Characterization Study of Carbonaceous Pitch Fumes and Their Condensates

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Abstract

Anode plants in China predominantly utilize Regenerative Thermal Oxidizers (RTOs) to incinerate pitch fumes. The incineration process requires the addition of natural gas. To reduce natural gas consumption, it is proposed to utilize an in-plant baking furnace for the synergistic co-combustion of Volatile Organic Compounds (VOCs) and condensates from pitch storage tanks, ensuring that emissions meet regulatory standards. Transport and combustion experiments were conducted on condensates from existing fume pipelines to determine the conveying temperature to the baking furnace and the required combustion temperature. Additionally, VOC transport experiments during the melting of solid pitch were carried out to establish the VOC flow rate for the baking furnace injection. These studies provide a foundation for the development of multi-pollutant synergistic control technologies in carbonaceous fume treatment.

Keywords: Anode plants, Condensate transport, Condensate combustion, VOC combustion, Synergistic control.

1. Introduction

In 2024, China's anode block production capacity reached 30.366 million tonnes per annum (MTPA), with an output of 23.10 million tonnes, corresponding to a capacity utilization rate of 76.07 %. China accounts for two-thirds of the world's anode block production, ranking first globally. The Aluminum Corporation of China (CHINALCO) maintained its position as China's second-largest producer, with a total production capacity of 3.138 MTPA and an annual output of 2.857 million tonnes.

During the forming process of anode production, the melting of solid pitch and the storage of liquid pitch release substantial amounts of pitch fumes. Field measurements [1] show that the concentration of pitch fumes during pitch melting ranges approximately 1 300–1 600 mg/Nm^3, while that emitted from liquid pitch storage tanks is approximately 800–1 000 mg/Nm^3. The composition of these fumes is highly complex, containing more than one hundred hazardous substances such as carbazole, pyridine, naphthalene, phenanthrene, anthracene, and phenol. In particular, benzopyrene is recognized as a strong carcinogen.

Moreover, the *Emission Standard of Pollutants for the Aluminum Industry* stipulates special emission limits for pitch fumes: 30 mg/m^3 for emissions from cathode baking furnaces and pitch melting operations, and 20 mg/m^3 for emissions from anode baking furnaces and green anode production. Pitch fumes must be purified before discharge to ensure compliance with the standard.

Primary treatment methods for pitch fumes include electrostatic precipitation, adsorption, absorption, condensation, and incineration. (1) The electrostatic precipitation method exhibits very low removal efficiency for benzopyrene in pitch fumes. Moreover, it produces hazardous waste tar during the removal of pitch fumes, which to some extent contributes to secondary pollution. (2) Adsorption can be categorized into dry adsorption and resin adsorption. In dry adsorption, pitch fumes pass through layers of activated carbon or calcined coke, where organic compounds are captured. Although this approach delivers high adsorption efficiency, the adsorbents require frequent regeneration or replacement once saturated, resulting in considerable long-term operating costs.

The resin adsorption method employs specialized adsorption resins to capture organic constituents from pitch fumes. While the adsorption capacity is high and the resins can be regenerated and reused, the method is limited by the high cost of resins, low mechanical strength, and proneness to damage during operation. (3) The absorption method produces a large amount of wastewater during the removal of pitch fumes, leading to secondary pollution. Wastewater is difficult to treat and entails high treatment costs, and the process also causes severe corrosion to equipment. (4)

The condensation method lowers the temperature to condense gaseous organic compounds in pitch fumes into a liquid form, achieving both recovery and purification. It is effective for recovering high-boiling-point organic compounds but performs poorly with low-boiling-point compounds. However, this method requires high capital investment and operating costs. (5) The incineration method includes direct combustion and catalytic combustion. In direct combustion, pitch fumes are introduced into a combustion chamber, where organic compounds are burned at high temperatures (typically 700–800 °C), producing carbon dioxide and water. This method is highly efficient and suitable for treating high-concentration pitch fumes, but it needs high energy consumption and operating costs.

