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Study of the Combustion , Pyrolysis Characteristics and Synergistic Effect of Co-hydrocharsation Products of Oil Shale and Rice Husk

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Abstract: Under the pressure of environmental problems and fossil energy shortage, countries all over the world are looking for fuel to replace fossil energy. Oil shale and rice husk are potential fuels, but they both have some problems, such as high ash content and low calorific value. In the present study, oil shale and rice husk were used as feedstock for the high quality fuel through hydrothermal approach, it provides a new way for the resource utilization of oil shale and rice. Thermogravimetric method was used to analyze the functional groups change and thermal transformation characteristics of mixed hydrochars prepared for oil shale(OS) and rice husk(RH) at different hydrothermal temperatures(150, 200 and 250°C), including combustion and pyrolysis processes, and analyze the synergistic effects. Results showed that the co-hydrocharsization pretreatment had a significant effect on the thermal transformation behavior of oil shale and rice husk. On the one hand, the mixture of hydrochar has higher volatile content than its calculated value. On the other hand, a synergistic effect (promoting combustion and pyrolysis behavior) was found in both combustion and pyrolysis processes, and this effect was the most obvious when the hydrothermal temperature was around 200 °C, and the characteristic peak of functional groups vibration was strong. Since the synergistic effect of pyrolysis process is lower than that of combustion process, co-hydrocharsation products are considered to be more suitable for combustion. These findings have positive significance of energy generation and utilization of organic waste by the combination of co-hydrocharsization modification and subsequent thermochemical process.

Keywords: oil shale; Rice husk; Hydrocharsization; Combustion characteristics; Pyrolysis characteristics; synergy

1. Introduction

Oil shale has been explored by researchers and found to be a fuel to deep development potential, and has huge reserves all over the world[1]. However, researchers also have found that oil shale has a high ash content, resulting in weak combustion reaction ability in the later stage, so it is difficult to large-scale combustion alone[2]. Biomass is the advantages of extensive sources, including renewable and less combustion pollutants, and it is considered to be an important component of the world energy in the future[3]. But it contains a number of alkaline metals easy to cause a large amount of corrosion of the heating surface of combustion equipment[4]. In recent years, hydrocharsization is an effective means of converting organic solid waste into solid fuel by heat treatment[5], it has attracted extensive attention to scholars at home and abroad. In fact, the high temperature and high pressure water vapor conditions in the reactor are similar to the natural carbonization process, which is considered to be the simulation of the natural carbonization process[6].

Researchers have the large body of research, use the different raw materials by co-hydrocharsization to produce solid hydrochars fuel, some scholars[7, 8] used sludge with lignite through hydrocharsization and research combustion and pyrolysis characteristics of hydrochars, found product of co-hydrocharsizations has higher carbon yield, and promoted the combustion and pyrolysis behavior. Some other scholars[9-11] studied the combustion performance of product by co-hydrocharsization of biomass and PVC, and found that the combustion performance of the hydrochars was better than that of raw materials at 200°C, but the removal of chlorine in PVC was impeded by biomass. Researchers who co-hydrocharsization of coal and biomass[12,13] found that, the hydrochars content

is the best at 230°C, and the combustion index which is close to bituminous coal is the highest. Most researchers have found that the co-hydrocharsization of two materials with different properties has more advantages than the hydrocharsization produced from a single material.

To sum up, oil shale and rice husk have huge reserves, and there are certain problems of the combustion and utilization of oil shale and rice husk alone. If improving the quality of the mixed fuel to oil shale and rice husk through hydrocharsization, can reduce the unfavorable factors of both and maximize the advantages of both as fuels. Therefore, in this paper, thermogravimetric method was used to conduct combustion and pyrolysis characteristics test and kinetics analysis on the mixture of oil shale and rice husk, which will provide some theoretical reference for the large-scale application of oil shale and rice husk in the future.

2. Materials and Methods

2.1 Test Materials

Oil shale (OS) was taken from a coal farm in Jilin Province, and rice husk (RH) was taken from a grain factory in Liaoning Province. The raw materials were natural air-dried and crushed to a particle size less than 0.2 mm. Previous studies have found that when the mass ratio of biomass to coal is 1:1, hydrothermal charcoal has great combustion characteristics and synergistic effect. Therefore, oil shale and rice husk are evenly mixed according to the mass ratio of 1:1, and the mixture is named Mix. Before the experiment, the sample was placed in a 105°C of constant-temperature drying oven (Shanghai light instrument equipment 101a-00) for 24 h, and then sealed for use. Proximate and ultimate analysis of samples are shown in Table 1.

Table 1. Proximate and ultimate analysis of the raw

Sample	Proximate analysis/wt. %				Ultimate analysis/wt. %				
	M	Ash	VM	FC ^a	C	H	O ^b	N	S
RH	8.48	19.62	59.98	11.92	35.34	5.37	30.11	0.95	0.13
OS	3.84	80.53	13.15	2.48	8.45	1.51	5.98	1.02	1.04

^a FC% = 100% - VM% - ash%

^b O% = 100% - C% - H% - N% - S% - Ash% - M%

2.2 Preparation of Hydrochars

The hydrocharsization test was carried out in a small high temperature and pressure reactor chamber. The material of the reactor chamber was Hastelloy alloy, the maximum working temperature was 300°C, the pressure was 20 MPa, and the volume of the chamber was 150 mL. To avoid the influence of impurities in water on the hydrolysis of raw materials and ensure the accuracy of the experiment, the solution was selected as deionized water. Considering the working conditions of the experimental equipment and the pyrolysis temperature of cellulose [14], the hydrothermal reaction temperatures were selected as 150, 200 and 250°C. Raw is the Raw material control, the specific reaction conditions are shown in the table.

