



Research Paper

Synergy in co-combustion of oil shale semi-coke with torrefied cornstalk



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HIGHLIGHTS

- A synergistic effect did exist in the co-combustion process.
- The synergy effect was confirmed by the evaluated values of the activation energies.
- Burnout times in a CFB were predicted by AKTS-Thermokinetics Software.

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ABSTRACT

Previous research has indicated that combing semi-coke with torrefied cornstalks can help to easily initiate combustion, and reduce the hazardous nature of semi-coke for disposal. Combustion experiments with oil shale semi-coke from Huadian retorts, torrefied cornstalk as well as their blends were conducted using a thermogravimetric analyzer under air atmosphere in order to assess the combustion behavior and synergy in the co-combustion process. Combustion kinetic parameters and predicted burn times in a circulating fluidized bed were then calculated using AKTS-Thermokinetics Software applying the differential isoconversional analysis of Friedman. The interaction index MR and an average activation energy values were used to analyze the synergy of the co-combustion process. The results showed that a synergistic effect was observed in the system: oil shale semi-coke and torrefied cornstalks during co-combustion. Interpretation of the MR curve indicates that the influence of the torrefied cornstalks on the combustion process is observed mainly during the second phase of the process. The shortest burnout time estimated in a circulating fluidized bed (CFB) was observed for a mixture of 70 wt% semi-coke and 30 wt% torrefied (275 °C) cornstalk.

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1. Introduction

Oil shale semi-coke is the solid waste formed during the thermal processing of oil shale. This material is a low-grade fuel (2500–4000 kJ/kg), with a low volatile content, minimal calorific value and high proportion of an ash. Oil shale semi-coke is difficult to ignite when attempting to burn it during disposal, therefore retorting solid waste occupies the large-area landfill sites [1]. This is actually an environmental concern because the retorting waste contains toxic environmental compounds [2,3], such as polycyclic aromatic hydrocarbons, phenolic compounds and sulfids, which can leach into the surrounding soil, waterways and aquifers.

Co-combustion of oil shale semi-coke has been extensively studied. Kuusik et al. [4] studied the co-combustion of Estonian oil shale semi-coke and oil shale in a circulating fluidized bed (CFB) and found that semi-coke with a moisture content <10%

can be combusted alone, while semi-coke with a moisture content >10% is difficult to burn even when incorporated into a small amount of shale. Wang et al. [5–7] studied the combustion behavior of oil shale semi-coke in a thermogravimetric analyzer and claimed that the combustion is a multistage process occurring in a few temperature ranges. Sun et al. [8] found that the combustion characteristics of ignition and burnout could be improved when semi-coke was mixed with bituminous coal. Liu et al. [9,10] studied the combustion characteristics and kinetic parameters of co-combustion of the Huadian oil shale retorting waste and cornstalks by the FWO (Flynn-Wall-Ozawa) method. The primary reaction period shifted from high to low temperatures as the amount of cornstalk mixed with the retorting waste increased. The activation energy and frequency factor of the volatiles combustion increased, while for the coke the combustion activation energy and frequency factor decreased.

For disposing the waste several effective ways of co-combustion of oil shale semi-coke with oil shale, coal or biomass in a CFB have been proposed. Many of them use the heat generated and reduce

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the levels of combustible bottom ash to below 2%, fulfilling requirements for use in building materials. Arro et al. [11] investigated the co-combustion of oil shale semi-coke with oil shale in a CFB. Kaljuvee et al. [12] studied the combustion of oil shale semi-coke in a CFB and found that SO₂ could be completely adsorbed. Liu et al. [13] studied the combustion of various mixtures of oil shale retorting solid waste and cornstalk in a CFB under various conditions and found low emissions levels of NO_x.

The co-combustion of semi-coke with cornstalks can fully utilize this undesired waste, decreasing potential environmental hazards, saving energy and protecting the environment. Sonobe et al. [14] studied the co-pyrolysis of lignite mixed with corn straw. The results indicate that synergy occurs in this system, and a studied mixture was more combustible than either alone. The corn straw is highly volatile and released a significant amount of heat while reducing the ignition temperature of the coal. However, raw biomass as a potential energy source also has certain drawbacks, stemming from its intrinsic properties. These include heterogeneity and a low energy density. In order to overcome these shortcomings, torrefaction is widely considered a promising pre-treatment for reducing some of these drawbacks. Torrefaction [15] increases the biomass energy density and reduce its moisture content, improves grindability, and produces lower NO_x and SO₂ emissions [16].