Catalytic combustion, on the other hand, burns pitch fumes at lower temperatures (typically 200–400 °C) in the presence of catalysts, such as noble metals or metal oxides. The advantages of this method include a lower ignition temperature and reduced energy consumption, but it comes with the disadvantages of high catalyst costs and the risk of catalyst intoxication and deactivation.

Compared to methods such as electrostatic precipitation, adsorption, absorption, and condensation, incineration is the method that offers the most thorough treatment of pitch fumes. However, it requires additional fuel and results in high energy consumption. According to the *Guidelines on Strengthening the Response to Heavy Pollution Weather and Consolidating Emergency Emission Reduction Measures*, carbon manufacturers shall be categorized as Class A, and are required to adopt incineration processes to treat organic exhaust gases, including pitch fumes. Therefore, under the premise of minimizing energy consumption, incineration is the most effective method for pitch fumes control in China's carbon industry.

Carbon manufacturers typically use pot baking furnaces, where the flue temperature can reach up to 1350 °C. Based on this, the project team proposed [2, 3] utilizing the high-temperature flues of these pot furnaces to directly incinerate pitch fumes, in order to reduce energy consumption. This approach eliminates the need for additional energy input, as the pitch fumes can serve as fuel for the furnace. The heat generated during combustion can be recovered and reused, thereby achieving emission reduction and carbon mitigation, and simultaneously lowering production costs.

2. Experiment

2.1 Experimental Methods

Condensates formed within the existing pitch fume pipelines in the plant tend to accumulate, hindering the smooth transport of the fumes. The key to implementing direct incineration of pitch fumes using the high-temperature flues of the pot furnaces lies in ensuring the reliable and continuous conveyance of the fumes. An experimental flowchart was developed accordingly, as shown in Figure 1.

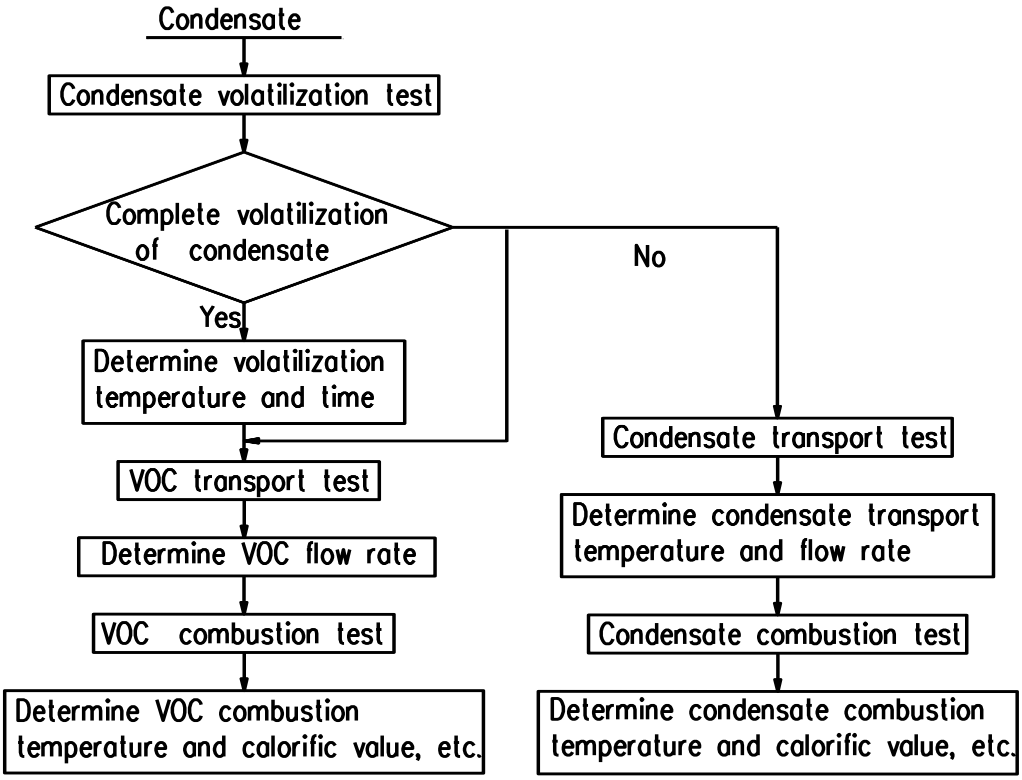

Figure 1. Schematic diagram of the experimental procedure.