Table 2. Sample reaction conditions

Sample		hydrothermal temperature / °C	RH/% (mass)	OS/% (mass)
OS	OS-Raw	0	0	100
	OS-150	150	0	100
	OS-200	200	0	100
	OS-250	250	0	100
RH	RH-Raw	0	100	0
	RH-150	150	100	0
	RH-200	200	100	0
	RH-250	250	100	0
Mix	Mix-Raw	0	50	50
	Mix-150	150	50	50

Mix-200	200	50	50
Mix-250	250	50	50

The test process was as follows: 10g sample was placed in the reactor chamber, 100mL deionized water was added, mixed evenly, nitrogen was pumped into the reactor chamber (30mL/min) for 5 min after the cover was put on, the air in the reactor chamber was drained, and the reactor chamber was sealed. It was heated at a rate of 10°C/min and kept for a certain reaction time (2h) after reaching the reaction temperature. When the time is up, take out the reactor chamber, cool it to room temperature, use metal screen to separate solid and liquid, collect solid sample, put the solid sample in 105°C of constant-temperature drying oven for 24h, and seal it for later use.

2.3 Characterization and Methods

Proximate analysis according to GB/T 28731-2012 (China) standard determination of ash and volatile content of the sample, fixed carbon subtraction method was used to calculate.

The combustion and pyrolysis tests were carried out with the thermogravimetric analyzer of Mettler Toledo, and the crucible material was alumina. The protective gas was high purity nitrogen, and the gas flow rate was 50mL/min. The combustion atmosphere is synthetic air, and the pyrolysis atmosphere is high purity nitrogen, and the gas flow rate is 50mL/min. The initial temperature was room temperature, and the termination temperature was 900°C. The heating rate was set at 20°C/min.

The surface functional groups were used by the Nicolet 67 Fourier transform infrared spectrometer made by Thermo Nicolet Company (U.S.). The scanning interval was 750~4000cm⁻¹, and the diamond crystal tablet was used. The test method is Fourier transform Attenuated total reflection infrared spectroscopy (ATR-FTIR).

3 Results and Discussion

3.1 Proximate Analysis of Hydrochars

Table 3 shows the Proximate analysis of Hydrochars under different reaction conditions. It can be seen that the fixed carbon content of the three raw materials increased significantly after hydrocharsization treatment, but the hydrothermal temperature had different effects on them. When the hydrothermal temperature is 150°C, the fixed carbon content in oil shale increases from 5.29% to 14.02%, the hydrothermal temperature continues to increase, the fixed carbon content increases less than 2%, and ash content increases. This is due to the fact that oil shale contains a large number of light volatile content. When the hydrothermal temperature is low, organic matter is hydrolyzed [15] and small molecular compounds are generated. Subsequently, some small molecular compounds in the liquid phase undergo condensation reaction. At the same time, a small amount of ash dissolved in the liquid phase increases the fixed carbon content. When the hydrothermal temperature is less than 200°C, the contents of fixed carbon and volatile matter in rice husk hydrochars change little, because the physical structure of cellulose is destroyed and hydrolyzed, hydrolyzed products undergo a series of chemical reactions such as dehydration, isomerization, etc. And generate some intermediate products of hydroxymethylfurfural or furfural and its derivatives [16]. However, due to the low reaction intensity and small decomposition amount, the change of fixed carbon and volatiles in hydrochars is small. As the temperature increased to 250°C, the fixed carbon content decreased from 15.75% to 25.35%, and the volatile content decreased from 64.23% to 50.92%. The main reason are that at this hydrothermal temperature, a large amount of cellulose hydrolyzes and deoxidizes, and functional groups such as CH and OH are destroyed. At the same time, aromatic chemical reactions to hydrochars further condense and recombine to generate macromolecular compounds [16].

Table 3 Proximate analysis of hydrochars

Sample	Proximate analysis/wt. %		
	FC	VM	Ash
OS-Raw	5.29	15.67	79.04
OS-150	14.02	10.21	75.77
OS-200	14.58	9.69	77.73

OS-250	15.72	6.09	78.19
RH-Raw	12.78	70.11	17.11
RH-150	12.47	69.22	18.31
RH-200	15.75	64.23	20.02
RH-250	25.35	50.92	23.73
Mix-Raw	9.82	41.67	48.51
Mix-150	12.29	40.53	47.18
Mix-200	13.28	35.87	50.85
Mix-250	14.91	30.33	54.76
Mix-Raw(th)	9.07	42.86	48.07
Mix-150(th)	13.25	39.71	47.04
Mix-200(th)	15.19	35.94	48.87
Mix-250(th)	20.56	28.49	50.95

Note: th is the calculated value.

Compared with the theoretical calculation value of the mixture hydrochars, the experimental mixture hydrochars is less affected by the hydrothermal temperature. With the increase in hydrothermal temperature, the fixed carbon content increases, while the volatile content decreases, which is consistent with the change of the first two raw materials with hydrothermal temperature. The fixed carbon content is lower than the theoretical value, while the volatile content is higher. This may be due to the carbonate or alkaline earth metal oxides in oil shale that hinder the hydrolysis of cellulose in rice husk [17] and inhibit the deoxidation and decarboxylation reactions.

