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Development of new technology for coal gasification purification and research on the formation mechanism of pollutants

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Abstract: Coal-fired power generation is the main source of CO₂ emission in China. To solve the problems of declined efficiency and increased costs caused by CO₂ capture in coal-fired power systems, an integrated gasification fuel cell (IGFC) power generation technology was developed. The interaction mechanisms among coal gasification and purification, fuel cell and other components are further studied for IGFCs. Towards the direction of coal gasification and purification, we studied gasification reaction characteristics of ultrafine coal particles, ash melting characteristics and their effects on coal gasification reactions, the formation mechanism of pollutants. We further develop an elevated temperature/pressure swing adsorption rig for simultaneous H₂S and CO₂ removals. The results show the validity of the Miura-Maki model to describe the gasification of Shenhua bituminous coal with a good fit between the predicted DTG curves and experimental data. The designed 8-6-1 cycle procedure can effectively remove CO₂ and H₂S simultaneously with removal rate over 99.9%. In addition, transition metal oxides used as mercury removal adsorbents in coal gasified syngas were shown with great potential. The techniques presented in this paper can improve the gasification efficiency and reduce the formation of pollutants in IGFCs.

Keywords: IGFC; coal gasification; H₂S-CO₂ removal; syngas mercury removal

Nomenclature

	DAEM	distributed activation energy model	
	DT	deformation temperature	
<i>Abbreviations</i>	ETPSA	elevated temperature pressure swing adsorption	
AD	adsorption		
AFT	ash flow temperature	FT	flow temperature
BD	counter-current blow down	HT	hemispherical temperature
CBK	carbon burnout kinetic model	IGCC	integrated gasification combined cycle
CHP	combined heat and power		

IGFC	integrated coal gasification fuel cell
MDEA	methyldiethanolamine
PE	pressure equalization
PG	N ₂ purge
PP	pressurization with product gas
PSA	pressure swing adsorption
RH	high pressure steam rinse
RPM	random pore model
SOFC	solid oxide fuel cell
ST	softening temperature
TGA	thermogravimetric analyzer
V	vacuum desorption
WGS	water gas shift

Symbols

R	universal gas constant
A	pre-exponential factor function
DTG	predicted combustion reaction rate function

E	activation energy function
H_g	Hg ⁰ concentrations [ng/L]
k_0	pre-exponential factor
K	reaction rate function
m	sample weight at time t
m_0	initial sample weight
m_∞	final sample weight
R^2	correlation coefficients
t	time
T	temperature

Greek symbols

α	gasification conversion factor
β	heating rate
η	mercury removal efficiency

Subscript

in	inlet
out	outlet

1. Introduction

Integrated coal gasification fuel cell (IGFC) power generation is a combination of integrated gasification combined cycle (IGCC) and solid oxide fuel cell (SOFC) technologies, which could greatly improve the efficiency of coal to electricity and achieve zero emission of CO₂ and pollutants. The SOFC is a critical component in the IGFC. In 2015, Daily (Daily 2015) developed an SOFC power generation system aiming at 5kW and reached a power output of 4.82kW. Its power generation and CHP efficiency were 48.5% and 79.7%, respectively. SOFCMAN developed an SOFC of 200kW in 2016 (Sofcman 2016). Another SOFC power generation system of 15kW was established by Shanxi Jincheng Anthracite Coal Mining Group in China (Li and Zhang 2019). In 2017, China approved an IGFC project and planned to build a MWth level demonstration station within four years, with a power efficiency higher than 50% and CO₂ capture rate higher than 91% (Dong et

al. 2019). The SOFC technology has been industrialized overseas as well. For example, Bloom Energy, Mitsubishi and Convion are able to produce SOFCs of 30-200kW (Cao et al. 2020). Base on the development of SOFC technology, many counties have made plans to promote the development and application of IGFC. In 2015, Japan (Strategy 2019) planned to establish an IGFC power generation of 100MW with power efficiency of 55% before 2025. In United States, the company Fuel Cell Energy planned to establish a demonstration IGFC station of 670MW (Cao et al. 2020). IGFC is regarded as the most promising near-zero CO₂ emission coal gasification power generation technology in the future (Peng and Han 2009).

The entrained-bed coal gasification process is the cleanest and most efficient coal gasification technology (Fan 2013; Liu et al. 2010; Wang 2014). At present, the entrained-bed coal gasification process is widely used in IGCC power stations over 250MW (Zhang and Yang 2019). Compared with fixed-bed and

fluidized-bed gasifiers, entrained-bed gasifiers have the advantages of coal adaptability and operation reliability. The entrained-bed gasifiers used in China nowadays mainly include Texaco, Shell and GSP gasifiers. How to improve the carbon conversion rate and cold gas efficiency has been a key difficulty in the entrained-bed coal gasification technology.

Entrained flow coal gasification technology, whose carbon conversion rate and cold gas efficiency can be as high as 98% and 80% respectively, represents a direction of coal gasification. Liquid slagging and dry feeding coal gasification technology has many advantages such as low oxygen consumption, high carbon conversion, high cold gas efficiency and large capacity for single furnace, which will be a mainstream of advanced coal gasification (Liu and Tian 2012). Pulverized coal with low ash melting point is often used in dry feeding entrained flow gasification. Gasifying temperatures should be higher than ash melting point to ensure the liquid ash removal (Krishnamoorthy and Pisupati 2015). The successful development of large energy efficient ultrafine pulverized coal preparation system establishes the foundation for the utilization of ultrafine pulverized coal. Microscale effect of ultrafine pulverized coal can increase the gasification rate and conversion efficiency (Liu et al. 2014; Luo et al. 2019). This paper intends to review the research on gasification characteristics of ultrafine pulverized coal under CO₂ atmosphere and to describe the basic kinetic characteristics of ultrafine pulverized coal, so as to provide theoretical guidance for improved effective gas yield, carbon conversion rate and cold gas efficiency.

At present, the general coal gasification reaction model does not consider the thermal deactivation effect of coal at high temperatures, high pressures and high conversion rates. The most commonly used kinetic models for coal gasification reaction include homogeneous

model, core-shrinking reaction model and random hole model. Homogeneous model can only describe a process in which the rate of gasification reaction decreases monotonously with the rate of carbon conversion. However, it is not applicable to the gasification process with extreme gasification reaction rates. Although the stochastic pore model can describe the extreme gasification reaction rates, it is not suitable to describe the catalytic gasification process of coal and the extreme value of gasification reaction rate occurs in the case of high conversion rate. So far, no model can accurately describe the process of gasification reaction rate changing with reaction time and conversion rate. Therefore, the establishment of a generalized and quantitative kinetic model to describe coal gasification reaction will be the focus of coal gasification reaction dynamics research.

The distributed activation energy model (DAEM) (Pitt 1962) and carbon burnout kinetic model (CBK) (Cloke et al. 2003; Hurt et al. 1998a; Hurt et al. 1998b) have been proven very successful for describing the kinetics of coal pyrolysis and combustion. The DAEM was originally proposed by Pitt (Pitt 1962) and later adapted by Anthony and Howard (Anthony and Howard 1976). It describes a complex reaction as a number of parallel first-order reactions, each occurring with its own rate coefficient. Usually, it is further assumed that all reactions share the same frequency factor and that measuring the relationship between the distributed activation energy and the burnout ratio requires at least three different heating rates. The CBK model was proposed by Hurt (Hurt et al. 1998b). It accurately describes the kinetics of heterogeneous char oxidation reactions. One of the main limitations of this type of research is that burning and burnout temperatures are always lower than the ash flow temperature (AFT). The kinetic characteristics of coal high-temperature combustion require further investigation. In this study, the kinetic

parameters of char combustion including the activation energy (E) and the pre-exponential factor (A) were obtained from thermogravimetric analyzer (TGA) data. A model that predicted the char combustion rate was then established using the kinetic parameters of char combustion and was validated with experimental data.

Combustion of syngas (mixtures of H_2 and CO) can greatly reduce CO_2 emissions in power generation systems (Sui et al. 2018; Sui et al. 2020a; Sui et al. 2019). In the field of syngas purification, there are several industrialized methods that could separately remove H_2S and CO_2 , such as Selexol, methyldiethanolamine (MDEA), rectisol and pressure swing adsorption (PSA) (Chaubey et al. 2013; Dincer and Acar 2015; Wiheeb et al. 2013; Yu et al. 2012). These techniques are widely used in coal chemical industry, providing a basis for the development of H_2S - CO_2 simultaneous removal methods. Selexol, rectisol and MDEA belong to the category of wet methods, in which impurities are absorbed by solvents at $-50\sim 60$ °C. The solvent in MDEA is a chemical absorbent while the others are physical absorbents. The devices of wet methods are complicated and costly. Impurity removal and absorbents regeneration are conducted in different units. The maintenance and operating costs are not economical either.

Consequently, some substitutes of conventional purification methods are proposed and studied. Using dry methods, RTI international (Denton and L 2014; Gupta and Raghubir 2010) separated H_2S and CO_2 from syngas at elevated temperatures and normal temperatures, respectively, with more than 99.9% H_2S and 90% CO_2 captured. Compared with Selexol and rectisol, the initial investment of this method decreased by 50% and the operating cost was also lower. The energy consumption of adsorbent/absorbent regeneration was only 72% of that in Selexol. Moreover, if H_2S and CO_2 could be simultaneously removed in one step,

the device can be further simplified. Still, the corresponding techniques are under development. Improvement of adsorbent performance, technique process design and adsorption bed structure optimization are all necessary at this stage.

