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THE EXPERIMENTAL STUDY ON THE INCINERATION OF THE ACRYLONITRILE EFFLUENT IN THE CFB BOILER BURNING OIL SHALE

YANG MA, JIANGUO LIU, CHAO FAN, SHA WANG, XIUMIN JIANG*

Institute of Thermal Energy Engineering, School of Mechanical Engineering, Shanghai Jiao Tong University, Shanghai, 200240, PR China

Abstract. *The production of acrylonitrile by using the process of propylene ammoxidation generates an effluent which contains acrylonitrile, acetonitrile and hydrocyanic acid and has an enormous adverse impact on the environment and human health. Circulating fluidized bed (CFB) incineration is an effective, well-improved and widely used method for the disposal of this hazardous material. In China, oil shale is an important source of energy alternative to oil and is rich in reserve. In this study, oil shale is utilized as fuel in the CFB test bed. The acrylonitrile effluent is injected into the furnace to be incinerated for the harmless disposal. The trial demonstrates that at 750 and 850 °C, respectively, the concentration of both acrylonitrile and acetonitrile in the flue gas meets Chinese national emission standards. However, the concentration of hydrogen cyanide does not conform to the standard, which problem needs to be further addressed.*

Keywords: *acrylonitrile effluent, incineration, circulating fluidized bed, oil shale.*

1. Introduction

Acrylonitrile is an essential raw material mainly for the synthesis of polyacrylonitrile fiber, ABS/SAN resin, adiponitrile, acrylamide and carbon fiber [1]. In China, the demand for and production of acrylonitrile are huge [2, 3], so investigation of the possibilities of disposal of the wastewater generated is of great practical significance. The by-products in the process of propylene ammoxidation are mainly hydrogen cyanide, acetonitrile, acrolein, carbon dioxide and carbon monoxide. Provided by Chinese Guangxi Keyuan Corporation, the effluent sample was from the 200,000 t/y acrylonitrile project, whose components and design flow values are given in Table 1.

* Corresponding author: e-mail *xiuminjiang@sjtu.edu.cn*

Table 1. The components of the effluent and design flows

Component	Design flow, kg/h
Acrylonitrile and hydrogen cyanide	4.5
H_2O	3098.6
CO	948.1
CO_2	2926.1
C_3H_6	254.4
C_3H_8	77.8
O_2	1910.8
N_2	84950.1
NO_X, mg/Nm^3	≤ 500
Total flow, kg/h	94165.9
Operating temperature, °C	36
Operating pressure, MPa	0.015
Average molecular weight	28

The acrylonitrile effluent has a very complex composition, consisting not only of acrylonitrile, acetonitrile and hydrocyanic acid, but also of acrylamide, acrylic acid, and acrolein [4]. The acrylonitrile, acetonitrile and hydrocyanic acid in the effluent are extremely harmful to human health. In direct contact, acrylonitrile is able to damage the skin and mucosa of the human body, inflict harm on the organs, and has proved to be carcinogenic [5, 6]. After entering the human body, cyanides generate the CN^- group, which can bind enzymes relevant for respiration, making cells unable to utilize oxygen normally [7].

The Chinese Integrated Wastewater Discharge Standard GB8978-1996 [8] sets the emission standards of cyanides, requiring that the first and secondary level emission should be below 0.5 mg/L and the third level emission should not exceed 1.0 mg/L. Therefore, the acrylonitrile effluent has to be treated to make it harmless.

Hitherto, there have been used various approaches for the harmless treatment of the acrylonitrile wastewater. These include enrichment by evaporation, hydrolysis, ozonation, ion exchange and activated carbon adsorption, as well as biochemical, ferrous sulfate, peroxide and liquid membrane methods. The incineration of the acrylonitrile effluent is able to oxidize the complex organic components, realizing the harmless treatment. The circulating fluidized bed (CFB) technology has many advantages, such as high combustion efficiency, greater flexibility in fuels use, high heat transfer efficiency, and low emissions [9, 10]. Besides, the huge amount of inert material present in the furnace at high temperature creates an ideal environment for the evaporation, pyrolysis and combustion of the wastewater, which is especially suitable for the incineration of the hazardous effluent.