3.2 Chemical Structure Analysis of Hydrochars

In Figure 1(a, b and c), the wide peak of wave number 3620~3300 cm⁻¹ corresponds to the O-H bending vibration peak, the absorption peak of wave number 2900~2850 cm⁻¹ is the stretching vibration peak of C-H bond between aliphatic group, and the characteristic peak of benzene ring structure in the range of 1700~1370 cm⁻¹. 1030~1060 cm⁻¹ is the stretching vibration of C-OH bond in hydroxyl, ester and ether [18]. As can be seen from Figure 1(a), the infrared spectra of the hydrochars obtained are basically similar to the characteristic peaks of the main groups except for some wave peak intensity changes. After hydrocharsization treatment for 150 °C, the light volatiles hydrolyzed and produced a large number of esters and ether compounds. The characteristic peak vibration intensity of functional groups of hydrochars of oil shale was intense. However, as the hydrothermal temperature continues to rise, O-H, C-H and C-O bonds break during further pyrolysis of oil shale, and the vibration intensity of characteristic peaks of functional groups becomes smaller and smaller, which is close to that of raw materials. As shown in Figure 1(b), the variation on characteristic peak vibration intensity of functional groups of rice husk hydrochars is basically consistent with that of oil shale hydrochars, but the characteristic peak intensity of benzene ring structure basically does not change with the increase of hydrothermal temperature, indicating that the benzene ring structure of rice husk hydrochars is relatively stable. Figure 1(c) shows the FTIR diagram of the hydrochars mixture. When the hydrothermal temperature is 200 °C, the characteristic peaks of C-H and C-O functional groups of the hydrochars show strong vibration, which is due to the hydrolysis of hemicellulose and cellulose in rice husk to generate a large number of fatty family compounds. The vibration of characteristic peak decreases from the increase in hydrothermal temperature, indicating that the macromolecule compounds are hydrolyzed further.

3.3 Combustion Characteristics of Hydrochars

2.2.1 Analysis of Combustion TG and DTG Curves

The TG and DTG curves of the three raw materials and their hydrochars combustion process is shown in Figure 2, Figure 3 and Figure 4. Taking the theoretical TG and DTG curves of the co-hydrochars with a mixture of 150 °C as an example, the TG and DTG curves are calculated by Formula (1).

$$TG_{th-150} = 0.5TG_{OS-150} + 0.5TG_{RH-150} \quad (1)$$

Where, 0.5 is the mixing ratio of OS and RH, and TG_{OS-150} and TG_{RH-150} represent the weight loss of OS-150

and RH-150 respectively.

According to the DTG curve in Figure 2, there are three obvious weightlessness peaks of oil shale. The first peak ($<150^{\circ}\text{C}$) is the mass loss caused by water evaporation. The second peak ($250\sim650^{\circ}\text{C}$) is mainly caused by the release of gaseous products caused by the volatilized analysis or decomposition of organic compounds[19] and the combustion of partially fixed carbon. The third peak ($650\sim750^{\circ}\text{C}$) was caused by the slow combustion of residual fixed carbon and the pyrolysis reaction to other inorganic materials such as carbonate and alkaline earth minerals. After hydrothermal treatment, part of salt and alkaline earth minerals are dissolved in water, resulting in a decrease in ash contents in oil shale and a downward TG curve. With the increase in hydrothermal temperature, the volatile content of hydrochars decreased slightly, while the ash content increased, showing that the second and third peak values of DTG gradually decreased, but the hydrothermal temperature had little influence on the variation range of DTG curve of hydrochars of oil shale.

Figure 3 shows that the hydrochars combustion process of rice husk is also divided into three stages. The first stage ($<150^{\circ}\text{C}$) is caused by water loss. In the second stage ($250\sim400^{\circ}\text{C}$), DTG curve showed a large peak value, indicating that rice husk hydrothermal charcoal may contain more lighter volatile matter[20], and a large amount of hemicellulose and cellulose are precipitated in the form of gas phase. Therefore, rice husk combustion is mainly light volatile matter; The third stage ($400\sim600^{\circ}\text{C}$) is mainly characterized by slow lignin combustion, which is characterized by small peak value and wide range of DTG curve. With the increase of hydrothermal temperature, volatile content decreased and fixed carbon content increased, showing that the second peak value of DTG curve gradually decreased and the third peak value gradually increased. When the hydrothermal temperature is 150°C , the hydrolysis reaction to organic matter is dominant and a large number of intermediates are generated. Some intermediates generate stabler carbon-carbon double bonds between polymerization[21], so the weight loss rate increases compared with raw materials. When the hydrothermal temperature is 250°C , the excessive hydrothermal temperature leads to the hydrolysis of hemicellulose and a large amount of cellulose, which is decomposed into small molecule compounds dissolved in water, and some small molecule compounds are condensed to generate pseudolignin substances[22], which leads to a significant decrease in the combustion rate of volatiles in THE DTG curve. In addition, the backward ignition temperature indicates that hydrothermal treatment can shorten the combustion time of hydrochars.

Figure 4 plots TG and DTG curves of oil shale and rice husk hydrochars combustion process, including experimental curves and calculation curves. From the image, it can be intuitively found that the combustion curve is similar to that of rice husk, indicating that rice husk plays a dominant role in the combustion process of mixed hydrothermal charcoal. There are two main combustion peaks at the DTG curve, which may be because some salts or alkaline earth metals in oil shale promote the pyrolysis of part of lignin in rice husk[23], leading to the transfer of fixed carbon combustion to low temperature, thus making the combustion process of the mixture of hydrochars more stable. Compared with the calculated curve, it can also be found that the fixed carbon combustion section is close to the volatile combustion section. With the increase in hydrothermal temperature, the combustion peaks of volatile and fixed carbon of hydrochars are obviously higher than the calculated curve. These results indicate that the synergistic effect between oil shale and rice husk makes the combustion process of the mixture of hydrochars more fully concentrated.