2.2 Experiment and Discussion of Results

2.2.1 Condensate Transport Experiment

Condensate Volatilization Experiment

A condensate volatilization experiment was conducted using condensate collected from a pitch fume transport pipeline of a domestic carbon manufacturer. A total of 125.94 g of condensate was placed into a flask (flask weight: 164.10 g). The flask was heated with a heating mantle at specified temperatures. At 110 °C, 120 °C, and 130 °C, the temperature was maintained for 20 and 40 minutes, respectively, after which the total weight including condensate and container was measured. Subsequently, the total weight was measured after maintaining temperatures of 140 °C, 150 °C, 160 °C, 180 °C, and 200 °C for 20 minutes each. The results of the condensate volatilization test are shown in Table 1.

Table 1. Condensate volatilization results.

Temperature °C	Total Mass g	Mass after 20 min g	Volatilization (0–20 min) %	Mass after 40 min g	Volatilization (20–40 min) %
110	290.04	289.92	0.10	289.84	0.06
120	289.80	289.74	0.05	289.68	0.05
130	289.68	289.52	0.13	289.38	0.11
140	289.38	289.29	0.07		
150	289.29	288.96	0.26		
160	288.96	288.74	0.18		
180	288.74	288.33	0.33		
200	288.33	287.31	0.82		

As shown in Table 1, within the temperature range of 110–200 °C, the volatilization rate of the condensate fluctuated irregularly with increasing temperature during the 20-minute residence time at each temperature point. At the same temperature, the amount volatilized during the 20–40 minutes was consistently not more than that during the 0–20 minutes. Over the entire 4.7-hour experiment, the total volatilization amounted to 1.36 %.

It can be seen that, to achieve rapid and complete volatilization of the condensate into the gas phase, the system must maintain an accompanying temperature of at least 200 °C, which aligns with the findings of Lingjie Cui et al. [4], who stated, "Most of the pitch fumes are pitch vapor, which has a relatively high condensation point (200 °C)." Given the high accompanying temperature (> 200 °C) required for the rapid and complete volatilization of the condensate, the experiment was designed to separately investigate the transport and combustion of both the condensate and the uncondensed pitch fumes (VOCs).

The viscosity of the condensate could not be measured, indicating that it is very low. During the heating test, visible residues and particles remained in the condensate at 70 °C, while above 85 °C, the condensate exhibited a flow behaviour similar to thick milk. Considering temperature variations, the recommended transport temperature for the condensate should be above 90 °C. The experimental results showed a coking value of 1.62 % for the condensate, suggesting that its return to the pitch storage tank would reduce the overall coking value of the pitch. Therefore, the combustion of the condensate was further investigated.

2.2.2 Combustion Experiment of the Condensate

The condensate was dried for 21.5 hours at 60 °C and 90 °C, respectively, yielding a water content of 1.19 %. It is inferred that the water content has no significant effect on the combustion of the condensate.

(1) Thermogravimetric (TGA) Experiment of Condensate

In an air atmosphere, the condensate was heated from ambient temperature to 900 °C at a rate of 30 °C/min. The thermogravimetric curve of the condensate in air is shown in Figure 2.