In China, along with the economic development and social advancement, the consumption of traditional fossil energies, mainly coal and oil, is increasing rapidly. Therefore, seeking substitutes for them is becoming more and more vital. Oil shale is an important alternative energy. China has

abundant oil shale resources and rich reserves [11]. The conventional methods of oil shale utilization in China include retorting and burning in the boiler [12]. Besides, oil shale is an ideal co-firing fuel, the mixture of which with high sulfur coal demonstrates good combustion characteristics [13]. However, there have been no investigations as yet on the co-combustion of oil shale and hazardous material in the CFB boiler for harmless treatment.

The originality of the trial described in this paper consists in that the simultaneous incineration of oil shale and the acrylonitrile effluent in CFB renders the latter harmless. The following two main objectives were set:

1) to verify whether the process of incineration can transform acrylonitrile, acetonitrile and hydrogen cyanide into harmless compounds;
2) to investigate the mechanism of transformation of the hazardous material by measuring the component concentrations in the flue gas.

At first, the current paper presents the characteristics of the effluent used, reports the results of proximate and ultimate analyses of oil shale, and gives the particle size distribution of the quartz bed material. Then, the experimental methods and measurement equipment are described. The third section discusses the measurement results and analyzes the regularities of transformation of hazardous substances.

2. Materials and methods

2.1. Material characteristics

For experiments, the Agilent 7890A Gas Chromatograph was used according to the U.S. Environmental Protection Agency method USEPA8031-1994, to measure the concentration of acrylonitrile and acetonitrile in the wastewater, the results are given in Table 2.

The oil shale sample used in the experiment was from Jilin Huadian City, the results of proximate and ultimate analyses of the sample are presented in Table 3.

The bed material was quartz. Its particle size distribution in weight is given in Table 4. The motionless height of the bed material was kept at 300 mm, which needed 2.95 L quartz sand.

Table 2. The concentration of acrylonitrile and acetonitrile

Compound	Concentration, mg/L
Acrylonitrile	1720
Acetonitrile	1180

Table 3. The proximate and ultimate analysis of oil shale

Proximate analysis, %					Ultimate analysis, %				
M_{ar}	V_{ar}	A_{ar}	FC_{ar}	$Q_{ar.net}$, kJ/kg	C_{ar}	H_{ar}	O_{ar}	N_{ar}	S_{ar}
11.54	36.21	48.24	4.02	11076.07	27.33	3.59	7.89	0.57	0.84

Table 4. The particle size distribution of quartz sand

Particle size, mm	> 4.0	4.0–3.0	3.0–2.5	2.5–2.0	2.0–1.38	1.38–1.1	1.1–0.8	< 0.8
wt%	0	18.02	25.37	29.21	16.85	7.13	2.08	1.34

2.2. Experimental methods

The test facility used in the experiment resembled a large CFB boiler, as shown in Figure 1. The height and inner diameter of the furnace were 5 m and 210 mm, respectively. Oil shale was added from the top of the furnace to

