil phase to internal phase: 1:1. The efficiency of tar removal was about 98 % at optimal operating conditions.

1. Introduction
Coke is mainly used in blast furnace iron smelting and blast furnace smelting of non-ferrous metals such as copper, lead, zinc, titanium, antimony and mercury acting as reducing agent, heating agent and material column framework. Tar in flue gas is a complex mixture consisting mainly of aromatic hydrocarbons carcinogens. If the coke oven flue gas with excessive tar content is emitted into the atmosphere, it will not only cause seriously environmental pollution, but also threaten people health. So, it is necessary to develop a method for removal tar from coke flue gas.

Emulsion liquid membrane (ELM) is an efficient and energy-saving separation technology. ELM provides several advantages such as a high interfacial area resulting in enhancement of mass transfer efficiency, high selectivity, relatively low cost due to the cycling usage of oil phase. ELM is widely used in the separation or extraction of target substances, such as removal heavy metal ion pollutant of gadolinium [1] and chromium (VI) [2], removal organic pollutant of phenol [3] and cationic dye [4], extraction organic compounds of lactic acid [5] ethylparaben [6]. ELM was used to removal tar from coke oven flue gas in this work and the parameters including the concentration of surfactant, the gas flow rate, the separation and emulsion stirring speed and the volume ratio of oil phase to internal phase, etc. were studied.

2. Experimental
2.1. Main drugs and instruments
Tar, Coking Plant in Tangshan city; kerosene, Tianjin Damao Chemical Reagent Factory; xylene, Tianjin Yongda Chemical Reagent Co., Ltd.; L-113B, Lanzhou Refinery Factory; homogenizer, JZ-II, Sifang Electrical Equipment Factory; QPA-5LP Air Generator, Shanghai Lingxi Instrument Co., Ltd.; UV-Vis Spectrophotometer, T6, Beijing Puxi General Instrument Co., Ltd.; high speed refrigerated centrifuge, SIGMA 3-30K, Sartorius Scientific Instruments (Germany) Co., Ltd.

2.2. The process of tar removal by ELM

The L-113B as surfactant and kerosene as solvent construct the membrane phase (oil phase). Water was used as inter phase and outer phase, respectively. The emulsion was prepared by high speed stirring method. Coke oven flue gas containing tar flow past through the separation vessel, in which the tar was absorbed by emulsion liquid membrane system. The removal efficiency was measured by increase of cotton weight in the pipe of discharge gas. The operation condition was as follows: absorption time for tar in coke oven flue gas was 40 min, tar concentration in coke oven flue gas was 62.5 mg/mL.

3. Results and discussions

3.1 Removal of tar by emulsion liquid membrane

3.1.1 Effect of the L-113B concentration

The effect of surfactant concentration on the removal efficiency for tar is shown in Fig. 1. The concentration of surfactant is an important factor that directly affects the stability of the W/O emulsion. At low surfactant concentration, the amount of surfactant is insufficient for emulsion well which causes more break-ups and instability of the W/O emulsion. However, excessive surfactant leads to emulsion will not disperse well in outer phase.

As shown in Figure 1, when the concentration of L-113B is 1 % to 3 % (v/v), the removal efficiency for tar is gradually increasing. This is because the larger the concentration of the L-113B, the better the stability of the W/O emulsion, and so the effect of tar removal is enhanced. When the L-113B concentration is increase over 3 %, the removal efficiency of tar remains almost unchanged. That is because the higher surfactant emulsion causes swelling during the separation stirring process, which causes instability of the W/O emulsion. So, the higher concentration of surfactant can worsen the emulsion swelling phenomenon [7]. Accordingly, the concentration of L-113B was selected as 3 % (v/v) for all subsequent experiments.

![Figure 1. Effect of the concentration of L-113B on tar removal (Experimental conditions: volume ratio of oil phase to internal phase: 3:2; separation stirring speed on tar removal: 600rpm; gas flow rate: 120mL/min; volume ratio of emulsion to external phase: 1:4; emulsification speed: 4000 rpm.)](image-url)
3.1.2 Effect of emulsification speed
Experiments with different emulsification speeds ranging from 2000 r/min to 5000 r/min were conducted. Figure 2 shows that the tar removal efficiency increases with an increase in the emulsification speed from 2000 r/min to 4000 r/min. For higher emulsification speed gives better mixing of membrane phase (oil phase) and internal phase, the stability of W/O emulsion is enhanced. Also, higher emulsification speed can yield smaller size of emulsion liquid droplets, which have larger interfacial surface area per unit volume of membrane phase and promote the diffusion of tar from the external phase to the oil phase. But when the emulsification speed is higher than 4000 r/min, the tar removal efficiency begins to decline for the formed emulsion liquid droplets easy swelling in separation process. So, the emulsification stirring speed was selected as 4000 r/min in the following experiments.