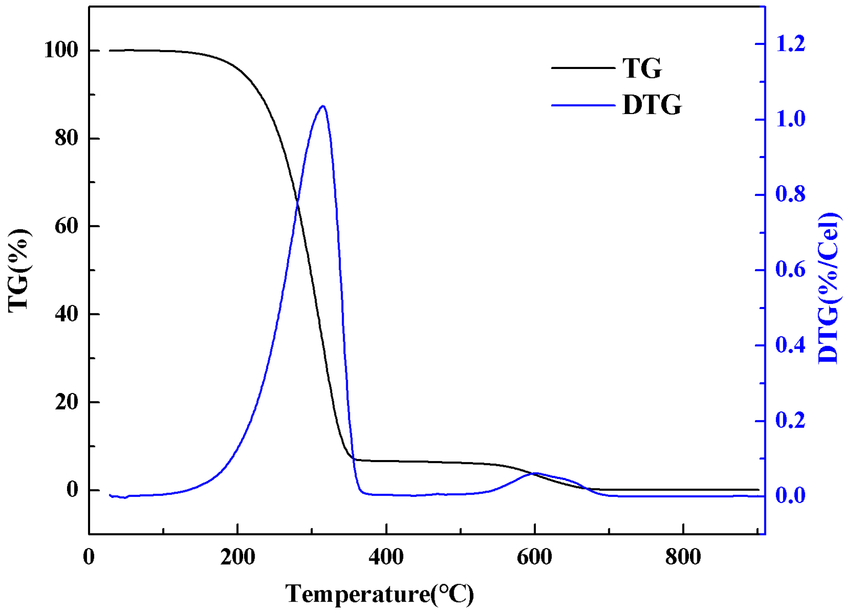

Figure 2. Thermogravimetric curve of the condensate in air.

As shown in Figure 2, the condensate exhibited the highest rate of mass loss at 320 °C, with the mass loss stabilizing around 700 °C. It is therefore inferred that combustion of the condensate occurs below 700 °C.

(2) Combustion Experiment of the Condensate

The condensate was placed in muffle furnaces at different temperatures, and the combustion results are shown in Table 2.

Table 2. Combustion results of the condensate.

Condensate mass, g	39.34	28.09	27.19
Temperature, °C	700	550	580
Mass loss of condensate, %	99.91	99.07	99.39

At 700 °C, the condensate began to combust approximately 1 minute after being placed in the muffle furnace chamber, with combustion lasting around 2.25 minutes and the chamber temperature reaching 731 °C. At 550 °C, visible fume appeared 17 seconds after the condensate was placed into the chamber, but no combustion was observed. A temperature drop in the furnace was noted in the process, and fume release continued for approximately 4.5 minutes. At 580 °C, combustion started about 1 minute after the condensate was placed into the chamber and lasted for around 2 minutes. As shown in Table 2, regardless of whether combustion or smouldering occurred, the residue content was always less than 1 %, and higher temperatures resulted in a smaller residual mass. In addition, according to the *Determination of Calorific Value of Coal* (GB/T 213-2008), the lower heating value (LHV) of the condensate was measured to be 37 250 kJ/kg. This provides a quantitative basis for evaluating the 'impact of condensate combustion on the thermal equilibrium of the furnace.

2.2.3 VOCs Transport Experiment

Solid pitch from the storage facility of a domestic carbon manufacturer was selected for the study. The results of routine characterization of the solid pitch are shown in Table 3 and Figure 3.

Table 3. Routine characterization results of solid pitch.

Test Item	Unit	Result	Test Method
Softening Point	℃	112	NB/SH/T 0739-2014
Density	g/cm^3	1.32	YS/T 63.9-2012
Toluene-Insolubles	%	31.6	GB/T 2292-2018
Quinoline-Insolubles	%	11.5	GB/T 2293-2019
Water Content	%	0.83	GB/T 26930.1-2011
Coking Value	%	59.59	GB/T 8727-2008