3.3.2 Analysis of Combustion Characteristics

Ignition and burnout temperatures are determined by TG-DTG curve joint definition method[24,25]. Combustion characteristics of samples are expressed by comprehensive combustion characteristics index S_N [26], which can be expressed as:

$$S_N = \frac{(dw/dt)_{max}(dw/dt)_{mean}}{T_i^2 T_b} \quad (2)$$

Where, $(dw/dt)_{max}$ and $(dw/dt)_{mean}$ are the maximum combustion rate and average combustion rate

respectively, %/min; T_i is the ignition temperature, K; T_b is burnout temperature, K.

Table 4. Combustion characteristics of hydrochars

Sample	Characteristic temperatures/°C		t_b / min	$(dw/dt)_{max}/$ (%(mass) • min ⁻¹)	$(dw/dt)_{mean}/$ (%(mass) • min ⁻¹)	$S_N \times 10^7$
	T_i	T_b				
OS-Raw	338.15	741.29	19.03	1.58	0.95	0.18
OS-150	309.34	751.26	22.51	1.70	0.97	0.23
OS-200	308.59	741.97	22.21	1.71	0.92	0.22
OS-250	308.91	741.64	22.22	1.64	0.90	0.21
RH-Raw	254.38	556.80	16.31	13.39	5.14	19.10
RH-150	253.87	585.22	17.08	16.36	4.54	19.69
RH-200	285.44	575.92	15.51	14.54	4.69	14.53
RH-250	265.42	595.89	15.55	6.78	4.27	6.90
Mix-Raw	265.64	712.22	22.52	6.51	2.20	2.85
Mix-150	265.67	702.50	22.02	7.62	2.32	3.57
Mix-200	286.95	702.26	21.07	8.27	2.22	3.18
Mix-250	276.87	692.52	21.01	5.56	2.10	2.20
Mix-Raw(th)	265.53	741.29	22.32	6.38	1.37	1.67
Mix-150(th)	256.01	740.94	21.95	7.35	1.42	2.15
Mix-200(th)	296.01	732.06	21.05	7.71	1.65	1.98
Mix-250(th)	297.73	750.65	21.03	3.38	3.38	1.72

Note: t_b is the time from ignition to burnout.

The comprehensive combustion index (S_N) of hydrochars was calculated in Table 4 to further to evaluate the combustion performance of the fuel. For oil shale, with the increase of hydrothermal temperature, the comprehensive combustion index S_N firstly increased and then decreased, from 1.8×10^{-8} when raw material to 2.3×10^{-8} (OS-150) and then decreased to 2.1×10^{-8} (OS-250). This may be due to the increase in ash content after hydrothermal treatment, which leads to some difficult-to-burn minerals blocking part of the pores [27], reducing its contact area with air, and thus limiting the combustion behavior of hydrothermal charcoal. After hydrothermal treatment, the comprehensive combustion index of rice husk has the same trend as that of oil shale, and reaches the maximum value (1.97×10^{-8}) at the hydrothermal temperature of 150 °C. However, with the increase of hydrothermal temperature, S_N decreases greatly. As expected, the composite combustion index of the mixture was higher than the calculated value, and also reached the maximum value at 150 °C (Calculated value: 2.15×10^{-8} ; Experimental value: 3.57×10^{-8}).

3.3.3 Analysis of Combustion Dynamics Parameters

The combustion reaction to oil shale and rice husk hydrochars is a typical gas-solid reaction, and the relationship between combustion rate and temperature conforms to Arrhenius law for such a reaction process with slow heating up [28]. Therefore, equations (3) and (4) can be used to describe the combustion process of hydrochars:

$$f(\alpha) = (1 - \alpha)^n \quad (3)$$

$$\alpha = \frac{m_0 - m_T}{m_0 - m_\infty} \quad (4)$$

Where, α is the conversion rate, which can be obtained from the thermogravimetric curve according to Equation (4). M_0 , M_T and M_∞ are the sample mass before the experiment, at the time of experiment T and at the end of experiment respectively, kg; n is the reaction order.

The combustion rate equation can be expressed by Equation (5):

$$\frac{d\alpha}{dT} = \frac{A}{\beta} \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (5)$$

Where, A is the pre-exponential factor, min^{-1} ; β is heating rate, K/min ; E is the activation energy, kJ/mol ; R is the gas constant, $\text{J/(mol}\cdot\text{K)}$; T is the absolute temperature, K .

The coats-Redfern equation[29] was used to analyze the dynamics, and $n=1$ was used to calculate. Equations (3) and (5) were integrated simultaneously to obtain:

$$\ln\left[-\frac{\ln(1-\alpha)}{T^2}\right] = \ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] - \frac{E}{RT} \quad (6)$$

Where, $1 - \frac{2RT}{E} \approx 1$, $\ln\left[\frac{AR}{\beta E}\left(1 - \frac{2RT}{E}\right)\right] \approx \ln\frac{AR}{\beta E}$, as a constant, define $y = \ln\left[-\frac{\ln(1-\alpha)}{T^2}\right]$, $b = \ln\frac{AR}{\beta E}$, $k = -\frac{E}{R}$, $x = -\frac{1}{T}$, Where k and b are constants, substituted into Equation (6), equation (7) is obtained:

$$y = kx + b \quad (7)$$

The slope and intercept of the line can be obtained by eq.(7) to calculate E and A . As can be seen from Figure 2, 3 and 4, oil shale hydrothermal charcoal contains combustion peak and inorganic pyrolysis peak, and only combustion peak is calculated here, while rice husk and hybrid hydrothermal charcoal have two obvious combustion peaks, so the combustion kinetics parameters of the two peaks are analyzed respectively. The results are shown in Table 5.