Co-combustion of various mixtures of semi-coke and differently torreficated cornstalks was analyzed using thermogravimetric analysis (TGA). The combustion kinetic parameters calculated using AKTS software was then used to estimate the co-combustion burnout time under an isothermal condition in a CFB furnace. Finally, the synergy of co-combustion between the semi-coke and variously torreficated cornstalks mixed in different ratios was evaluated using the interaction index MR (mean of the absolute error divided by the mean of the calculated value) in order to analyze the effect of each material in the combustion process.

2. Experimental

2.1. Materials

Oil shale semi-coke was obtained from the Huadian oil shale retort factory. Torreficated cornstalks were collected from Jilin City. The particle size of the blends was <0.2 mm.

Torrefaction experiments were carried out in an OTL1200 tube furnace under nitrogen flow. The cornstalks were heated to 250 °C, 275 °C or 300 °C at a heating rate of 10 °C min⁻¹ and held at these temperatures for 22 min. During tube furnace cooling to

Table 1
Samples labels and blending ratios of semi-coke (SC) to cornstalk (CS).

Temperature	0:10	5:5	6:4	7:3	8:2	9:1	10:0
SC/250 °C CS	A1	A2	A3	A4	A5	A6	A7
SC/275 °C CS	B1	B2	B3	B4	B5	B6	B7
SC/300 °C CS	C1	C2	C3	C4	C5	C6	C7

Table 2
Proximate and ultimate analyses of samples.

Sample	Proximate analysis/mass%				LHV Q _{net,v,ar} (kJ/kg)	Ultimate analysis/mass%				
	M _{ad}	V _{ad}	A _{ad}	FC _{ad}		C _{ad}	H _{ad}	O _{ad}	N _{ad}	S _{ad}
A1	1.91	70.10	6.98	21.02	17020.03	48.06	6.55	35.68	0.66	0.16
B1	1.50	66.82	7.82	23.86	17852.78	48.17	5.96	35.71	0.70	0.14
C1	1.60	60.12	8.94	29.35	19162.65	51.87	6.23	30.54	0.68	0.14
SC	0.89	10.44	82.62	6.09	3868.29	11.29	0.35	4.21	0.11	0.53

ad air dry basis, M moisture, A ash, V volatile matter, FC fixed carbon, LHV low heating value, SC semi-coke (no added cornstalk).

room temperature, the N₂ flow was stopped. Temperatures of torrefication of the cornstalks were chosen to be between 250 and 300 °C because torrefaction of biomass below 250 °C tends to produce the products with poor grindability whereas above 300 °C the cellulose and lignin decompose [17]. Sample labels and applied blending ratios are shown in Table 1.

2.2. TG/DSC experiment

Combustion characteristics of the samples containing the mixtures of torreficated cornstalk and oil shale semi-coke were determined by a Mettler-Toledo TGA/DSC 1 analyzer. The flow rate of purging gas air was kept at 50 ml min⁻¹. About 5 mg sample were heated from 50 °C up to 950 °C with different heating rates: 10, 20, 40, 80 °C min⁻¹.

2.3. Calculation of combustion kinetic parameters and estimating burnout time

Combustion kinetic parameters for each sample were calculated using TG traces by AKTS-Thermokinetics Software [18–20] applying differential isoconversional Friedman [21] method. The logarithm of the conversion rate as a function of the reciprocal temperature at any conversion α :

$$\ln \frac{d\alpha}{dt} = \ln[A(\alpha)f(\alpha)] - \frac{E(\alpha)}{RT} \quad (1)$$

where T, t, A, E and R are the temperature, time, pre-exponential factor, activation energy and gas constant, respectively. As $f(\alpha)$ is a constant in the last term at any fixed α , the dependence of the logarithm of the conversion rate over $1/T$ is a straight line with the slope $m = E(\alpha)/R$ and the intercept on Y-axis is equal to $\ln[A(\alpha)f(\alpha)]$.

Using AKTS-Thermokinetics Software it is also possible to estimate the burnout time needed for each sample under different experimental conditions. Here, we considered:

- (i) The research subject is the small sample particles that escape from the CFB classifier.
- (ii) Small sample particles burned already during first passage through the furnace.

3. Results and discussion

3.1. The analysis of the samples

The data on proximate and ultimate analyses of oil shale semi-coke and torreficated cornstalks blends are presented in Table 2.

As seen from Table 2, the torreficated cornstalk has much higher volatile matter content (70.10%, 66.82% and 60.12%, for samples calcined at temperatures of 250 °C, 275 °C and 300 °C, respectively) than oil shale semi-coke (10.44%). On the contrary, oil shale semi-coke has much greater ash content (82.62%) than differently torreficated cornstalk (6.98%, 7.82% and 8.94%, respectively). With an increasing temperature of torrefication the light

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