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Dust removal and purification of calcium carbide furnace off-gas

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ABSTRACT

A large amount of CO contained in calcium carbide furnace off-gas can be recycled and used as an important raw material for C1 (one carbon) industrial chemical manufacturing. The key to the recovery is the removal of dust and gaseous impurities from the off-gas. For this purpose, an industrial device has been used for removing the dust. This consists of a laboratory-scale fixed-bed reactor with two kinds of adsorbents, prepared in our laboratory, for removing HCN and COS. The results show that the dust content after the dedusting process was less than 20 mg/m^3. The dust particles are composed of microspheres, with an obvious tendency to agglomerate, and with an average diameter of about 6.71 μm. After adsorption, the outlet concentrations of both HCN and COS were less than 1 mg/m^3. In order to remove HCN, activated carbon (AC) was used, impregnated with 0.15 mol/L $Cu(CH_3COO)_2$ solution. The optimum calcination temperature was 350 °C. The AC, modified with $Cu(CH_3COO)_2$, was examined by means of N_2-BET and X-ray photoelectron spectroscopy (XPS) before and after off-gas treatment. The results indicate that the chemisorption products were mainly present in the AC micropores and mesopores, with radius 0.81–1.51 nm. After dust removal and purification, the calcium carbide furnace off-gas is fit for use as a raw material in the C1 chemical manufacturing industry.

1. Introduction

China has little petroleum but is rich in coal. In recent years, the price of petroleum has risen sharply. Following the Chinese energy development strategy, chemical industry using coal as a feedstock will gradually substitute for the petrochemical industry. Chemical industry using coal is developing rapidly, especially in the production of calcium carbide (CaC_2). In developed countries, polyvinyl chloride (PVC) is normally manufactured from petroleum. In China, nearly 78% of PVC is synthesized using acetylene derived from calcium carbide [1]. Calcium carbide is a basic raw material for producing acetylene gas, using the following reaction [2]:

$$CaC_2 + 2H_2O \rightarrow C_2H_2 + Ca(OH)_2 \quad (1)$$

Calcium carbide is manufactured from lime (CaO) and carbonaceous material (petroleum coke or metallurgical coke) in a electric arc furnace at 1800–2200 °C, according to the following equation [3]:

$$CaO + 3C \xrightarrow{1800-2200\ ^{\circ}C} CaC_2 + CO \quad (2)$$

When 1 t calcium carbide is produced, about 400 Nm^3 (standard cubic meter at 0 °C and 1.013 bar) of off-gas is simultaneously emitted [4,5]. The temperature of the off-gas is 700–1100 °C. It contains about 70–80 vol% of CO and 130,000–200,000 mg/m^3 of dust [6]. This causes serious air pollution and a huge waste of a CO resource when the off-gas is burnt and released into the atmosphere. With the development of C1 (one carbon) chemical manufacturing, CO can be used to synthesize many organic chemical products. After dedusting and purification of the off-gas, it can also be used as a raw material for these syntheses. This recycling method not only minimizes the air pollution but also reduces the cost of calcium carbide production and increases economic return.

For effective treatment and comprehensive utilization of the calcium carbide furnace off-gas, two difficulties must be solved. The first is the removal of dust from the off-gas because of the viscosity and corrosion produced by the dust. The dust is mostly composed of fine particles (0.1–20 μm) [6] with coke tar adhering to their surfaces. The second difficulty is the elimination of gaseous

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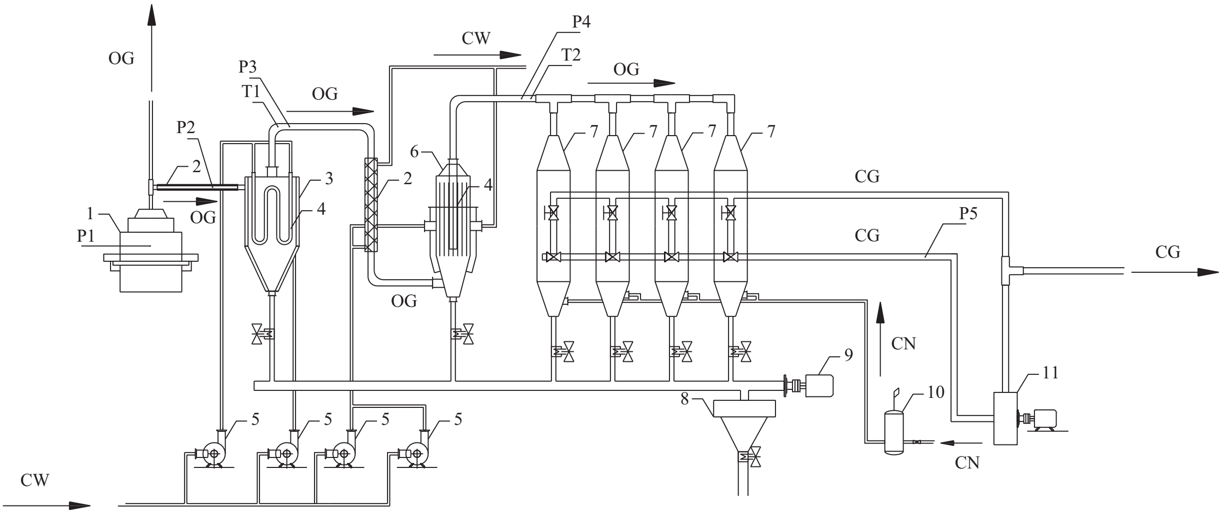