With the rapid development of human society, energy and environmental problems are becoming more and more serious. The fact that China is rich in coal resources but poor in oil and natural gas determines that coal will be the main fossil energy source to maintain the rapid development of the whole society in a long period of time. Accordingly, sulfur, nitrogen, chlorine and other pollutants generated in the processes of coal utilization have been widely concerned (Xu and Wei 1999); The trace and volatile metal elements (such as Hg, Pb, As, Se, etc.) has also been paid more attention. Mercury is the most volatile heavy metal pollutant in coal. Although its concentration in coal is relatively low, considering the total consumption of coal is huge and mercury is mainly discharged in the form of gas, the latter in the process of coal utilization accounts for a large proportion of the mercury released by human activities.

With increased attention paid to mercury pollution in the atmosphere, mercury emission in the processes of coal utilization has become an urgent environmental problem. There are three forms of mercury released from coal utilization: Hg^p , Hg^{2+} and Hg^0 . Hg^p can be removed by particulate control and Hg^{2+} can be removed by wet scrubbing or SO_2 control, while elemental mercury is not easy to dissolve, making it difficult to be removed via ordinary dust removal equipment (Pavlish et al. 2003). In the recent years, the research works of mercury removal are mainly focused on the removal of mercury from coal-fired flue gas. The main methods are: (a) adsorption method: adsorption of mercury in flue gas with activated carbon, fly ash, mineral adsorbents, etc. (Granite et al. 2000; Liu 2015); (b) catalytic adsorption method:

metal oxides (such as TiO₂, CeO₂, ZnO, MoO₃, CuO, MnO₂, etc.) (Li et al. 2011; Liu 2016; Wen et al. 2011) or precious metals (Ag, Pd, Pt, etc.) (Liu et al. 2008) are loaded on Al₂O₃ or molecular sieve and other carriers to remove mercury. The two methods show a certain ability of mercury removal in different temperature ranges, while the components of flue gas (SO₂, SO₃, NO, NO_x, HCl, etc.) have a great influence on the mechanism of mercury removal. The gases produced by coal gasification are composed of reducing agents (usually containing trace O₂) and the content of elemental mercury that is difficult to remove is higher than that of coal-fired flue gases (Pavlish et al. 2003; Reed et al. 2001). Therefore, the removal of mercury from coal gas exhausts has gradually become a research hotspot at home and abroad.

The paper is organized as follows: in Section 2, coal gasification models and syngas purification methods are presented. Subsequently, in Section 3, experiments and calculations of CO₂ gasification of ultrafine pulverized coal particles, H₂S-CO₂ removal and syngas mercury removal are discussed. Finally, the conclusions are summarized in Section 4.

2. Methods and Experiments

2.1 Kinetic models of coal gasification

Bituminous coal obtained from Shenhua mine was used in this work. Screening equipment was used to separate materials with five particle sizes, whose average particle sizes were determined by Malvern Mastersizer 3000. Thermogravimetric analysis was conducted via a TG (Setsys Evolution, SETARAM, France). Each sample was heated in CO₂ environment from ambient temperature to 1300 °C with four different heating rates (5, 10, 20, and 40 °C/min). The integral iso-conversional model proposed by Miura-Maki (Miura and Maki 1998) has been widely used to obtain kinetic parameters for thermal-conversion of coal. The previous work

(Song et al. 2016) proved the validity of Miura-Maki model by comparing the experimental and the reproduced conversion degree versus temperature based on the calculated kinetic parameters.

$$\ln\left(\frac{\beta}{T^2}\right) = \ln\left(\frac{k_0 R}{E}\right) + 0.6075 - \frac{E}{RT} \quad (1)$$

Where β is the heating rate, k_0 the pre-exponential factor, E the activation energy, R the universal gas constant.

At low operating temperatures, the chemical reaction rates are slow and the oxygen supply rate is much faster than the oxygen consumption rate. Therefore, the combustion process consisted of a slow heating zone and a combustion reaction zone, which can be considered a dynamic area where chemical kinetic factors control the reaction rate (Sun and Chen 1991). The reaction rate can be expressed with the Arrhenius with the following assumptions (Zhang et al. 2000):

(a) The sample particles are spherical. The particle diameter and density are constant during the combustion process. The impact of the ash layer on the combustion is not considered.

(b) The combustion reactions only occur on the particles' surfaces and the reaction rate is calculated based on the particles' outside surface area.

(c) The oxygen pressure is distributed evenly throughout the sample layer.

(d) The total surface oxidation reaction product is CO₂.

The combustion rate function can be expressed as follows (Hecker et al. 2003; Sima-Ella et al. 2005):

$$\alpha = \frac{m_0 - m}{m_0 - m_\infty} \quad (2)$$

$$-\frac{d\alpha}{dt} = K(\alpha)\alpha \quad (3)$$

The reaction rate function $K(\alpha)$ is usually assumed via the Arrhenius equation (Pilling and Seakins 1995):

$$K(\alpha) = A(\alpha) \exp(-E(\alpha) / (RT)) \quad (4)$$

where α is the burnout ratio, which is the mass ratio of the burned combustible matter to the total combustible matter in the coal. m_0 is the initial mass weight of the sample and m is the sample's mass weight at time t . m_∞ is the final sample weight. $K(\alpha)$ is the combustion reaction rate as a function of α . $A(\alpha)$ is the pre-exponential factor function and $E(\alpha)$ is the activation energy function.

The curves of char combustion at two temperatures T_1 and T_2 can be obtained from TGA experiments including $TG_1(\alpha)$, $TG_2(\alpha)$, $DTG_1(\alpha)$, and $DTG_2(\alpha)$. $E(\alpha)$ and $A(\alpha)$ from T_1 to T_2 can be calculated as:

$$E_{T_1, T_2}(\alpha) = - \frac{R \ln \frac{DTG_1(\alpha)}{DTG_2(\alpha)}}{\left(\frac{1}{T_1} - \frac{1}{T_2} \right)} \quad (5)$$

$$A_{T_1, T_2}(\alpha) = \frac{DTG_2(\alpha)}{\exp(-E_{T_1, T_2}(\alpha) / (RT_2))} \quad (6)$$

From Eqs. (5) and (6), the predicted combustion reaction rate function $DTG'(\alpha)$ at a combustion temperature of T_3 ($T_3 \in [T_1, T_2]$) is as follows:

$$DTG'(\alpha) = A_{T_1, T_2}(\alpha) \exp(-E_{T_1, T_2}(\alpha) / RT_3) \quad (7)$$

To validate the predicted model's veracity, the predicted results are compared with experimental data and an error analysis is conducted.

Hulunbeier lignite coal was utilized in the present work. The average diameter of the coal samples was 76 μm and all samples were less than 200 μm . The coal properties, ash components, and fusion characteristic temperatures are presented in **Table 1**.

Table 1 Coal properties (as received basis, wt.%) and ash components analysis

Item	Value	Item	Value
Coal proximate analysis		Ash compositions	
(%, w/w ar)		(wt %)	
Fixed carbon	44.86	SiO ₂	55.63
Volatile matter	35.44	Al ₂ O ₃	11.51
Ash	11.05	Fe ₂ O ₃	14.22
Moisture	8.65	CaO	11.24
Ultimate analysis		MgO	2.14
(%, w/w ar)		TiO ₂	0.76
Carbon	59.46	SO ₃	3.02
Hydrogen	3.35	P ₂ O ₅	0.06
Oxygen	16.44	K ₂ O	0.48
Nitrogen	0.80	Na ₂ O	0.94
Sulfur	0.25	Fusion characteristic temperature	
Lower heating value	25.6	(°C)	
(MJ/kg)		DT ^a	1090
		ST ^b	1100
		HT ^c	1110

^a Deformation Temperature. ^b Softening Temperature. ^c Hemispherical Temperature. ^d Flow Temperature.

A TGA from Beijing Henven Scientific Instrument Factory was used. The minimum sensitivity was 0.1 μg and the data was collected every second in a temperature range of 25 $^{\circ}\text{C}$ to 1450 $^{\circ}\text{C}$.

All coal samples were measured with 20 mg, dewatered at 100 $^{\circ}\text{C}$ for 30 min and heated at a fixed heating rate of 80 $^{\circ}\text{C}/\text{min}$, starting from 100 $^{\circ}\text{C}$ and rising to the temperature T_H in N_2 environment (200 mL/min). The samples were then held at T_H for 30 min for complete volatile devolatilization. Air (100 mL/min) was injected into the TGA after 30 min and the temperature was kept constant until the mass weights of the samples remained constant. The temperature T_H in each case was divided into 25 levels in the range of 500–1450 $^{\circ}\text{C}$, with heating intervals of 50 $^{\circ}\text{C}$ in the range of 500–1200 $^{\circ}\text{C}$ and 25 $^{\circ}\text{C}$ in the range of 1200–1450 $^{\circ}\text{C}$.

2.2 H₂S-CO₂ removal

The authors had proposed elevated temperature pressure swing adsorption (ETPSA)

process operating at 150–400 $^{\circ}\text{C}$ for H₂S-CO₂ simultaneous removal. It is similar to PSA but with higher working temperatures. As a dry method, the device of ETPSA is less complex than that in wet methods. Furthermore, compared with regular PSA, ETPSA is more energy efficient due to a higher product gas recovery rate and less sensible heat loss (Gazzani et al. 2013).

A small scale (6 Nm³/h) ETPSA unit has been developed in the ammonia plant of Quanji Energy Co., Ltd., Shanxi province, China. On-site CO₂-H₂S simultaneous removal is realized on this device. Syngas coming for water gas shift (WGS, which converts CO to CO₂ for pre-combustion capture (Sui et al. 2020b)) unit flowed to this unit with a flow rate of 1–10 Nm³/h. The WGS is approximately 50 m away from ETPSA, and hence the temperature decreased from 216 $^{\circ}\text{C}$ to around 180 $^{\circ}\text{C}$ during the transport. A part of the steam was condensed and separated by a gas-liquid separator. The compositions of final feed gas are listed in **Table 2**.