Table 5. kinetic parameters of hydrochars combustion

Sample	Temperature $T/^{\circ}\text{C}$	Fitted equation	Activation energy $E/(\text{kJ}\cdot\text{mol}^{-1})$	Frequency factor A/min^{-1}	Correlation coefficient R^2
OS-Raw	338.15~643.21	$y = -4292.42x - 8.222$	35.69	2.31×10	0.99
	662.73~741.29	$y = -6354.72x - 6.379$	52.83	2.16×10^2	0.93
OS-150	309.34~643.28	$y = -3406.96x - 9.174$	28.33	7.06	0.99
	672.59~751.26	$y = -5785.83x - 6.957$	48.10	1.1×10^2	0.93
OS-200	308.59~643.73	$y = -3352.86x - 9.196$	27.88	6.78	0.99
	653.51~741.97	$y = -5293.14x - 7.402$	44.01	6.45×10	0.92
OS-250	308.91~643.56	$y = -3623.28x - 8.866$	30.12	1.02×10	0.99
	653.56~741.64	$y = -4296.11x - 8.382$	35.72	1.97×10	0.93
RH-Raw	264.8~381.86	$y = -6703.57x - 2.419$	55.73	1.19×10^4	0.94
	391.87~584.48	$y = -3488.22x - 7.881$	29.01	2.64×10	0.92
RH-150	264.24~391.25	$y = -6237.83x - 3.433$	51.86	4.03×10^3	0.94
	420.67~603.64	$y = -4291.89x - 7.007$	35.68	7.77×10	0.95
RH-200	285.44~380.85	$y = -6802.38x - 2.638$	56.56	9.73×10^3	0.96
	390.74~594.13	$y = -3047.32x - 8.772$	25.34	9.44	0.93
RH-250	286.85~361.29	$y = -5299.37x - 5.458$	44.06	4.51×10^2	0.98
	371.34~613.71	$y = -4291.12x - 7.397$	35.68	5.26×10	0.93
Mix-Raw	265.64~380.74	$y = -7026.22x - 2.221$	58.42	1.52×10^4	0.93
	390.73~712.22	$y = -2263.48x - 9.945$	18.82	2.17	0.97
Mix-150	265.67~381.60	$y = -7813.59x - 0.970$	64.96	5.92×10^4	0.97
	391.52~702.50	$y = -1834.27x - 10.35$	15.25	1.17	0.92
Mix-200	286.95~383.21	$y = -8526.12x - 0.086$	70.89	1.56×10^5	0.96

	393.20~662.90	$y=-2236.34x-9.821$	18.59	2.43	0.93
Mix-250	276.87~362.46	$y=-9807.56x+1.916$	81.54	1.33×10^6	0.98
	372.49~692.52	$y=-2380.95x-9.756$	19.79	2.76	0.91
Mix-Raw(th)	265.53~381.86	$y=-5671.62x-4.456$	47.15	1.32×10^3	0.93
	381.86~741.29	$y=-1944.94x-10.41$	16.17	1.17	0.95
Mix-150(th)	256.01~400.98	$y=-5045.39x-5.714$	41.95	3.32×10^2	0.98
	400.98~740.94	$y=-2106.81x-10.33$	17.52	1.37	0.94
Mix-200(th)	296.01~390.82	$y=-5412.64x-5.223$	45.00	5.83×10^2	0.95
	390.82~732.06	$y=-2095.66x-10.35$	17.42	1.34	0.92
Mix-250(th)	297.73~361.29	$y=-4236.97x-7.462$	35.23	4.87×10	0.99
	361.29~750.65	$y=-3141.24x-9.231$	26.12	6.15	0.97

From table 5 shows, in addition to the oil shale, in a fixed carbon combustion activation energy of other samples are lower than in volatile combustion activation energy, this is mainly because of volatile combustion period, low temperature, low molecular energy, need high heat to promote molecular thermal motion, which leads to a high activation energy, and volatile part and fixed carbon combustion, also absorb more heat. In coke combustion section, lignin decomposition is slow, and coke with porous structure generated by pyrolysis of volatile combustion section [30] is conducive to the contact between oxygen molecules and carbon. Meanwhile, the combustion of volatile combustion section has fully preheated the sample, resulting in low activation energy in fixed carbon combustion section. The activation energy of the combustion section of the volatiles in the actual mixture of hydrochars is higher than the theoretical value, which is because the synergistic effect on the two generates more volatiles and requires more heat of absorption. The combustion segments of fixed carbon are all lower than the theoretical values, which may be due to the existence of a small amount of salt or alkaline earth minerals in hydrochars which promotes the combustion behavior and reduces the activation energy.

3.3.4 Analysis of Synergistic Effect in Combustion Process

In order to further clarify the synergistic effect of hydrochars mixture in the combustion process, taking the co-hydrocharsization of the mixture at 150°C as an example, the theoretical calculation of hydrochars loss ($TG_{MIX-150}$) and deviation ($Deviation_{150}$) [31] are shown in Formula (1) and (8) respectively.

$$Deviation_{150} = \frac{(TG_{exp-150} - TG_{th-150})}{TG_{th-150}} \times 100\% \quad (8)$$

Where, $TG_{EXP-150}$ is the experimental weight loss of Mix150. The theoretical calculated values and deviations of other parameters can be obtained by "weight loss ($TG_{\times \times}$)" in substitution Equation (8), and the results are shown in the figure 5.