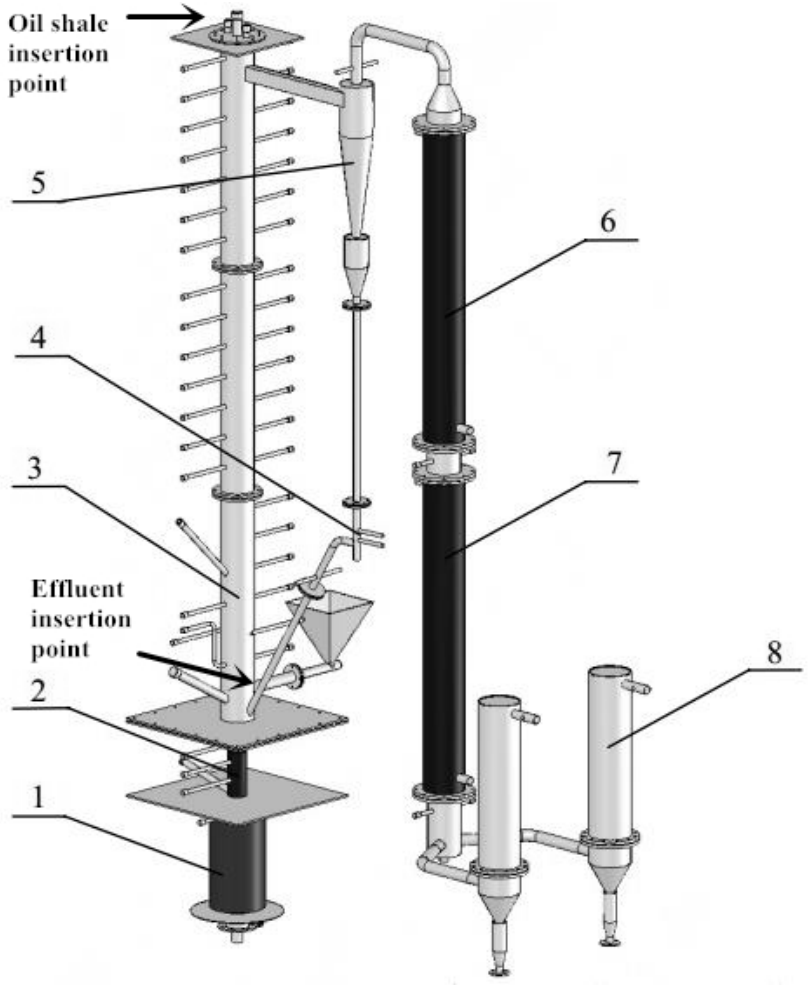

Fig. 1. The structure of the test bed. 1 – air heater; 2 – dense-phase zone; 3 – dilute-phase zone; 4 – material valve; 5 – cyclone; 6. – upper heat exchanger; 7 – lower heat exchanger; 8 – bag-type dust collector.

prevent blocking. The effluent was injected from the bottom of the furnace. The distance between the two points was 3.8 m. The effluent injection point was 1.2 m above the grid. Silicon carbide bars, which were used to heat the furnace, were placed outside it. The tail flue was collected into a bag-type dust collector.

During the trial, the furnace was heated to 300 °C by silicon carbide bars. After oil shale was added, the temperature was controlled by the air volume and feed rate to maintain the combustion. Depending on whether the wastewater was injected, as well as on whether the temperature of the dense-phase zone was 750 or 850 °C, the experiment was carried out with four material groups: two blank groups and two experimental groups. During the measurement of concentrations, the combustion of each group was maintained for 15 minutes. In the two experimental groups, the acrylonitrile effluent was injected into the furnace as a flow of 35 ml/min by a peristaltic pump.

The component concentrations of the flue gas were measured. The measuring points were all situated at the exit of the separator. Acrylonitrile and acetonitrile in the flue gas were detected by the PerkinElmer Clarus 500 gas chromatograph according to the solvent desorption and gas chromatography method recommended by the Chinese national standard Determination of nitriles in the air of workplace GBZ/T160.68-2007 [14]. The concentration of hydrogen cyanide (HCN) was measured by a UV/Vis spectrophotometer according to the Iso-nicotinic-acid-3-methyl-1-phenyl-5-pyrazolone spectrophotometric method as described in the Chinese national standard Determination of hydrogen cyanide of the Stationary source emission HJ/T28-1999 [15]. The concentrations of conventional gas were measured by a flue gas analyzer Gasmet FTIR DX4000. All the measured concentrations were converted into concentrations in dry flue gas and the 1.4 excessive air coefficient based on Chinese Emission standard of air pollutants for coal-burning, oil-burning, gas-burning boiler GB13271-2001 [16].

3. Results and discussion

3.1. The decomposition rate of acrylonitrile and acetonitrile

The main hazardous components of the effluent were hydrogen cyanide, acrylonitrile and acetonitrile, whose measured and converted concentration values are given in Table 5.

According to the results of analysis of the wastewater and the measured concentrations of hazardous components in the flue gas, the conversion rates of acrylonitrile and acetonitrile after combustion were calculated, the results are presented in Table 6.

From Table 5 and Table 6 it can be seen that the conversion rates of the two compounds are over 95% at both 850 and 950 °C, however, being higher (97.5%) at 750 °C. The average concentration of oxygen in the exit of the separator at 850 °C is only 3.76%, remaining far below the 8.06% at 750 °C.