Table 2 Details of the feed gas

Temperature	Pressure	Composition
180 $^{\circ}\text{C}$	2-3MPa	54% H ₂ , 36% CO ₂ , 5% H ₂ O, 0.4% CO, 700 ppm H ₂ S, 1% N ₂ , 3% CH ₄ , Trace Ar

There were four adsorption beds and four buffer tanks (same size columns packed with SiO₂ particles of similar sizes) in this rig. The tanks were used for pressure equalization. The height of adsorption beds were 1.8 m and the inner diameter was 79 mm. The adsorbent was 207C activated carbon (Calgon Carbon Co., Ltd), which had undergone some special surface treatment (Li et al. 2019). The hydrophobicity of the adsorbent was significantly higher than the pristine activated carbon. The outlook of this

rig is shown in **Fig. 1**.



Fig. 1 Outlook photo of the ETPSA device

Step	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Bed1	AD	AD	AD	AD	AD	RH	PEA	PE1	PEB	PEC	PE2	PED	BD	PG	V	PEC	PE2	PEC	PEB	PE1	PEA	PP	PP	PP
Bed2	PEB	PE1	PEA	PP	PP	PP	AD	AD	AD	AD	AD	RH	PEA	PE1	PEB	PEC	PE2	PEC	BD	PG	V	PED	PE2	PEC
Bed3	BD	PG	V	PED	PE2	PEC	PEB	PE1	PEA	PP	PP	PP	AD	AD	AD	AD	AD	RH	PEA	PE1	PEB	PEC	PE2	PED
Bed4	PEA	PE1	PEB	PEC	PE2	PED	BD	PG	V	PED	PE2	PEC	PEB	PE1	PEA	PP	PP	PP	AD	AD	AD	AD	AD	RH
Tank1	PEA		PEA																					
Tank2	PEB		PEB																					
Tank3				PEC		PEC																		
Tank4				PED		PED																		
Cycle 544s	50	30	14	14	14	14	50	30	14	14	14	14	50	30	14	14	14	14	50	30	14	14	14	14
Cycle 456s	43	19	13	13	13	13	43	19	13	13	13	13	43	19	13	13	13	13	43	19	13	13	13	13
Cycle 360s	34	18	11	11	11	5	34	18	11	11	11	5	34	18	11	11	11	5	34	18	11	11	11	5
Cycle 468s	40	25	14	15	15	7	40	25	14	15	15	7	40	25	14	15	15	7	40	25	14	15	15	7

Fig. 2 8-6-1 ETPSA cycle procedures. AD: adsorption; RH: high pressure steam rinse; PE: pressure equalization with columns (1, 2) or tanks (A, B, C, D); BD: counter-current blow down; PG: N₂ purge; V: vacuum desorption; PP: pressurization with product gas.

According to elevating the working temperature, the reversibility of H₂S adsorption was improved (Hao et al. 2019). Adsorbed H₂S could be detached from the adsorbent and collected during vacuum desorption or purge step. Although the sulfur capacity of activated carbon was lower than metal oxides, the breakthrough times of H₂S was still much longer than CO₂. Hence as long as CO₂ did not penetrate the adsorption bed, the H₂S could be removed thoroughly.

Herein, an 8-6-1 (eight adsorption beds/tanks, six pressure equalization, one adsorption in each cycle) ETPSA cycles were designed. The schedules are shown in **Fig. 2**, where the step sequence and the corresponding duration lengths are listed. The time length of each cycle here is 468 s (the last line in the chart). Because N₂ is a material of ammonia synthesis, N₂ purging was adopted in this study.

2.3 Syngas mercury removal

The precursor Mn(NO₃)₂•4H₂O of 10 g manganese oxide was dissolved in deionized water in a 100 ml bottle, creating a 100 ml Mn(NO₃)₂ solution with a mass fraction of 10 wt.%. 10g activated alumina and 10 ml

manganese nitrate aqueous. Then the activated alumina was added to manganese nitrate aqueous solution, stirred manually for 30 min, and followed by ultrasonic shock for 20 min. The activated alumina impregnated with manganese nitrate solution was heated in the electric furnace of 200 W and was placed in the oven at 100 °C for 1 h until water was fully evaporated. After drying, alumina loaded with manganese oxide precursor was placed in a tubular furnace at a constant temperature of 400 °C and removed after calcining for 3 h in air. Subsequently, it was cooled to room temperature in a drying dish. The obtained Mn₂O₃/Al₂O₃ mercury removal adsorbent was stored in silica gel. Similarly, Co₂O₃/Al₂O₃ and Fe₂O₃/Al₂O₃ adsorbents were prepared by the same method with Co(NO₃)₂ and Fe(NO₃)₂ as precursors, respectively.

The experiment was carried out in the fixed bed reactor system, as shown in **Fig. 3**. The apparatus mainly includes 6 parts: simulated syngas control system, mercury vapor generation system, water vapor generation system, tubular reactor system, tail gas treatment system and mercury analysis system. An MAX-L cold atomic absorption mercury analyzer produced by Labtech company was used in the experiments to

access the mercury concentrations.

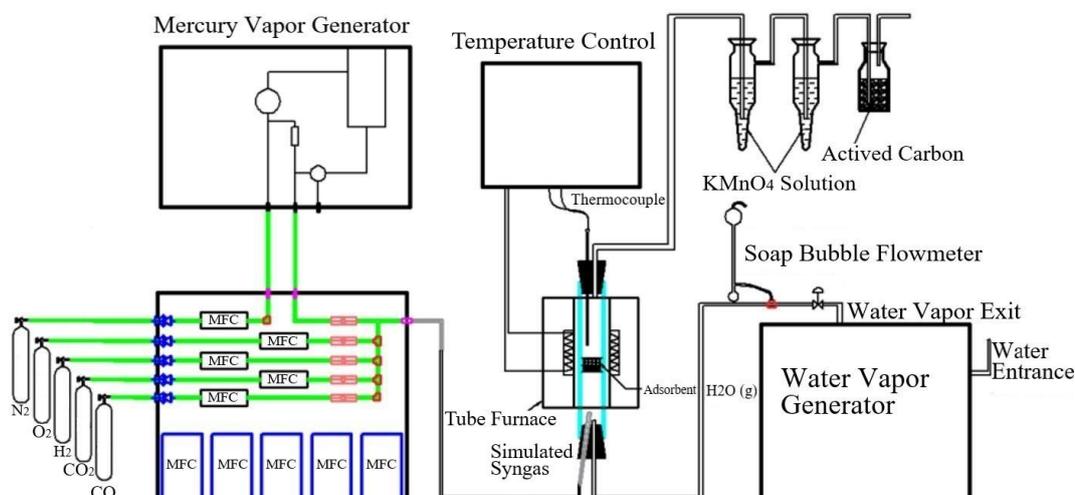


Fig. 3 Schematic diagram of simulated syngas mercury removal system

The mercury removal activity of the adsorbent was evaluated in a fixed bed reactor at 200 °C in a simulated gas (N₂, CO, H₂, H₂S, H₂O and Hg) environment. The experimental apparatus is shown in **Fig. 4**. The simulated gas was selected in the experiment. Hg steam concentration was 60 µg/m³. The stable concentration was provided by mercury permeation tube through the dynamic gas calibration instrument. The permeation temperature was set at 60 °C. The carrier gas was N₂ and the flow rate was 200 mL/min. The simulated gas was provided by standard gas distribution cylinders with H₂S concentration of

200 ppm, H₂ volume fraction of 30%, CO volume fraction of 60%, CO₂ volume fraction of 5% and H₂O vapor volume fraction of 5%. The total gas flow rate was 1 L/min (nitrogen as the equilibrium gas). The adsorbent dose was 0.5 g and the bed temperature was set as 200 °C.

The mercury removal efficiency (η) of the adsorbent was used as the evaluation index, whose calculation formula was as follows:

$$\eta = \frac{H_{gin} - H_{gout}}{H_{gin}} \quad (8)$$

where H_{gin} and H_{gout} denote the inlet and outlet Hg⁰ concentrations (ng/L), respectively.