In general, when the deviation is greater than 2% (98% confidence), it indicates low weight loss rate and high heat loss. When the deviation value is less than -2%, it indicates a strong synergistic effect, which is beneficial to the combustion process of the mixture [32]. According to the above rules, it can be observed that the mixture pretreated by hydrocharsization has a low ignition point T_i ($<290^\circ\text{C}$), and no synergistic effect occurs to the initial combustion stage ($<300^\circ\text{C}$). When the combustion temperature is higher than 350°C , the synergistic effect is obvious. This is due to the interaction between raw materials: (1) oil shale catalyzes more decarboxylation reaction, improves the degree of coalification of the mixture, thus accelerating the actual combustion of the mixture; (2) The first release and combustion of light volatile compounds from rice husk can effectively improve the reactivity of oil shale and promote the combustion process of the mixture. With the increase in hydrothermal temperature, the synergistic effect is enhanced, and the maximum negative deviation is 10.12% at 250°C , indicating that oil shale and rice husk achieve the maximum synergistic effect at this temperature. With the increase in hydrothermal temperature, there is a large positive deviation from volatile combustion stage ($250\sim350^\circ\text{C}$) and salt or alkaline earth metal decomposition stage ($600\sim900^\circ\text{C}$) [33], and the overall synergic effect of Mix-250 is smaller than that of Mix-200. Therefore, considering

the combustion behavior, comprehensive combustion index and synergistic effects of hydrochars, Mix-200 is more suitable as a solid fuel.

3.4 Pyrolysis characteristics of hydrochars

3.4.1 TG and DTG Curve Analysis of Hydrochars Pyrolysis

When the carrier gas is pure N_2 , except for a simple thermal decomposition process similar to combustion, the pyrolysis process does not include the oxidation of the sample, but includes a thermochemical process combining heat and oxygen effects. Figure 6, Figure 7 and Figure 8 show the TG and DTG curves of raw material and hydrochars pyrolysis process.

Figure 6 shows that oil shale pyrolysis can be divided into three parts: The first part ($<150^\circ C$) is the mass loss caused by water evaporation, and the weight loss is less than 3%. The second part ($200\sim 600^\circ C$) is the stage of volatilization and partial fixed carbon pyrolysis. The maximum weight loss rate is around $450^\circ C$, and a small weight loss peak to occur to $550^\circ C$ for some samples. This is mainly due to the chemical bond fracture of organic compounds in oil shale and the transformation and degeneration of some functional groups to generate combustible gas and certain condensable volatiles[34]. The weight loss rate of the whole part 2 is about 10%, which is the main stage of oil shale pyrolysis process. The third part ($600\sim 750^\circ C$) is mainly caused by the secondary cracking of the pyrolysis products (mainly tar and coke) in the second stage. At this stage, the tar and coke molecules are cracked and cracked into non-condensed gas phase products, and the weight loss in this stage is about 7%. However, the oil shale contains a large amount of ash, including salts and alkaline earth metal oxides, and the mass is still decreasing after $750^\circ C$. After hydrocharsization treatment, the weight loss curve of oil shale changes obviously, TG curve shows an overall upward shift, and with the increase of hydrothermal temperature, ash content increases, TG curve continues to move up. The DTG curve also changed significantly, and the maximum weight loss rate increased from 1.18 to 1.46. With the increase in hydrothermal temperature, the peak value of $720^\circ C$ gradually decreased. The results showed that the hydrothermal process resulted in the decrease of light volatile and the increase of heavy volatile and fixed carbon in oil shale, which was similar to that of Kambo H.S. The research conclusions[35] is relatively consistent. At the same time, the pyrolysis interval moves backward with the increase in hydrothermal temperature.

Figure 7 shows the weight loss curve (TG) and weight loss rate curve (DTG) of rice husk pyrolysis. The pyrolysis of rice husk is different from its combustion process, which is divided into two stages: 1) Water evaporation is consistent with the combustion process of $150^\circ C$. 2) $250\sim 450^\circ C$ is the main range of rice husk pyrolysis, the weight loss process is the most intense, mainly the decomposition reaction of cellulose and lignin in rice husk. After hydrocharsization treatment, TG curve moved upward and ash content increased. With the increase in hydrothermal temperature, the pyrolysis peak of hydrochars shifts slightly to a higher temperature than that of raw material. The maximum fuel rate is reached at the RH-200. Minimum in RH-250. This is because when the hydrothermal temperature is low, hemicellulose and a small amount of cellulose hydrolyze and accelerate the pyrolysis reaction, while when the hydrothermal temperature is high ($250^\circ C$), the main components of hydrochars are lignin and macromolecular compounds, so the pyrolysis reaction is slow.

Figure 8 shows the theoretical and experimental TG-DTG comparison curve of the pyrolysis process of the hydrochars mixture. According to the TG curve, the weight loss rate is high in the range of $250\sim 350^\circ C$, and the experimental weight loss rate is higher than the theoretical calculation value. This is because the oil shale mainly occurs in the process of pyrolysis two competing reaction, condensation and cracking of rice husk pyrolysis temperature is lower than that of the oil shale, needed to generate the H_2 produced its first H_2 inhibit shale condensation reaction, so as to promote the mixture to a certain extent of cracking reaction[36], finally accelerate the weight loss rate of the pyrolysis process. In addition, the alkali metal elements in rice husk can catalyze the pyrolysis process, which can promote the mixture pyrolysis and release gas products. DTG curve also shows that there is a certain synergistic effect of the pyrolysis process. With the increase in hydrothermal temperature, the

maximum weight loss rate of pyrolysis increases first and then decreases, reaching the maximum at Mix-200, which is consistent with the pyrolysis change of rice husk hydrothermal charcoal.