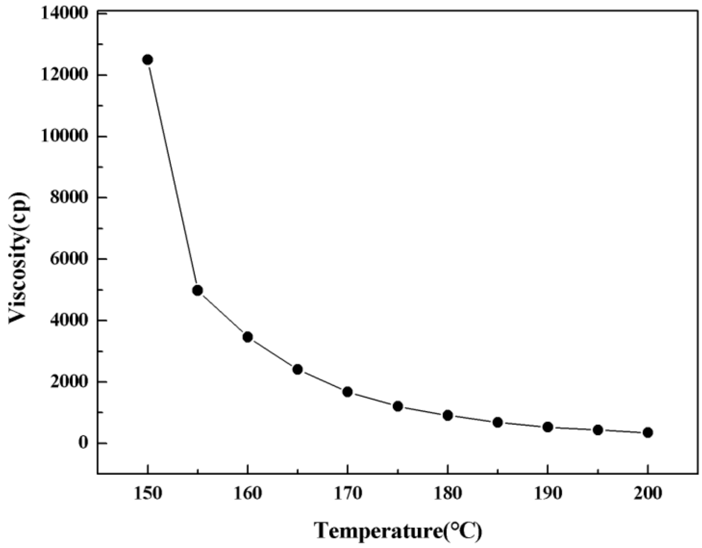

Figure 3. Viscosity of solid pitch.

(1) Experiment on pitch fumes generation rate
The volatilization rates of parallel samples of dried solid pitch at 180 °C are shown in Figure 4.

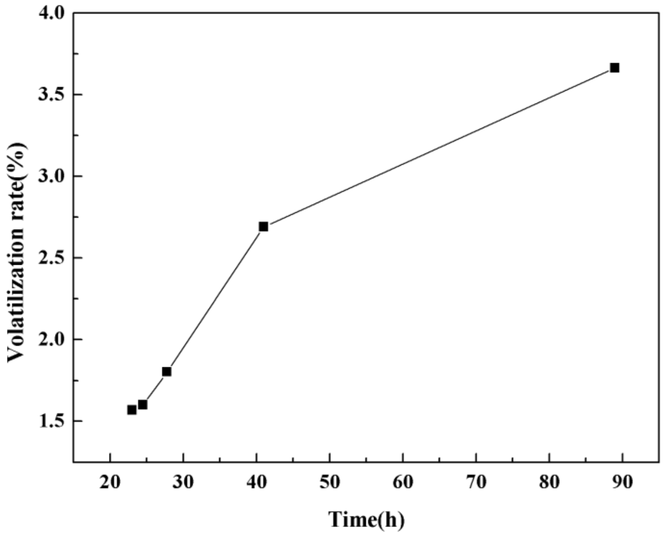

Figure 4. Volatilization rate of solid pitch.

After being heated at a constant temperature of 180 °C in a forced-air drying oven for approximately 89 hours, the solid pitch exhibited a volatilization rate of 3.66 %, indicating that the generated pitch fumes accounted for 3.66 % of the mass of the solid pitch.

According to reference [5], pitch fumes do not condense at temperatures above 400 °C. Given the practical difficulty of maintaining accompanying temperatures above 400 °C, condensation of pitch fumes in the transfer line is deemed acceptable. The critical requirement is that the condensate must be able to flow out of the pitch fumes pipeline, which can be ensured by maintaining the temperature inside pipeline above 90 °C. In this study, the uncondensed gas in the pitch fumes is referred to as VOCs, while the condensed material is termed condensate. The mass ratio of VOCs to condensate is 1:4 [6]. This provides a theoretical basis for selecting the induced draft fan for VOCs transport and determining the appropriate size for the condensate storage tank in the experimental setup.

2.2.4 Combustion Experiment of VOCs

VOCs refer to the substances remaining after the condensation of pitch fumes. Due to their similar combustion characteristics to pitch fumes and their feature to combust at temperatures above 800 °C, further experimental investigation was deemed unnecessary.

3. Conclusions

This study addresses the high energy consumption associated with incineration of pitch fumes in anode plants. Through an investigation of the characteristics of carbonaceous pitch fumes and their condensate, the following key conclusions were drawn:

1) For the synergistic treatment of pitch fumes, condensation is permitted, with separate processing of VOCs and condensate.

2) During transport, the condensate temperature should be maintained above 90 °C.

3) The combustion temperature of the condensate should be above 580 °C.

4) The yield of pitch fumes should be determined through volatilization experiments of the pitch.

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