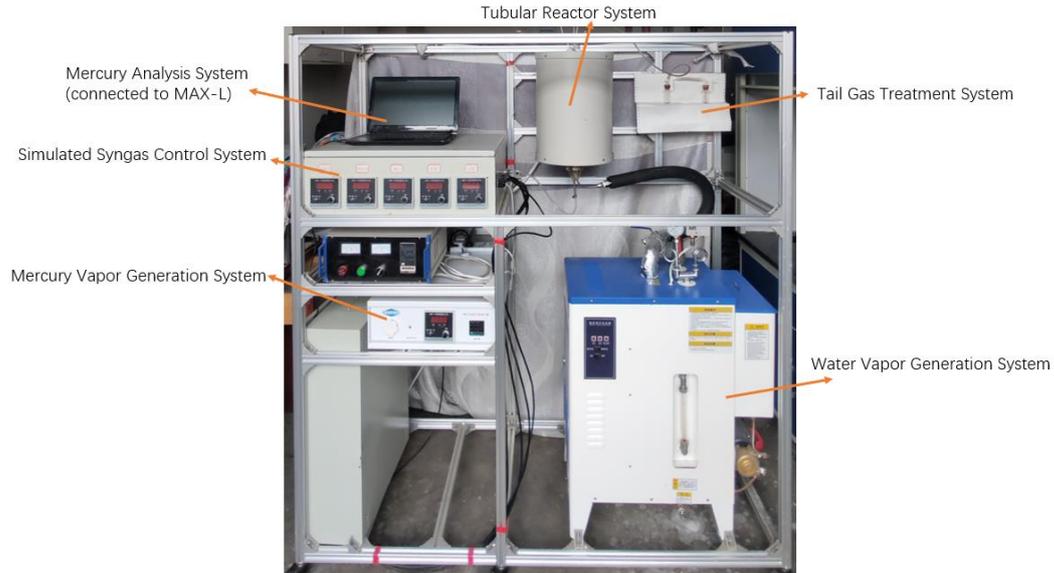


Fig. 4 Test bench of syngas mercury removal system

3. Results and discussions

3.1 CO₂ gasification of ultrafine pulverized coal particles

It can be seen from the particle size distribution curves (as shown in **Fig. 5a**) and microscopic appearance (as shown in **Fig. 5b**) that the average particle sizes for Samples 1#, 2# and 3# were smaller than Samples 4# and 5#. Further, the surfaces of 4# and 5# was smooth, while the surfaces of 1#, 2# and 3# was rather rough. The rough surfaces would promote the gasification process and enhance the reaction activity. The gasification conversion factor (α) curves for the five samples with different particle sizes (as shown in **Fig. 5c**) almost overlapped when the temperature was lower than 850 °C. However, when the temperature was higher than 850 °C, there existed significant differences for coal samples with different particle sizes. As for the effect of particle size on the gasification conversion factor, it can be found that the smaller the particle size, the larger value of conversion factor. According to the plot of $\ln(\beta/T^2)$ vs $1/T$ at a particular conversion factor (α) (as shown in **Fig. 5d**), a linear equation with the slope of $-E/R$ and intercept of $\ln(k_0R/E)+0.6075$ can be fitted, which gives the values of activation energies, pre-exponential factors, and correlation coefficients

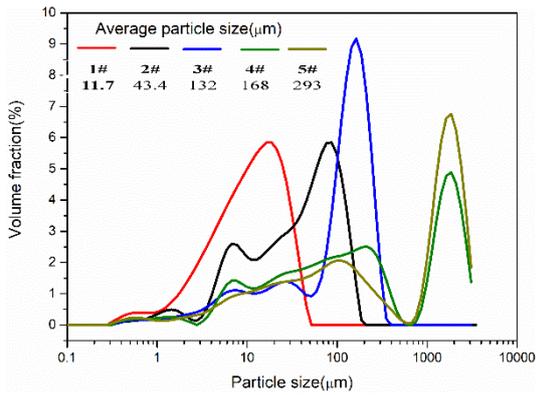
(R^2). The calculated values of correlation coefficient for all the five samples were all higher than 0.97, showing that the Miura-Maki model is applicable to Shenhua bituminous coal for gasification kinetic analysis.

3.2 Predicted DTG model

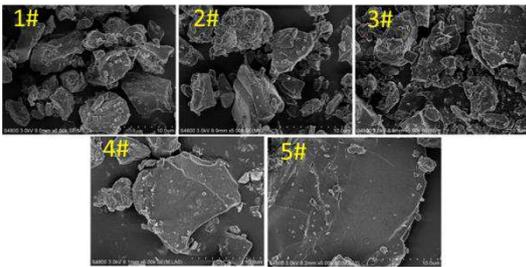
Fig. 6 depicts the $T(t)$, $1-\alpha(t)$, $DTG(t)$, and $DTG(\alpha)$ profiles for the Hulunbeier lignite coal. As shown in **Fig. 6** (b) and (c), the weight loss ratio $1-\alpha$ and the reaction rate $DTG(t)$ exhibit a regular distribution as the combustion temperature increases. The peaks in the $DTG(\alpha)$ profiles shown in **Fig. 6** (d) can be observed when the burnout ratio α is around 0.1, which was also observed by Bhatia et al. (Bhatia and Perlmutter 1980). The authors proposed a random pore model (RPM), which stated that the reaction rate responded to the change in pore structure and that a positive relationship existed between changes in the reaction rate and pore superficial area. The changes in the pore superficial area were the result of the competition between the pore extension and the pore overlap. The pore extension benefited from the increase in pore superficial area while the result for the pore overlap was the opposite. At the beginning of char combustion, the pore extension dominated and the

reaction rate increased rapidly with the rising pore superficial area. After the peak of the reaction rate, which occurred at α_{max} , the pore overlap began to dominate the reaction and the reaction rate decreased with the reduction in the pore superficial area. The peak of the reaction rate predicted by the RPM occurred at $0 < \alpha_{max} < 0.393$, which matched the observations shown in **Fig. 6 (d)**.

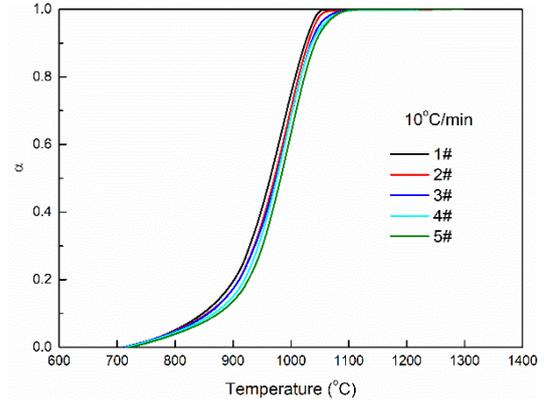
$E(\alpha)$ and $A(\alpha)$ are obtained by Eqs. (5) and (6) and are shown in **Fig. 7**. The result shows that both $E(\alpha)$ and $\log A(\alpha)$ exhibited a U-shaped with a gentle fluctuation in the range of $0.2 < \alpha < 0.9$. As the burnout ratio increased from 0 to 0.3, the char began to burn and the combustion rate increased significantly. This resulted in the decrease in E and $\log A$. As the combustion continued, the flammable matter burned first and heated the flame retardant matter. The combustion rate, E , and $\log A$ were relatively stable in the range of $0.2 < \alpha < 0.9$. As the



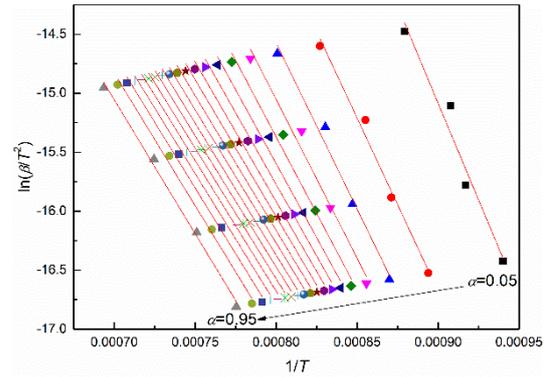
(a) particle size distribution curves



(b) the micro surface morphology

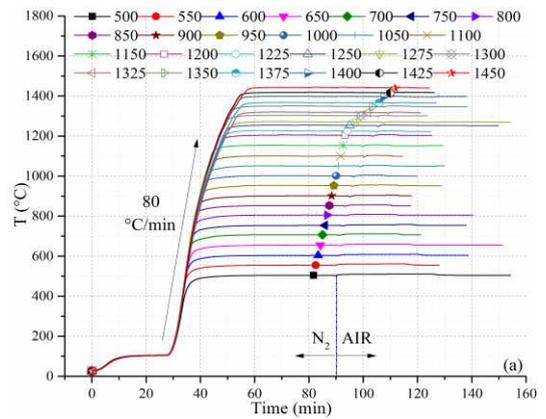


(c) gasification conversion factor curves

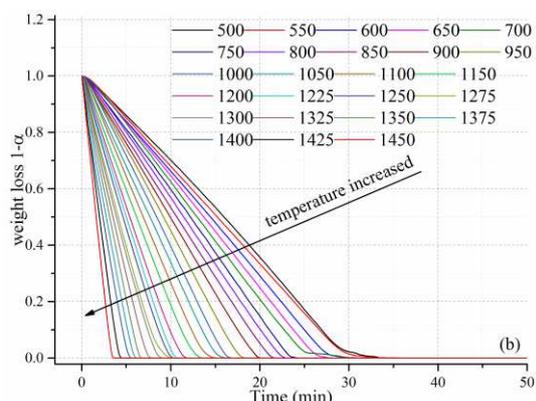


(d) the plots of $\ln(\beta/T^2)$ vs $1/T$

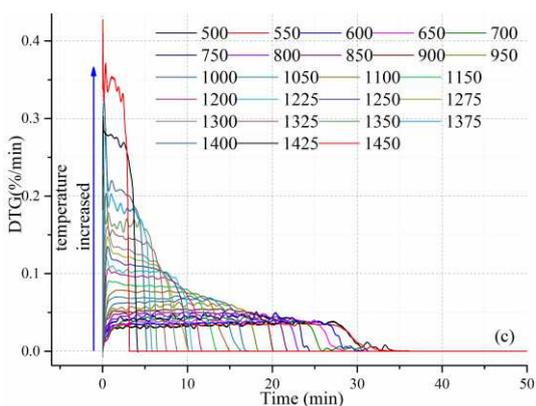
Fig. 5 Experimental results of five coal samples with different particle sizes: (a) particle size distribution curves, (b) micro surface morphology, (c) gasification conversion factor curves and (d) the plots of $\ln(\beta/T^2)$ vs $1/T$ at a particular conversion factor.



