



## Research Paper

## Catalytic characteristics of the pyrolysis of lignite over oil shale chars



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## HIGHLIGHTS

- Effect of oil shale chars on lignite pyrolysis are experimentally assessed.
- Oil shale chars restrain the thermal degradation of organic matters in lignite.
- Kinetic constant estimation using Friedman and Flynn-Wall-Ozawa method.
- Oil shale char is a promising candidate for trace metal adsorption.

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## ABSTRACT

In this paper, the non-isothermal thermogravimetric method (TGA) was applied to study the effect of oil shale chars on catalytic thermal decomposition of lignite. After oil shale chars being added, the trough temperature of the rate of weight loss ( $T_{max}$ ) increased by about 10 °C, and corresponding mass loss rate experienced an increase as high as 29.67%. The devolatilization time was longer as well as less concentrated as the value of the characteristic index of the pyrolysis products gained 28.936% increase. The characteristic of oil shale chars' effect on lengthening the time of pyrolysis indicated that oil shale char compounds may restrain the process of thermal degradation of organic matters in lignite. Noticeable increasing in  $-S=O$ ,  $-C=O$ ,  $-CH$  (Both aliphatic and aromatic),  $CH_4$  and decreasing in  $CO_2$  were observed in the co-pyrolysis of lignite with the oil shale char produced at slow heating rate of 30 °C/min from ambient temperature to 510 °C. Combining with the appearance of the lowest active energy and the increase of the trace metal concentration (38.89% to Tl and 22.98% to Ga) in the sample of lignite mixed with SC510, a conclusion can be achieved that employing the oil shale char as a catalyst has potential application prospect in co-utilization with other fuels.

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## 1. Introduction

As China the largest coal producer and consumer in the world, it depends heavily on coal [1]. Low-rank coals (i.e., lignite, brown coal and sub-bituminous coals) possess a special place in the energy system of China, since the reserves of lignite are about 41.18% in the total amount in the country [2]. In other words, it is the most important domestic source and thus, the main fuel for power generation [3,4]. Therefore, the exploitation of lignite is necessary for the growing energy demands and the depletion of high-rank coals. Lignite is a highly reactive coal due to the abundance of free radicals that are formed during thermal transformations of its oxygen functional groups [5]. Pyrolysis is generally considered as the most effective for low rank coal upgrading. Catalytic pyrolysis of coal is an attractive way to

achieve commercially acceptable low-pollution pyrolysis products at low temperatures [6].

Oil shale is a type of natural sedimentary rocks which is composed of organic contents distributed in an inorganic matrix [7]. Due to their natural low fixed carbon and high ash content, 4.71% for fixed carbon and 70% for ash in proximate analysis (air dry basis), a proper strategy for ash handling, disposal and utilization of oil shale char, which is a by-product of oil shale processing and also considered a serious environmental problem related to this ash. In general, oil shale char is used for production of cement and concrete, asphalt shingle, quarry-fill and sludge stabilization, soil treatment for agricultural purpose, while the large portion is dumped in landfills [8]. In recent years, char, or similar materials such as activated carbon, has been reported to have catalytic activity for reforming or cracking of hydrocarbons [9–13].

Thermo-gravimetric analysis (TGA) is a common technique used to investigate thermal events during the combustion, pyrolysis and gasification of solid raw materials, such as coal, and wood.

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Moreover, quantitative methods can be applied to TGA curves in order to obtain kinetic parameters of the thermal events. A precise knowledge of the kinetic characteristics of the pyrolysis process is essential for understanding and modelling pyrolysis at industrial scale [11,12].

This research investigates utilization of oil shale char in high value applications, such as catalysis in lignite pyrolysis. Char properties vary with gasification conditions, so it is important to understand how these properties influence the catalytic activity of char. This enables one to identify which torrefied processes produce char is appropriate for use in catalytic applications. For this purpose, the combined TG–FTIR technique was employed to dynamically record the species ejected from the thermal degradation of lignite over oil shale char and thereby derive the catalytic effect of oil shale char. Two model-free methods were used to determine the kinetic parameters which represent the pyrolysis of lignite [14]. Furthermore the oxygen functional groups, minerals composition, inorganic oxides and selected trace metals (Co, Cu, Cr and Zn) may affect the catalytic activity and are also studied here [13].