![Figure 2. Effect of emulsification speed on tar removal (Experimental conditions: volume ratio of oil phase to internal phase: 3:2; separation stirring speed on tar removal: 600 rpm; gas flow rate: 120mL/min; volume ratio of emulsion to external phase: 1:4.)](image)

3.1.3 Effect of volume ratio of emulsion to external water phase
The influence of volume ratio of emulsion to external phase on the removal efficiency of tar is shown in Figure 3. The volume ratio of the emulsion to the external phase directly affects emulsion dispersion effect in external phase and so effect the mass transfer surface. The tar removal efficiency increases remarkably by increasing the volume ratio of emulsion to external phase from 1:8 to 1:5. This is owing to the fact that with the increasing amount of emulsion in the external water phase, the amount of available droplets and interfacial surface area per unit volume of external phase increase and hence the transfer rate of tar and tar removal efficiency are promoted. But, when the volume ratio of emulsion to external phase increases from 1:5 to 1:3, the tar removal efficiency not increase apparently. The higher the volume ratio of emulsion to external phase will the more likely result the emulsion liquid membrane swelling and the larger the volume ratio of emulsion to external phase will result the higher the operational cost. Therefore, 1:5 was selected as the optimum volume ratio of emulsion to external water phase.
Figure 3. Effect of volume ratio of emulsion to external water phase on tar removal  
(Experimental conditions: volume ratio of oil phase to internal phase: 3:2; separation stirring speed on tar removal: 600 rpm; gas flow rate: 120 mL/min.).

3.1.4 Effect of gas flow rate  
The effect of gas flow rate on tar removal efficiency is shown in Figure 4. It is observed that the tar removal efficiency becomes lower and lower with the gas flow rate increasing. For the increased gas flow rate reduces the residence time of the gas in the absorber, and so shorter the contact time between the tar with emulsion and so result more tar could not absorbed. In the later experiment, 100 mL/min was recommended as gas flow rate.

Figure 4. Effect of gas flow rate on tar removal (Experimental conditions: volume ratio of oil phase to internal phase: 3:2; separation stirring speed on tar removal: 600 rpm.)

3.1.5 Effect of stirring speed  
The influence of stirring speed on the removal efficiency of tar is shown in Figure 5. For the fact of the size of emulsion liquid droplets is reduced by increasing the mixing intensity, more interfacial surface area is available between the external water phase and the oil phase. So, the tar removal efficiency increases gradually as the stirring speed increases from 420 to 630 r/min. But, the tar removal efficiency starts to decrease as stirring speed increasing from 630 to 840 r/min. This can be explained by that as the stirring speed increased the shear on the emulsion liquid membrane increased, and so the emulsion membrane might be unstable and even broken [8]. Also, membrane swelling might be aggravated by higher stirring speed. The stirring speed 630 r/min was recommended in the following experiment.
3.1.6 Effect of volume ratio of oil phase to internal phase

The effect of the volume ratio of oil phase to internal phase on removal efficiency of tar is shown in Figure 6. The experiments with different volume ratios of the oil phase to internal phase in the range of 1:4 to 7:3 were conducted while maintaining a fixed emulsion volume.

As shown in the Figure 6, the removal efficiency of tar increases with the volume ratio of oil phase to internal phase increase from 1:4 to 1:1. The viscosity for the emulsion is higher at larger volume ratio, which leads to a decrease of the diameter of internal phase droplets and so leads to the thicker of the emulsion membrane. The higher thickness membrane makes the emulsion more stability, which increases the tar removal efficiency. In addition, at high volume ratio, absorption and dissolution of tar are strengthened due to the relatively high organic phase. However, when the volume ratio of oil phase to internal phase is higher than 1:1, the tar removal efficiency begins to decrease. This is because the higher the volume ratio will not make the oil phase and inter phase emulsion well. Therefore, 1:1 volume ratio was the optimum volume ratio of oil phase to internal phase for this emulsion liquid membrane system in tar removal from flue gas.

4. Conclusions

The emulsion liquid membrane (ELM) process for the removal of tar from coke oven flue gas was experimentally studied. The removal efficiency for tar from coke oven flue gas was about 98 % at optimal operating conditions.
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