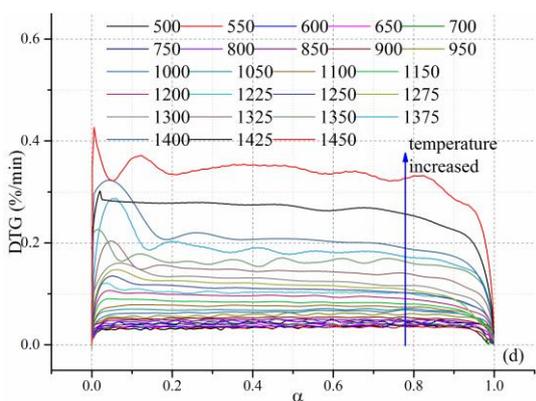
(a) $T(t)$



(b) $1-\alpha(t)$

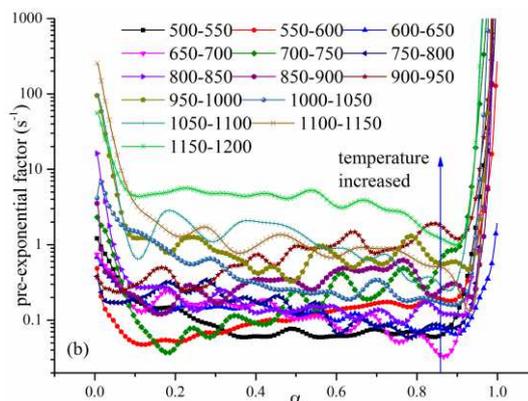


(c) $DTG(t)$

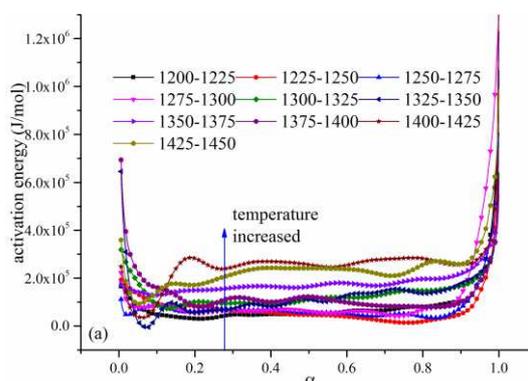


(d) $DTG(\alpha)$

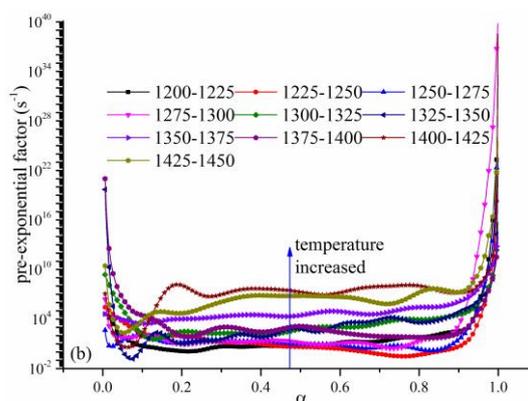
Fig. 6 The (a) $T(t)$, (b) $1-\alpha(t)$, (c) $DTG(t)$, and (d) $DTG(\alpha)$ profiles for the Hulunbeier lignite coal.



(b) pre-exponential factor $A(\alpha)$

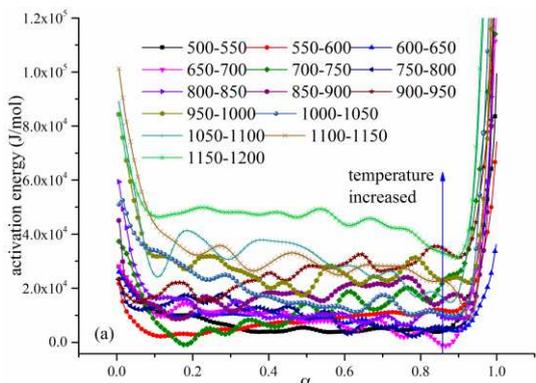


(a) activation energy $E(\alpha)$



(b) pre-exponential factor $A(\alpha)$

Fig. 7 The results for (a) activation energy $E(\alpha)$ and (b) pre-exponential factor $A(\alpha)$.



(a) activation energy $E(\alpha)$

combustion temperature increased from 500 °C to 1200 °C, E and $\log A$ curves progressively decreased in the range of $0.2 < \alpha < 0.9$ and increased in the range of $1200-1450$ °C. At the end of the combustion $0.9 < \alpha < 1$, E and $\log A$ curves increased exponentially for all temperatures.

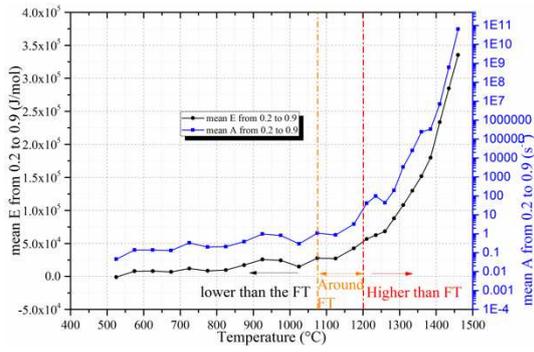
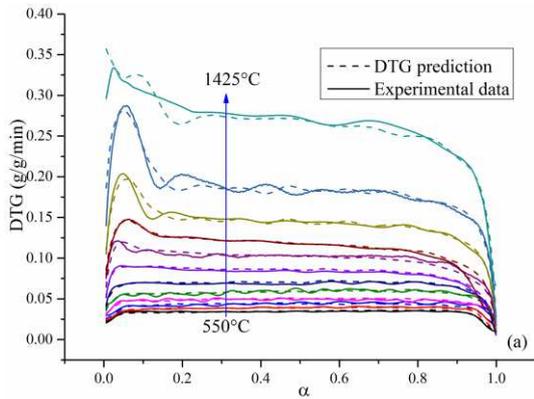
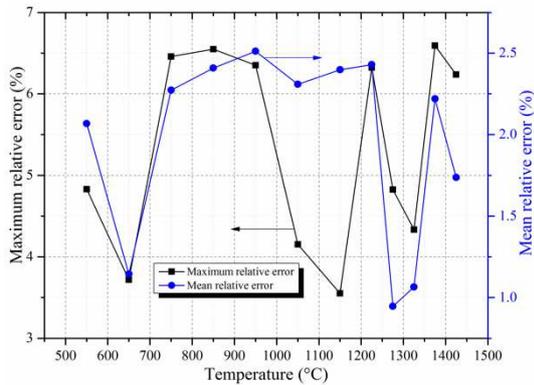


Fig. 8 Mean E and A values in the range of $0.2 < \alpha < 0.9$.



(a) DTG predicted and experimental results



(b) Error analysis in the range of $0.2 < \alpha < 0.9$.

Fig. 9 Comparisons of (a) DTG predicted and experimental results and (b) error analysis in the range of $0.2 < \alpha < 0.9$

The E and $\log A$ curves were stable in the range of $0.2 < \alpha < 0.9$ and mean E and $\log A$ in this range are shown in **Fig. 8**. At a combustion temperature lower than the AFT (1160 °C), the E and $\log A$ values fluctuated within the same order of magnitude. However, when the combustion temperature exceeded the AFT, the E and $\log A$ values increased

exponentially. It is noteworthy that the mean E and A values in the range of $0.2 < \alpha < 0.9$ varied with different temperatures, especially when the combustion temperature exceeded the AFT.

The values of T_1 and T_2 were identified as close as possible to avoid the effect of the AFT on the results of E and A . Using Eqs. (5), (6), and (7), $DTG'(\alpha)$ at a combustion temperature of T_3 ($T_3 = (T_1 + T_2)/2$) was obtained. The comparisons of the predicted and experimental results are shown in **Fig. 9(a)**. **Fig. 9(b)** shows the error analysis for the range of $0.2 < \alpha < 0.9$. The predicted DTG curves fit the experimental data well. The maximum and mean relative errors were less than 6.5% and 2.5%, respectively. This indicated that the DTG predicted model proposed in this study was validated to predict the char combustion in the TGA; the model performed especially well for high-temperature ($T > 1200$ °C) char combustion.

3.3 H₂S-CO₂ removal

The compositions of the product gas are listed in **Table 3**. Steam was removed via cooling before the evaluation. It is seen that the concentration of CO₂ was lower than 500 ppm, attesting 99.9% of CO₂ was captured by the adsorbent. The concentration of H₂S was lower than the detection accuracy of chromatographic (0.1 ppm). Hence, H₂S removal by activated carbon seems to be feasible. After running for several months, H₂S did not penetrate the adsorption bed, indicating the adsorption of H₂S did be reversible. As a physical adsorbent, activated carbon could more or less adsorb all kinds of gas. Therefore, not only CO₂ and H₂S but also CO and CH₄ were partially removed during this process. Because N₂ was adopted as the purging gas, the concentration of N₂ is higher than the feed gas. Small amount of inert gas is acceptable when H₂ is used in IGCC and IGFC.

Table 3 Working condition and purification outcomes of 8-6-1 ETPSA

Temperature	Pressure	Flow rate	Product gas composition (dry)
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170°C	2MPa	5.7 Nm ³ /h	1~2% N ₂ , <500 ppm CO ₂ , <0.1% CO, <0.1 ppm H ₂ S, <100 ppm CH ₄ , H ₂ as balance gas
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The H₂ recovery rate during this purification process is 97%, which is much higher than regular PSA (Lopes et al. 2011; Shen et al. 2012; Wang et al. 2012). It could be attributed to the introduction of vacuum desorption and steam rinse. In order to explore the influence of rinse and vacuum desorption, we changed the cycle procedure and evaluated the corresponding product gas compositions and recovery rates. The case shown above is the best

one and is named as Case 4 and the others are marked Case 1-3. The results are as shown in Table 4 for comparisons. The conditions and parameters were same as Case 4 if not specifically mentioned. We regulated the cycle time to make the product purity close Case 4 so that the recovery rate could represent the separation efficiency. The time length of each step is also given in Fig. 2.