The low oxygen concentration causes a relatively low oxygenolysis, which leads to a low conversion rate of acrylonitrile and acetonitrile. In the process of the acrylonitrile effluent incineration, the excessive air coefficient can be increased to enhance the decomposition rate of both compounds. The emission limits of the three contaminants as set in Chinese standards are listed in Table 7.

The Chinese standard GB16297-1996 [17] stipulates that the emission limit of acrylonitrile is 22 mg/m^3, the results obtained at the two different

Table 5. The measured and converted concentrations of hazardous components in the flue gas

Temperature, °C	750		850	
Average concentration of oxygen at the exit of the separator	8.06		3.76	
Gas	Concentration, mg/m^3			
	Measured value	Converted value	Measured value	Converted value
Hydrogen cyanide	36.6	42.43	45.1	39.24
Acrylonitrile	2.39	2.77	3.86	3.36
Acetonitrile	1.78	2.06	3.89	3.38

Table 6. The conversion rate of hazardous components

Parameter	Unit		Temperature 750 °C	Temperature 850 °C
Fuel feed rate	kg/h		6.3	10.3
Effluent flow rate	ml/min		35	35
Air flow rate	m^3/h		21.6	29.2
Flue gas flow rate	m^3/h		34.29	44.46
Feed rate of hazardous components	mg/min	Acrylonitrile	60.2	60.2
		Acetonitrile	41.3	41.3
Hazardous components residue	mg/min	Acrylonitrile	1.37	2.05
		Acetonitrile	1.02	2.07
Conversion rate of hazardous gas	%	Acrylonitrile	97.72	96.59
		Acetonitrile	97.53	94.99

Table 7. The emission limits of three contaminants

Contaminant	Chinese standard	Concentration limit, mg/m^3
Acrylonitrile	Integrated emission standard of air pollutants GB16297-1996 [17]	22
Acetonitrile	Occupational exposure limits for hazardous agents GBZ2.1-2007 [18]	30
Hydrogen cyanide	Integrated emission standard of air pollutants GB16297-1996 [17]	1.9

temperatures prove that the incineration process can make the concentration of acrylonitrile meet the Chinese standard. However, GB16297-1996 [17] does not set the specific emission concentration limit of acetonitrile. Therefore, the limit value of 30 mg/m^3 in the Chinese national standard Occupational exposure limits for hazardous agents GBZ2.1-2007 [18] was employed as the emission limit. Similarly, after the incineration the acetonitrile concentration in the flue gas met the standard.

From Table 5 it is clear that the concentration of HCN in the flue gas at both the temperatures was almost 40 mg/m^3. According to the Chinese Integrated emission standard of air pollutants GB16297-1996 [17], the hydrogen cyanide emission limit of a polluting unit built after January 1, 1997 must be lower than 1.9 mg/m^3. In this work, the corresponding measured figure was far beyond this value, which means that the incineration process is unable to meet the national standard. The trial demonstrated that the direct incineration of the flue gas with low HCN concentration gave no desired disposal effect. So, the flue gas needs further treatment. Besides, the combustion of the fuel containing elemental nitrogen generates hydrogen cyanide [19]. Hence the most effective way to remove HCN is to subject the flue gas to purification treatment.

3.2. The transformation of hazardous materials

The analysis of different experimental compound groups showed that the main oxygenolysis products of acrylonitrile, acetonitrile and hydrogen cyanide were NO and N_2O. The four experimental conditions were as follows: 750 °C without effluent, 750 °C effluent added, 850 °C without effluent and 850 °C effluent added. The emission concentrations of NO and N_2O were converted into concentrations in dry flue gas and the 1.4 excessive air coefficient and are given in Figure 2.