3.4.2 Analysis of Pyrolysis Characteristics

In order to quantitatively evaluate the pyrolysis characteristics of samples, a comprehensive pyrolysis index (D)[37] was defined to compare the release characteristics of each sample during pyrolysis. The calculation formula is (10), and the calculation results are shown in Table 6.

$$M_1 = 1 - M_r / 100 \quad (9)$$

$$D = \frac{(dw/dt)_{\max} (dw/dt)_{\text{mean}} M_1}{T_i T_m \Delta T_{1/2}} \quad (10)$$

Where, $(dw/dt)_{\max}$ and $(dw/dt)_{\text{mean}}$ are the maximum and average weight loss rates of the pyrolysis process, % (mass) · min⁻¹; M_1 is the amount of pyrolysis mass loss, % (mass), M_r is the amount of residue after pyrolysis, % (mass); T_i represents the initial pyrolysis temperature, °C; T_m represents the temperature point corresponding to the maximum weight loss rate, °C; $\Delta T_{1/2}$ is Temperature interval of $(dw/dt)_{\max}/(dw/dt)_{\text{mean}}=0.5$, °C.

Table 6. Pyrolysis characteristics of hydrochars

Sample	Residue/ %(mass)	Characteristic temperatures/°C		$(dw/dt)_{\max}/$ (%(mass) · min ⁻¹)	$(dw/dt)_{\text{mean}}/$ (%(mass) · min ⁻¹)	$\Delta T_{1/2}/$ °C	$D \times 10^7$
		T_i	T_m				
OS-Raw	80.66	386.10	711.56	1.18	0.58	301.12	6.67
OS-150	81.04	405.45	455.18	1.46	0.62	192.21	20.68
OS-200	82.18	405.48	455.14	1.48	0.58	207.25	18.44
OS-250	82.93	396.05	455.77	1.48	0.56	200.31	19.01
RH-Raw	33.15	253.66	345.08	12.26	4.61	100.42	2131.49
RH-150	32.85	254.32	355.62	15.38	5.51	101.54	3031.37
RH-200	39.02	202.79	354.82	16.28	3.60	100.7	3176.04
RH-250	53.43	204.13	366.22	6.48	2.07	140.55	682.10
Mix-Raw	57.05	264.55	345.61	6.38	1.17	211.11	220.63
Mix-150	56.66	264.65	365.71	7.74	1.21	201.53	272.05
Mix-200	57.55	295.26	365.78	11.26	1.20	160.92	447.44
Mix-250	66.35	305.53	366.04	5.98	0.98	207.59	167.49
Mix-Raw(th)	56.91	263.83	345.08	6.24	2.23	261.42	332.73
Mix-150(th)	56.95	243.99	355.38	7.74	1.13	221.09	259.82
Mix-200(th)	60.60	213.53	355.35	8.20	0.99	200.14	323.95
Mix-250(th)	68.18	214.30	366.22	3.32	0.82	250.37	94.46

The comprehensive pyrolysis index (D) can be used to describe the pyrolysis release characteristics of samples. Maximum weight loss Rate of oil shale and Rice Husk Raw materials (OS:1.18% · min⁻¹; 12.26% · min⁻¹), With the increase of hydrothermal temperature, the D index of hydrochars increases first and then decreases. When the hydrothermal temperature was 200 °C, the maximum weight loss rate (11.26% · min⁻¹) appeared, and the comprehensive pyrolysis index reached the maximum value of 447.44 × 10⁷. Except for Mix-Raw, the comprehensive pyrolysis indices of the hydrocharsaceous mixtures are all higher than their theoretical values. This indicates that the co-hydrocharsization of oil shale and rice husk has a synergistic effect, which effectively improves the overall pyrolysis releases characteristics of the mixture. The optimal hydrothermal temperature is around 200 °C.

3.4.3 Pyrolysis Kinetics Analysis

Hydrochars pyrolysis is a chemical reaction to a relatively slow reaction rate, and a large number of references[38] shows that the Coats-Redfern equation is also suitable for calculating pyrolysis kinetic parameters. Therefore, formulations(3) and (4) in section 2.2.3 are used to describe the pyrolysis process of hydrochars, and

Formulations(6) are used to calculate the pyrolysis kinetic parameters of hydrochars. As shown in Figure 5, the DTG curve of hydrochars of oil shale is the pyrolysis of salts and alkaline earth metal oxides at 600-750°C, so it is not analyzed here. The calculation results are shown in Table 7.

As shown in Table 7, the activation energy of hydrochars of oil shale reaches the maximum at 150°C, and the variation range of activation energy is small as the temperature continues to rise, which again indicates that hydrothermal temperature has little influence on hydrochars of oil shale. The activation energy of rice husk hydrochars decreases first and then increases from the increase in hydrothermal temperature, because cellulose hydrothermal reduces volatile content. However, when the temperature reaches 250°C, a large number of small molecules react to form lignin-like substances, which increases the activation energy required for pyrolysis. Comparing the experimental activation energies with the theoretical values, except Mix-200, the hydrothermal activation energies of the other mixtures were all higher than the theoretical values, mainly due to the synergistic effect of oil shale and rice husk when they were co-hydrothermal, and more macromolecular compounds were generated.