Table 4 Separation efficiencies of different cases with and without vacuum desorption and steam rinse

Case	Temperature	Flow rate	Cycle time	H ₂ S	CO ₂	H ₂ recovery	Procedure
1	170°C	5.2 Nm ³ /h	456 s	<0.1ppm	~0.3%	79.3%	Without V and RH
2	120°C	6.8 Nm ³ /h	544 s	<0.1ppm	~0.3%	86.4%	Without V and RH
3	170°C	5.7 Nm ³ /h	360 s	<0.1ppm	~0.3%	93.3%	Without V

After replacing V and RH with PG and AD, respectively, the H₂ recovery decreased to 79.3%, which was close to some regular PSA operated at normal temperatures (Mivechian and Pakizeh 2013; Rahimpour et al. 2013). Considering the adsorption capacity of activated carbon could deteriorate with the rising temperature, we set the temperature as 120 °C and the H₂ recovery rate is thus improved in Case 2. Subsequently, steam rinse was added and H₂ recovery increased to over 90% immediately. This means steam rinse was a significant factor. However, although the cycle time of Case 3 is shorter, CO₂ concentration in product gas was up to 0.3%, which was much higher than Case 4. It was mainly due to the remained impurities in adsorption bed after regeneration steps. Vacuum desorption is demonstrated to be effective in promoting adsorbent regeneration and hence compensates the defect in desorption kinetic performance. The introduction of vacuum desorption results in extra power consumption and the cost of high pressure steam in rinse step will also lead to more energy consumption. Consequently, the energy efficiency of ETPSA should be further discussed in our following studies.

3.4 Syngas mercury removal

3.4.1 α -Al₂O₃ measurement

α -Al₂O₃ was selected as the carrier in the experiments, with the parameters as shown in

Table 5. It can be seen that specific surface area of α -Al₂O₃ may reach as high as 237 m²/g. Such a large value manifested α -Al₂O₃ as an ideal carrier material.

Table 5 Properties of the carrier α -Al₂O₃

Sample	Size/mm	specific surface area (m ² /g)
α -Al ₂ O ₃	1.5	237

3.4.2 Mercury removal test of the carrier

Mercury removal experiments were carried out at different temperatures with α -Al₂O₃, which was not impregnated with the active component. The experimental result are shown in **Fig. 10**. It could be seen that at the temperature of 150 °C mercury removal efficiency was about 5%. Counter-intuitively, mercury removal efficiency decreased with the increase of temperature. When the temperature reached 400 °C, the mercury removal efficiency was almost zero. The reason was probably because α -Al₂O₃ was full of the microchannel and had very large specific surface area, which possessed strong physical adsorption capacity. Therefore, α -Al₂O₃ presented the mercury removal capacity in lower temperature, but does not possess chemical adsorption capacity and the mercury removal capacity was lost when the temperature reached 400 °C.

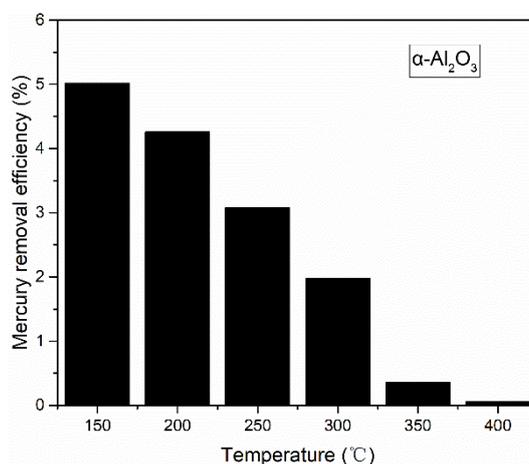


Fig. 10 Mercury removal performance of α -Al₂O₃ at different temperatures

3.4.3 Evaluation of prepared adsorbents

The prepared Mn₂O₃/Al₂O₃, Co₂O₃/Al₂O₃ and Fe₂O₃/Al₂O₃ loaded with active components were evaluated individually under the simulated gas condition at 200 °C. The evaluation results are shown in **Fig. 11~Fig. 13**.

As shown in **Fig. 11~Fig. 13**, the mercury removal efficiency of the prepared Mn₂O₃/Al₂O₃ could reach 90.4% in the first 10 min, and then slowly decreased and finally dropped to a stable

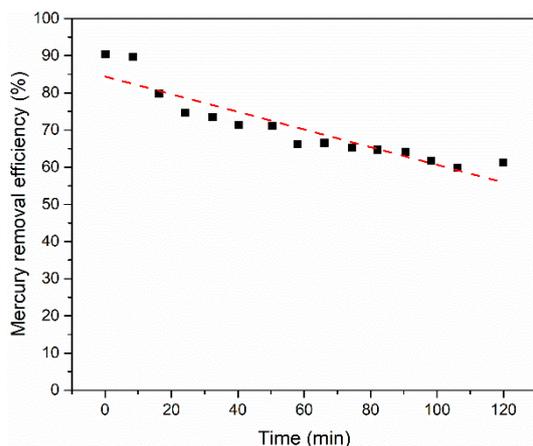


Fig. 11 The test curve of mercury removal performance of Mn₂O₃/Al₂O₃

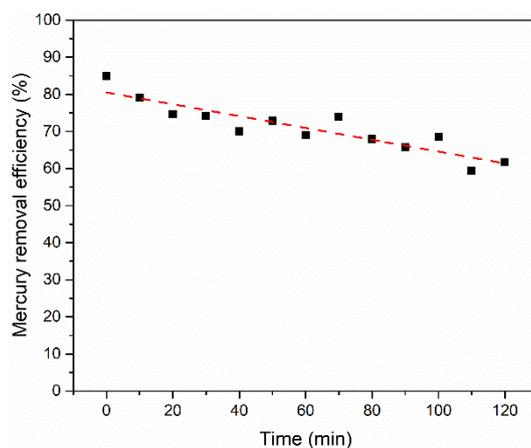


Fig. 12 The test curve of mercury removal performance of Co₂O₃/Al₂O₃

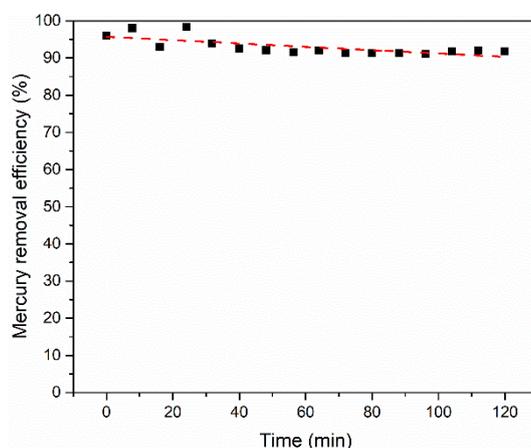
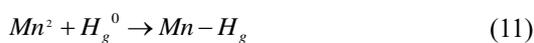
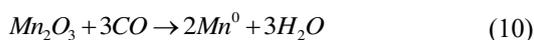
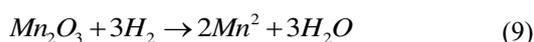


Fig. 13 The test curve of mercury removal performance of Fe₂O₃/Al₂O₃

level at ~ 60%. The initial mercury removal efficiency of the prepared Co₂O₃/Al₂O₃ was 86%, and the final mercury removal efficiency was stable at about 60%. The mercury removal agent Fe₂O₃/Al₂O₃ had the best mercury removal performance, with its initial mercury removal efficiency reaching 95.4%. In the two-hour test, the mercury removal agent was maintained at about 90% with no attenuation.

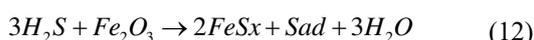
It could be seen in Figs. 11 and 12 that the mercury removal efficiency of Mn₂O₃/Al₂O₃ and Co₂O₃/Al₂O₃ both showed very big promotion compared to pure Al₂O₃, indicating the original physical adsorption was changed and could suggesting that physical adsorption and chemical adsorption synergy effected co-existed (Huo et al. 2017; Mao et al. 2018). The mechanism was speculated as follows

(Mn₂O₃ as example):



Meanwhile, the mercury removal efficiency of Mn₂O₃/Al₂O₃ and Co₂O₃/Al₂O₃ both displayed the trend of decreasing during 2 h test. Finally, the mercury removal efficiency was stabilized at a certain value, suggesting that the reaction of Hg⁰ and the active component reached reaction equilibrium.

The mercury removal mechanism of Fe₂O₃/Al₂O₃ was obviously different from that of Mn₂O₃/Al₂O₃ and Co₂O₃/Al₂O₃. The mechanism was proposed as follows:



It could be seen that because of its existence in coal gasification syngas, H₂S improved the mercury removal efficiency and stability of Fe₂O₃/Al₂O₃ mercury removal agent. Hence, H₂S replaced the combination of transition metal oxides with Hg⁰, making its mercury removal efficiency reached more than 90%.

4. Conclusions

In this paper, the gasification reaction characteristics of ultrafine coal particles, the formation mechanism of pollutants, and H₂S and CO₂ simultaneous removal in the process of IGFC were studied. The following conclusions can be obtained.

(1) The surface became coarser with the decrease of coal sample particle size, which could promote the gasification process and improve the reaction activity. The gasification kinetic parameters of Shenhua bituminous coal were obtained from the Miura-Maki Model. The value of activation energy decreased with reducing particle size of the coal samples.

(2) A database of the kinetic characteristics functions of char combustion and a DTG model was established. The maximum and mean relative errors were less than 6.5% and 2.5%, respectively. The predicted DTG curves fit the experimental data well because the effect of the AFT on the *E* and *A* values was taken into account.