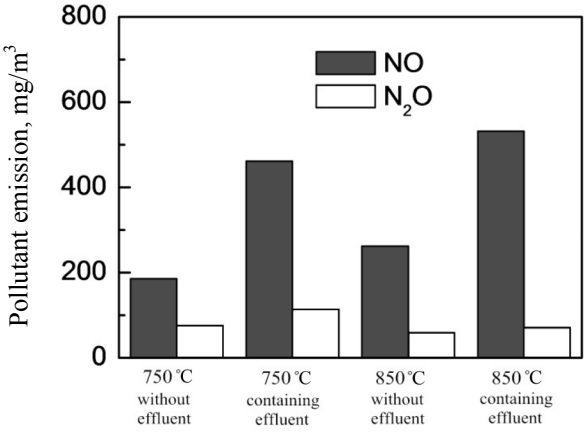

Fig. 2. The emission of NO and N_2O after conversion.

The main decomposition products of the three hazardous materials were NO and N_2O generated from two sources: oxygenolysis of the oil shale organism containing elemental nitrogen, and conversion of acrylonitrile, acetonitrile and hydrogen cyanide in the wastewater. The measured concentration values of the flue gas demonstrated that after the injection of the effluent, the concentrations of NO and N_2O increased significantly, which proves that the hazardous components in the wastewater underwent oxidative decomposition. The overall incineration process proceeded through the following reaction sequence:

$$CH_2 = CH - CN + O_2 \longrightarrow CO_2 + H_2O + HCN \quad (1)$$

$$CH_3 - CN + O_2 \longrightarrow CO_2 + H_2O + HCN \quad (2)$$

$$HCN + O_2 \longrightarrow H_2O + CO_2 + NO + N_2O \quad (3)$$

After the addition of the wastewater, the concentration of NO increased much more than that of N_2O. Due to the injection of the acrylonitrile effluent into the oil shale CFB, the concentration of NO and N_2O in the flue gas no longer met the limit standard for nitrogen oxide [16]. The flow rate of the wastewater has to be dealt with more thoroughly in order to make the concentrations of emitted NO and N_2O acceptable for practical applications. The water in the effluent evaporated rapidly after the injection. Thus acrylonitrile, acetonitrile and hydrogen cyanide went through rapid gasification. Due to the high triple bond energy, the cyano in the cyanides was unable to react with other chemicals. Therefore, the gaseous acrylonitrile and acetonitrile were converted into hydrogen cyanide [20], a major intermediate from the reaction of the cyano with hazardous NO and N_2O [19, 21]. In the reaction process, the oxidation product of HCN was NCO. Then, NCO was converted into NO after oxidation. The reaction of NCO with NO gave N_2O [22, 23]. A large amount of NCO was oxidized to generate NO in a competing way. This is why the NO concentration rose significantly after the addition of the wastewater, whereas the N_2O concentration increased negligibly.

The increase of the N_2O emission concentration was more noticeable at 750 °C, being smaller at 850 °C. This might be due to that the decomposition of N_2O occurred more easily at a higher temperature [24] and the conversion of N_2O took place in a lower oxygen concentration atmosphere [25]. Also, with rising temperature the concentration of NO increased and that of N_2O decreased. This may be explained by that the concentration of oxygen in the furnace was lower at 850 °C than at 750 °C. The production of NO increased with increasing temperature, while the generation of N_2O decreased with decreasing excessive air coefficient and increasing temperature [26, 27].

4. Conclusions

In this work, the oil shale sample from Jilin Huadian City was used to incinerate the acrylonitrile effluent. The effluent was provided by the Guangxi Keyuan Corporation, China. In the experiments, the bed temperature of the dense-phase zone was maintained at 750 and 850 °C, respectively. Based on the results of analysis of the acrylonitrile effluent composition and the measured values of the flue gas, as well as comparisons with Chinese national standards, the following conclusions can be drawn.

Under the experimental conditions, the conversion rates of the acrylonitrile and acetonitrile in the wastewater were both slightly over 95%. Most of the hazardous material underwent oxygenolysis, whose major product was NO and minor, N_2O. The incineration of the effluent caused an evident increase of the NO concentration and only a slight rise in the N_2O concentration. The harmless treatment carried out during the experiment showed that the concentrations of acrylonitrile and acetonitrile in the flue gas were lower than the emission limits set in Chinese national standards. However, the hydrogen cyanide concentration in the flue gas did not meet the requirements, which indicates that the direct incineration of this compound is not a suitable method for harmless treatment and the flue gas needs further disposal.

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