## 2. Materials and methods

### 2.1. Fuel samples

The raw materials used in this work were an oil shale from Guangdong Maoming oil shale mining area in China with an ash ratio of 70% and a lignitous coal from Indonesia. Maoming Mine is located at Maoming basin which is a Cenozoic faulted basin with semi-deep lacustrine sediment environment. Aquatic organism and terrestrial advanced plants are the majority source of the organic matters in oil shale. The stable and consistent warm and moist paleoclimate leads to its specific lithology association which is lignite and carbonaceous shale interlayer with gray oil shales [15]. Most Indonesian lignites and low rank coals are liptinite-rich (averaging about 10% liptinite by volume) with low inertinite and high vitrinite (often perhydrous) contents [16]. These materials were ground, sieved to size range of 0–0.18 mm and then dried in an oven at 105 °C for 24 h for the catalytic pyrolysis tests. All samples were stored in a desiccators for further use. The proximate and ultimate analysis of oil shale and lignite were performed using GB212-91 standard and ASTM D5373 standard methods which were shown in Table 1.

### 2.2. Char preparation

The oil shale chars were prepared by devolatilizing the raw fuels in a quartz fixed-bed reactor (90 mm internal diameter, 1400 mm length) heated by an electric furnace under a stream of nitrogen (100 N mL/min). A thermocouple in contact with the sample bed was used to control the devolatilization temperature. Two groups of ripped oil shale chars were obtained by different process: the chars which obtained by pyrolysis under a constant temperature of 450, 510, 530, 560 °C for 30 min, respectively were

classified into the FC, short for fast char, group; the one produced at slow heating rate of 30 °C/min from ambient temperature to 510 °C were labelling as the SC group. Afterwards, all the chars were cooled down under a flow of nitrogen to room temperature. Therefore, no measurable reactions would have taken place on the char surface with room air, since the char was only exposed to air at room temperature, where kinetics of such reactions would be immeasurably slow.

The char samples would be referred to throughout this paper using names indicated in Table 2, which described the gasification process and the final temperature. For example, FC-510 referred to chars derived from pyrolysis at constant temperature at 510 °C while SC-510 referred to that heated to the 510 °C at a heating rate of 30 °C/min. The proximate analysis of the char samples are given in Table 2.

### 2.3. Experimental procedure and methods

The catalytic pyrolysis process of lignite over ripped oil shale chars under N<sub>2</sub> atmosphere was studied by using a METTLER TGA thermogravimetric simultaneous thermal analyzer with a flow rate of 80 mL/min in the temperature range 100–950 °C. The samples, blends of lignite (80 wt%) and oil shale char (20 wt%) were loaded into the reactor to each experiment. All tests were experimented at heating rates of 20, 30, 40 °C/min, respectively for the sake of kinetic analysis.

A Fourier transform infrared measurements (Nicolet™ iS™ 10 FTIR spectrometer) coupled to the thermal analyzer was conducted for the identification of the gaseous species and their evolution profiles during catalytic pyrolysis. Evolved gases from TGA passed through a heated transferred line, which heated to 215 °C in order to prevent the condensation of gases, into a beam conforming flow cell for the FTIR to collect the spectra characteristics in the range of 4000–1000 cm<sup>-1</sup> IR absorption band to 6 cm<sup>-1</sup> resolution [14]. Duplicate experiments for each test were performed in order to test the reproducibility of the results.

### 2.4. Kinetic theory

Kinetics analysis methods were used to further study the catalytic pyrolysis of lignite. The rate of fuel's conversion,  $d\alpha/dt$ , was the linear function of a temperature-dependent rate constant and function of conversion, which was described as  $k(T)$  and  $f(\alpha)$ , respectively [17],

$$d\alpha/dt = k(T)f(\alpha) \quad (1)$$

where  $\alpha$  was the conversion degree,  $t$  (s) was experimental time,  $T$  (K) was the absolute temperature,  $k$  (T) usually described by the Arrhenius equation [18,19]:

$$k = A \exp(-E/RT) \quad (2)$$

where  $A$  (s<sup>-1</sup>) was pre-exponential Arrhenius factor,  $E$  (kJ/mol) was the apparent activation energy,  $R$  (kJ/mol·K) was the universal gas constant.

The degree of conversion,  $\alpha$ , was described as [20],

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (3)$$

where  $m_0$  was the initial mass of the sample,  $m_t$  was the mass of the sample at the time  $t$  and  $m_f$  was the final mass of the sample. The combination Eqs. (1) and (2) gives [21,22]

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (4)$$

while the temperature of the sample was controlled at a constant heating rate,  $\beta = dT/dt$  (°C/min).

**Table 1**  
The proximate analysis and elemental analysis of oil shale and lignite.

	Proximate analysis <sup>a</sup> (wt%)		Elemental analysis <sup>b</sup> (wt%)		
	Oil shale	Lignite		Oil shale	Lignite
Moisture	4.15	16.8	C	14.56	63.31
Volatile	24.25	45.79	H	2.46	5.187
Ash	70	15.83	N	0.47	0.97
Fix carbon <sup>c</sup>	4.71	37.18	S	3.022	0.415

<sup>a</sup> On air dry basis.

<sup>b</sup> On dry ash free basis.

<sup>c</sup> Calculated by difference.

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