(3) A small scale ETPSA rig was built in an ammonia plant and on-site syngas H₂S-CO₂ simultaneous removal was realized. An 8-6-1 cycle procedure with steam rinse and vacuum desorption was designed and demonstrated to be efficient. The concentration of CO₂ and H₂S in the product gas was lower than 500 ppm and 0.1 ppm, respectively, indicating a removal rate over 99.9%. The corresponding H₂ recovery rate was 97%. The importance of steam rinse and vacuum desorption was verified after changing the cycle procedure. However, the energy efficiency of ETPSA should be analyzed in detail in future studies.

(4) Three kinds of mercury removal adsorbents were prepared, Mn₂O₃/Al₂O₃, Co₂O₃/Al₂O₃ and Fe₂O₃/Al₂O₃, which showed diverse degrees of mercury removal performance. Among them, the mercury removal efficiency of Fe₂O₃/Al₂O₃ was basically stable at more than 90% under the 2 h condition at 200 °C medium temperature test. The use of transition metal oxides as mercury removal adsorbents in coal gasification syngas had great potential and was hence the main direction of the research on mercury removal in IGFC gas purification system.

Acknowledgements:

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Figures



Figure 1

Outlook photo of the ETPSA device

Step	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18	19	20	21	22	23	24
Bed1	AD	AD	AD	AD	AD	RH	PEA	PE1	PEB	PEC	PE2	PED	BD	PG	V	PEC	PE2	PEC	PEB	PE1	PEA	PP	PP	PP
Bed2	PEB	PE1	PEA	PP	PP	PP	AD	AD	AD	AD	AD	RH	PEA	PE1	PEB	PEC	PE2	PED	BD	PG	V	PEC	PE2	PEC
Bed3	BD	PG	V	PED	PE2	PEC	PEB	PE1	PEA	PP	PP	PP	AD	AD	AD	AD	AD	RH	PEA	PE1	PEB	PEC	PE2	PED
Bed4	PEA	PE1	PEB	PEC	PE2	PED	BD	PG	V	PED	PE2	PEC	PEB	PE1	PEA	PP	PP	PP	AD	AD	AD	AD	AD	RH
Tank1	PEA		PEA																					
Tank2	PEB		PEB																					
Tank3				PEC		PEC																		
Tank4				PED		PED																		
Cycle 544s	50	30	14	14	14	14	50	30	14	14	14	14	50	30	14	14	14	14	50	30	14	14	14	14
Cycle 456s	43	19	13	13	13	13	43	19	13	13	13	13	43	19	13	13	13	13	43	19	13	13	13	13
Cycle 360s	34	18	11	11	11	5	34	18	11	11	11	5	34	18	11	11	11	5	34	18	11	11	11	5
Cycle 468s	40	25	14	15	15	7	40	25	14	15	15	7	40	25	14	15	15	7	40	25	14	15	15	7

Figure 2

8-6-1 ETPSA cycle procedures. AD: adsorption; RH: high pressure steam rinse; PE: pressure equalization with columns (1, 2) or tanks (A, B, C, D); BD: counter-current blow down; PG: N2 purge; V: vacuum desorption; PP: pressurization with product gas.

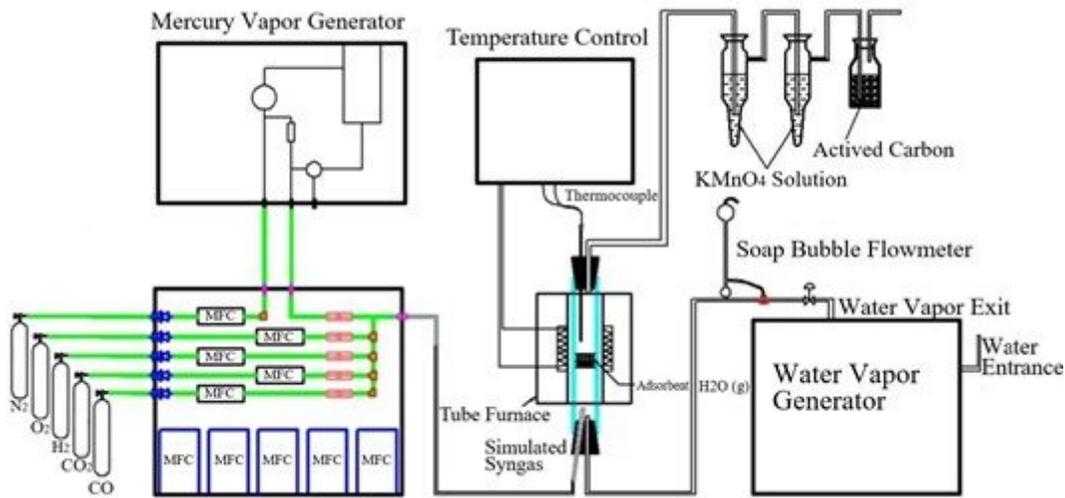


Figure 3

Schematic diagram of simulated syngas mercury removal system

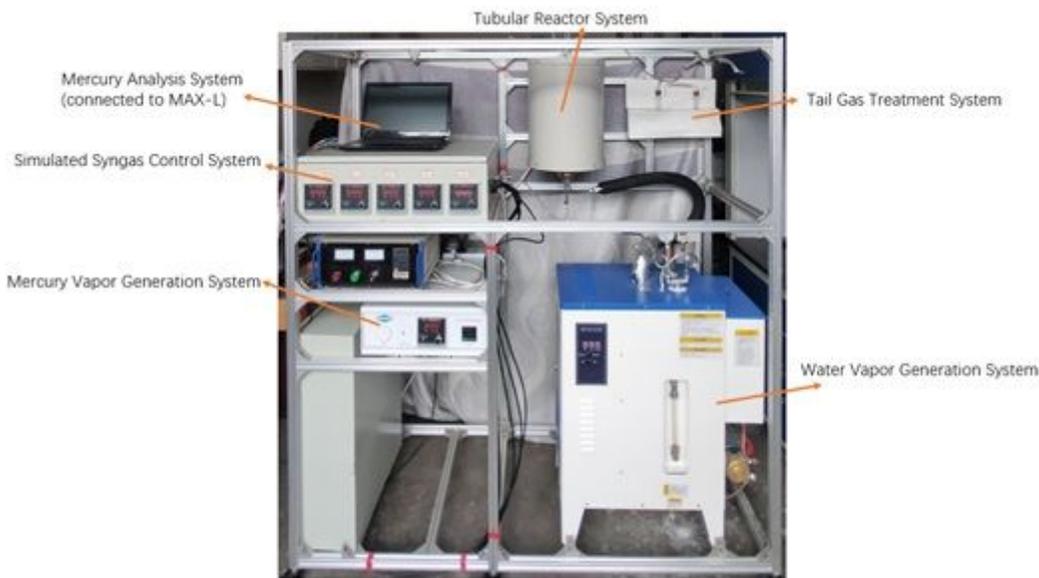
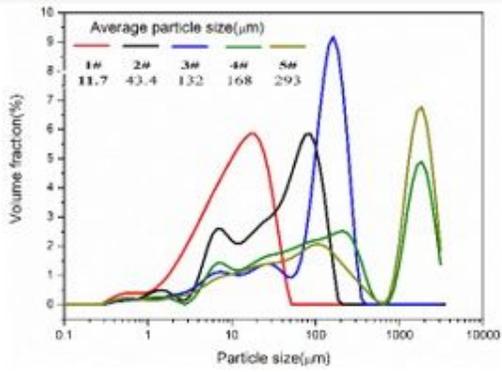
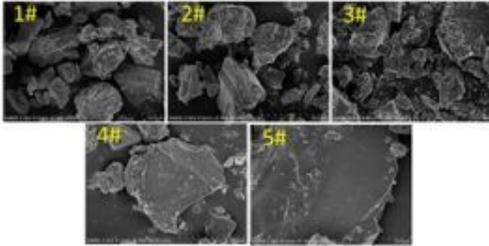


Figure 4

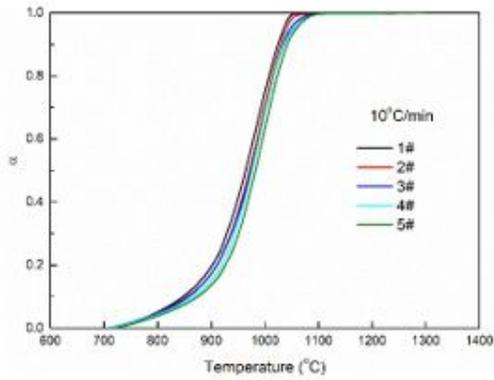
Test bench of syngas mercury removal system



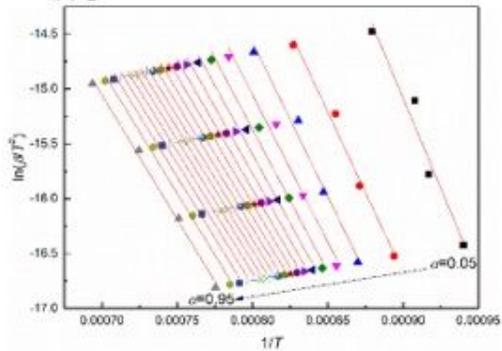
(a) particle size distribution curves



(b) the micro surface morphology



(c) gasification conversion factor curves



(d) the plots of $\ln(\beta/T^2)$ vs $1/T$

Figure 5

Experimental results of five coal samples with different particle sizes: (a) particle size distribution curves, (b) micro surface morphology, (c) gasification conversion factor curves and (d) the plots of $\ln(\beta/T^2)$ vs $1/T$ at a particular conversion factor.