Fig. 1. Schematic diagram of the industrial dedusting device. (1) Calcium carbide furnace; (2) water cooled tube; (3) cyclone separator; (4) circulation water pipe; (5) pump; (6) wet settler; (7) bag filter; (8) dust collection hopper; (9) motor; (10) N_2 gasholder; (11) induced fan; OG – off-gas; CW – circulating water; P – pressure gauge; T – thermometer; CN – compressed nitrogen; CG – clean gas.

impurities from the off-gas, such as HCN, COS, PH_3 and H_2S [7]. These impurities can seriously influence carbonylation synthesis and result in catalyst poisoning. Of these impurities the removal of HCN is the most important, because of its high concentration and toxicity. In general, researchers have focused on removing HCN from air and exhaust gas by adsorption [8–12], catalytic oxidation [13,14], catalytic hydrolysis methods [15,16], and have also studied the oxidation of HCN from water [17,18]. However, at low temperatures, HCN removal from industrial off-gas, which contains high concentration of CO, has not been reported.

In our previous work, it was found that modified activated carbon has good adsorption performance for removing the impurities (PH_3, H_2S, COS, CS_2) from yellow phosphorous off-gas [19–25]. The impurity concentrations in the yellow phosphorous off-gas after purification were less than 1 mg/m^3. Since the main components of this off-gas are similar to those from calcium carbide furnace off-gas [19–22], a laboratory-scale fixed-bed reactor, with modified activated carbon, was also used in this work for the removal of the gaseous impurities.

2. Materials and methods

2.1. Experimental materials

Two kinds of modified activated carbon were prepared. Commercial virgin activated carbon (VAC) was used as the support. The grain diameters were 4 ± 0.5 mm, bulk density 450–550 g/L, specific surface area 800–900 m^2/g, crushing strength 7 kg/cm and pore volume 0.4–0.7 cm^3/g. Firstly, the VAC was stirred and washed with distilled water at room temperature for 3 h, dried at 110 °C for 24 h. Then a known amount of dried activated carbon was impregnated with equal molar concentrations of NaOH or $Cu(CH_3COO)_2$ aqueous solution at room temperature for 48 h, dried at 110 °C for another 24 h, then calcined in a furnace for 6 h.

2.2. Analytical methods

A flue gas analyzer (TR-9700, Xian Juneng Instrument Co. Ltd., China) was used to detect CO, H_2, and O_2. A gas chromatograph (SQ-206, Beijing Analysis Instrument Factory, China) equipped with a thermal conductivity detector (TCD) was used to detect CO_2 and N_2. A gas chromatograph (HC-6, Hubei Chemistry Research Institute, China) equipped with a flame photometric detector (FPD) was used to detect H_2S, PH_3, and COS. A dust sampler (FC-3, Beijing Municipal Institute Labour Protection, China) was used to detect dust. HCN was analyzed using a CN^- ion selective electrode (pCN-1Q9, Shanghai Ruosull Technology Co. Ltd., China).

2.3. Industrial dedusting device

A schematic diagram of the industrial dedusting device is shown in Fig. 1. This consists of three sections. The first section is the cyclone dedusting system, including some water cooled tubes (the diameter of each tube is 0.35 m) and a cyclone separator (The vertical cylindrical body is 8.94 m in height and 2.12 m in diameter. The height of the conical body is 5.84 m and the diameter of conical bottom is 0.40 m); the second section is the wet settling system (The wet settler is consist of a vertical cylindrical body and two conical body. The vertical cylindrical body is 6.20 m in height and 1.32 m in diameter. The height of the upper conical body is 2.20 m and the diameter of conical top is 0.48 m. The height of the lower conical body is 3.26 m and the diameter of conical bottom is 0.48 m); the third section consists of four shake-deflate filters (The filtering area and height of the each bag filter are 460 m^2 and 11.7 m, respectively). The hot off-gas (between 600 °C and 1000 °C), from the calcium carbide furnace, with dust content between 150 g/m^3 and 200 g/m^3, was pumped into the cleaning system through a water cooled tube. The temperature of the off-gas was maintained in the range 550–600 °C. Coarse particles in the off-gas were removed by the cyclone separator (whose efficiency was about 50%) and the off-gas entered into another water cooled tube, before flowing into the wet settler. In the wet settling chamber, the off-gas was not in contact with water but the temperature of the off-gas was reduced to 400 °C. In order to prevent the coke tar from condensing and clogging the bag filters, the temperature of the off-gas was held at 250 °C. Compressed nitrogen was used for deflating the bag filters from the opposite direction and cleaning them.

2.4. Laboratory-scale fixed-bed reactor

After dedusting, the off-gas was pumped into a buffer tank (The buffer tank is 1000 mm in height and 200 mm in diameter) and a dust collector (The dust collector is 800 mm in height and 100 mm in diameter. The height of the glass fiber layer is 600 mm). In the dust collector, dust (15–20 mg/m^3) in the off-gas was removed