Table 7. Kinetic parameters of hydrochars pyrolysis

Sample	Temperature $T/^\circ\text{C}$	Fitted equation	Activation energy $E/(\text{kJ} \cdot \text{mol}^{-1})$	Frequency factor A/min^{-1}	Correlation coefficient R^2
OS-Raw	386.10~564.36	$y=-3237.41x-9.945$	26.92	3.08	0.99
OS-150	405.45~554.19	$y=-4581.35x-8.1347$	38.09	2.69×10	0.96
OS-200	405.48~554.06	$y=-4499.48x-8.2052$	37.41	2.46×10	0.94
OS-250	396.05~564.56	$y=-4506.9x-8.28196$	37.47	2.28×10	0.92
RH-Raw	253.66~395.49	$y=-7322.44x-1.3307$	60.88	3.87×10^4	0.99
RH-150	254.32~395.46	$y=-6847.06x-2.1923$	56.93	1.53×10^4	0.99
RH-200	202.79~354.49	$y=-2026.62x-10.706$	16.85	0.91	0.91
RH-250	204.13~396.34	$y=-3358.74x-8.2611$	27.92	1.74×10	0.96
Mix-Raw	264.55~405.86	$y=-6514.34x-3.0319$	54.16	6.28×10^3	0.96
Mix-150	264.65~405.88	$y=-7622.54x-1.4648$	63.37	3.52×10^4	0.98
Mix-200	295.26~406.01	$y=-9251.59x+0.800$	76.92	4.12×10^5	0.97
Mix-250	305.53~406.13	$y=-8040.07x-1.4053$	66.85	3.94×10^4	0.98
Mix-Raw(th)	263.83~395.49	$y=-5449.09x-4.8153$	45.30	8.83×10^2	0.98
Mix-150(th)	243.99~396.34	$y=-4788.87x-6.0853$	39.81	2.18×10^2	0.99
Mix-200(th)	213.53~315.46	$y=-1007.35x-12.939$	83.75	1.05	0.91
Mix-250(th)	214.30~405.48	$y=-2226.77x-10.626$	18.51	1.08	0.93

The correlation coefficients R^2 of kinetic parameters are all above 0.91, indicating that the pyrolysis kinetics results of hydrochars studied by the above kinetic equation are reliable.

3.4.4 Analysis of Synergistic Effect of Pyrolysis Process

Many scholars have conducted a lot of research on the synergistic mechanism of biomass and other fuels in the process of co-pyrolysis, but due to the large differences in the composition of different types of biomass and other fuels, the current conclusions are not clear[39-41]. In this study, it was found that the oil shale and rice husk mixed hydrothermal char exhibited a slight synergistic effect in the pyrolysis process when the hydrothermal temperature was lower than 150°C. When the hydrothermal temperature is higher than 200°C, the synergistic effect is strong, although the synergistic effect is obviously lower than the combustion process. In the pyrolysis process of the mixture, the devolatilization of rice husk occurred earlier than that of oil shale in stages. Compared with rice husk, shale is a poor hydrogen material, released by rice husk pyrolysis of O-H groups (mainly from dehydroxylation reaction) and H as a hydrogen donor transferred to the structure of oil shale, suppress the secondary reaction, condensation and crosslinking reaction, etc.) [42] reduce secondary coke and tar in the shale formation. These obvious synergy may promote the pyrolysis behavior of the mixture. At the same time, the raw materials of rice

husk and oil shale contain certain alkali metals and minerals, and these inorganic substances also have a certain catalytic effect on the thermal transformation of the mixture. Therefore, the synergistic effect of the pyrolysis process can be attributed to the hydrogen supply and the potential catalytic effect of alkali metals in rice husk on the pyrolysis of oil shale. It can be observed from Figure 9 that the synergistic effect at 250°C is not significantly better than that at 200°C, because at a higher hydrothermal temperature, the total volatile content of hydrochars decreases and the polymerization of hydrolyzed intermediates is enhanced, thus weakening the hydrogen supply effect in the pyrolysis process. Therefore, from the perspective of pyrolysis efficiency and economy, the hydrothermal temperature of 200°C is considered more appropriate.

4 Conclusion

In this paper, the effects of hydrothermal temperature on combustion and pyrolysis characteristics of cohydrocharsation products of oil shale and rice husk were studied, and significant synergistic effects were found during these heat utilization processes. The following conclusions were drawn according to the research content:

1) Different hydrothermal temperatures have little influence on the contents of fixed carbon and volatile matter in oil shale, and the characteristic vibration peaks of O-H, C-O and C-H groups have little change, but they have great influence on the contents of rice husk hydrochars, especially when the hydrothermal temperature is 250°C. The volatile content of the mixture hydrochars is higher than its theoretical value. With the increase in hydrothermal temperature, the volatile content increases and the vibration of functional group characteristic peaks to weaken.

2) The combustion reaction parameters of the mixture are all higher than the corresponding theoretical values, indicating that there is an obvious synergistic effect of oil shale and rice husk during the cohydrocharsization process, which promotes the mixture to burn more thoroughly and release more heat. About 200 °C is the optimal hydrothermal temperature for the carbonization pretreatment of cohydrothermal to produce solid fuel to combustion.

3) Due to the hydrogen supply of oil shale and rice husk and the catalysis of minerals and alkali metals, a certain synergistic effect also occurs to the pyrolysis process to promote the pyrolysis reaction. Similarly, these interactions are the most obvious when the hydrothermal temperature is around 240°C.

Since the synergistic effect of pyrolysis process is lower than that of combustion process, cohydrocharsation products are considered to be more suitable for combustion. The co-hydrocharsization pretreatment effectively improved the fuel characteristics of the mixed feedstock and proved to have the potential to provide more suitable fuel to further heat utilization. These findings have important guiding significance of the efficient utilization of organic waste with low fuel quality and the reduction of energy consumption of thermochemical utilization.

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Figures

Figure 1

FTIR spectrum of hydrochars

Figure 2

TG and DTG curves of hydrochars combustion in oil shale

Figure 3

TG and DTG curves of rice husk hydrothermal char combustion

Figure 4

TG and DTG curves of actual and theoretical combustion of mixed hydrochars

Figure 5

Deviation analysis of experimental and theoretical TG curves during hydrochars combustion process

Figure 6

TG and DTG curves of hydrochars pyrolysis of oil shale

Figure 7

TG and DTG curves of rice husk hydrothermal char pyrolysis

Figure 8

TG and DTG curves of oil shale and rice husk hydrothermal char pyrolysis

Figure 9