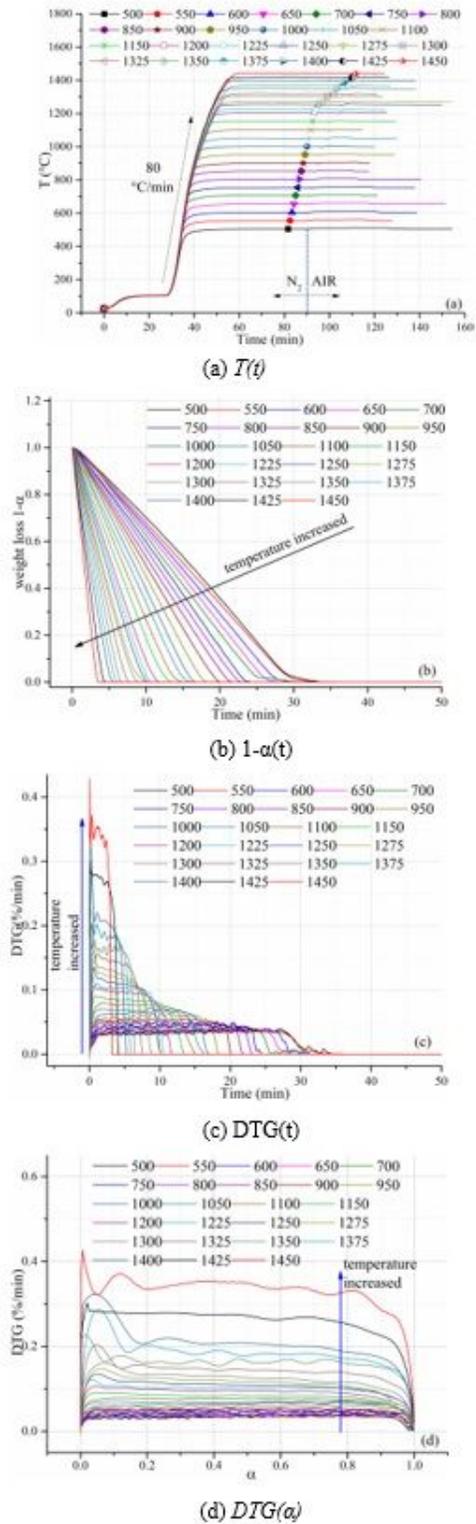
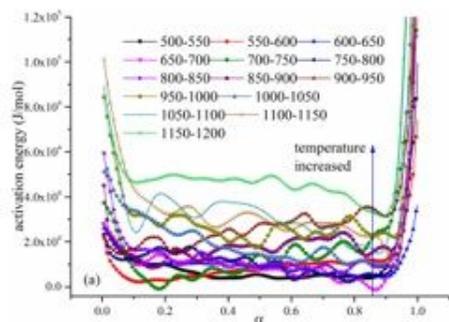
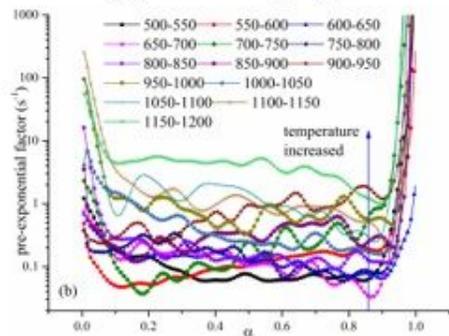


Figure 6

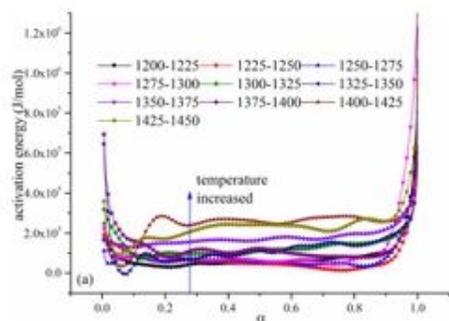
The (a) $T(t)$, (b) $1-\alpha(t)$, (c) $DTG(t)$, and (d) $DTG(\alpha)$ profiles for the Hulunbeier lignite coal.



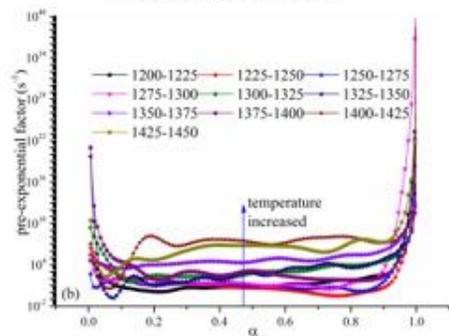
(a) activation energy $E(\alpha)$



(b) pre-exponential factor $A(\alpha)$



(a) activation energy $E(\alpha)$



(b) pre-exponential factor $A(\alpha)$

Figure 7

The results for (a) activation energy $E(\alpha)$ and (b) pre-exponential factor $A(\alpha)$.

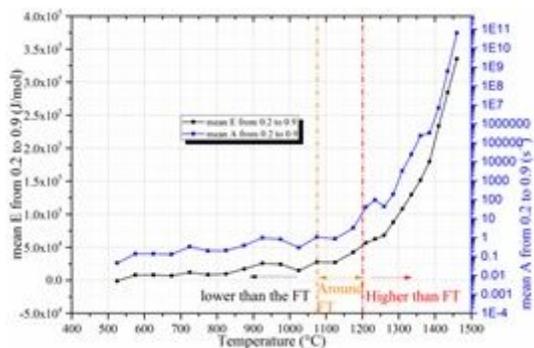
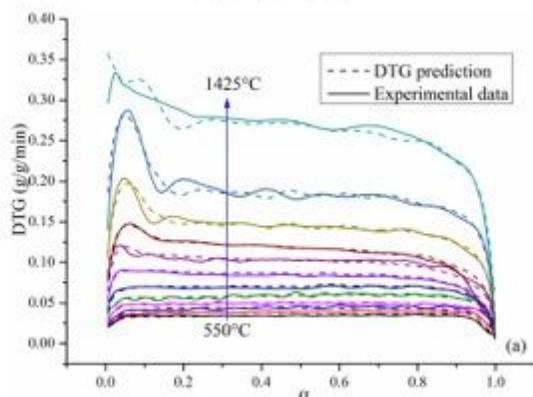


Figure 8

Mean E and A values in the range of $0.2 < \alpha < 0.9$.



(a) DTG predicted and experimental results

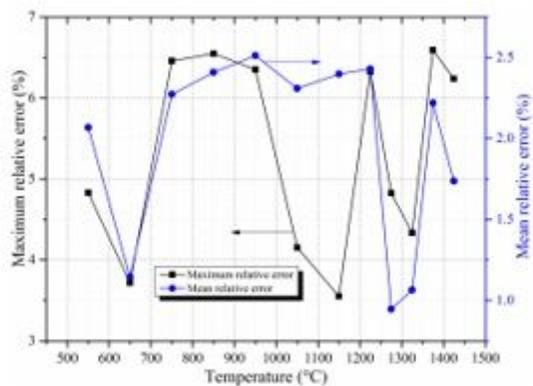


Figure 9

Comparisons of (a) DTG predicted and experimental results and (b) error analysis in the range of $0.2 < \alpha < 0.9$

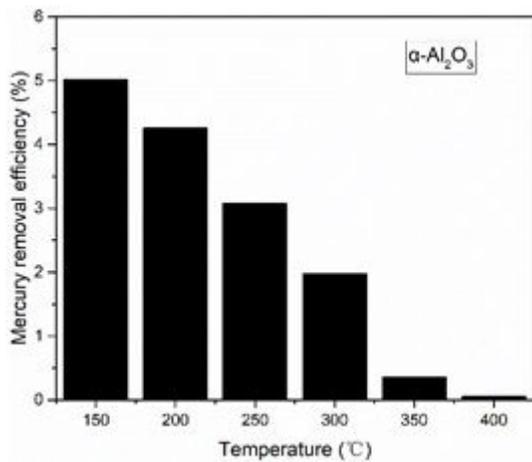


Figure 10

Mercury removal performance of $\alpha\text{-Al}_2\text{O}_3$ at different temperatures

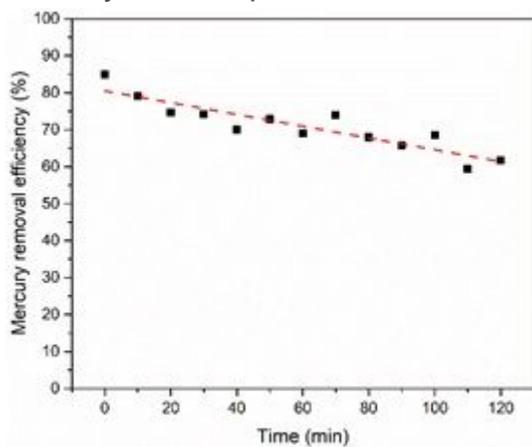


Figure 12

The test curve of mercury removal performance of $\text{Co}_2\text{O}_3/\text{Al}_2\text{O}_3$

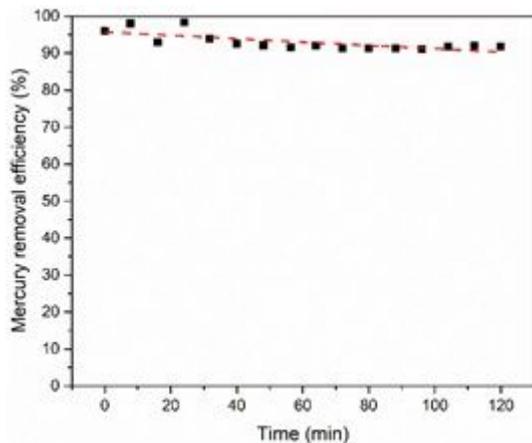


Figure 13

The test curve of mercury removal performance of $\text{Fe}_2\text{O}_3/\text{Al}_2\text{O}_3$