

Article

Effects of O₂ Concentration on Oxy-Fuel Combustion Characteristics and Kinetics of Changji and Fushun Oil Shales

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Abstract

This study investigates how O₂ concentration affects the combustion performance and kinetic response of Changji and Fushun oil shales under CO₂-based oxy-fuel atmospheres. Coupled TGA–DSC–MS analysis was performed to characterize thermal decomposition, heat release and absorption, gaseous product evolution, and apparent kinetic parameters. The results show that raising the O₂ concentration facilitates oil shale combustion. The TG–DTG and heat flow profiles move to lower-temperature regions as O₂ concentration increases. At 20 °C·min^{−1}, increasing the O₂ concentration from 35% to 100% reduced T_{p1} and T_{p2} from 357.3 and 519.7 °C to 331.2 and 491.5 °C for CJ oil shale, and from 352.3 and 484.0 °C to 326.6 and 429.7 °C for FS oil shale, respectively. These shifts were accompanied by decreases in ignition and burnout temperatures and an increase in the comprehensive combustion index. Fushun oil shale shows a more concentrated main mass-loss and heat-release region than Changji oil shale. It also exhibits lower ignition and burnout temperatures, indicating stronger overall combustion reactivity. By contrast, Changji oil shale displays more evident mass loss and thermal responses at high temperatures, suggesting a greater contribution from carbonate mineral decomposition in the later reaction stage. MS results further show that CO₂, H₂O, SO₂, and NO₂ release mainly occurs within 300–600 °C. Their release peaks shift toward lower temperatures as the O₂ concentration increases, indicating that oxygen-enriched atmospheres promote the oxidative conversion of organic carbon, hydrogen-containing structures, and S- and N-containing functional groups. The Vyazovkin nonlinear iso-conversional analysis provides conversion-dependent apparent activation energies rather than a single global kinetic parameter. The substantial variation in E_{α} with conversion highlights the overlapping and multi-stage nature of oil shale combustion. When the O₂ concentration is raised from 21% to 75%, E_{α} generally follows an upward trend; under pure O₂, however, it drops sharply. This non-monotonic variation suggests that O₂ concentration changes not only the combustion rate but also the dominant reaction routes at different conversion stages. These findings provide experimental support for selecting suitable oxy-fuel combustion conditions and improving the clean and efficient utilization of oil shale.



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Keywords: oil shale; oxy-fuel combustion; TGA–DSC–MS; O₂ concentration; combustion characteristics; gaseous products; kinetics; Vyazovkin method

1. Introduction

Driven by rising energy demand and the transition toward green, low-carbon development, the clean and efficient utilization of unconventional energy resources has become increasingly important. Oil shale, with substantial reserves and broad distribution in China, represents an important unconventional fossil resource. Fushun and Changji oil shales are representative examples. Owing to its potential for power generation, shale oil production, and comprehensive utilization, oil shale is of great significance for ensuring energy security and expanding alternative energy sources [1–3]. However, oil shale has a complex organic structure and a high mineral content. Its thermal conversion usually involves volatile release, semi-char combustion, mineral decomposition, and other multiphase coupled reactions. These features pose considerable challenges to its clean and efficient utilization. Compared with conventional air combustion, O_2/CO_2 oxy-fuel combustion increases the O_2 concentration in the combustion atmosphere and uses CO_2 instead of N_2 as the main diluent. This can improve fuel ignition, burnout, and heat release behavior. Oxy-fuel combustion also enriches CO_2 in the flue gas, thereby facilitating downstream CO_2 separation and offering a feasible pathway for low-carbon solid-fuel combustion and CO_2 capture [4–8]. For oil shale, oxy-fuel conditions can affect not only the oxidation of organic matter but also volatile release, semi-char combustion, and carbonate mineral decomposition. Therefore, oil shale combustion generally exhibits a multistage, heterogeneous, and strongly coupled thermochemical conversion process [1,3,9,10]. Its characteristic temperatures, mass-loss rate, gaseous product distribution, and apparent kinetic parameters may change markedly with O_2 concentration. Clarifying how oil shale burns and responds kinetically in O_2/CO_2 atmospheres is therefore essential for interpreting its reaction pathways and refining oxy-fuel combustion parameters.

Previous studies have shown that oxy-fuel atmospheres can reshape oil shale combustion by affecting ignition–burnout behavior, mineral evolution, and reaction kinetics. Loo et al. [11] reported that, for Estonian oil shale, higher O_2 concentrations lowered the ignition and burnout temperatures, shortened the overall combustion process, and changed the decomposition behavior of carbonate minerals. Baqain et al. [12,13] further reported that oxy-fuel combustion changed volatile release, gaseous emissions, and ash evolution during oil shale combustion and its co-combustion with biomass. Their work also indicated enhanced formation of mineral phases such as silicates and anhydrite. Bai et al. [14,15] examined Huadian oil shale combustion under O_2/CO_2 and O_2/N_2 atmospheres. Their results indicated that increasing the O_2 level enhanced combustion reactivity, and they identified 30% O_2 /70% CO_2 as an appropriate atmosphere for Huadian oil shale combustion. Liu et al. [16] investigated the combustion behavior and kinetic response of Fushun and Changji oil shales in air and 21% O_2 /79% CO_2 atmospheres by coupling thermogravimetry–mass spectrometry with a nonlinear iso-conversional method. Their results indicated that CO_2 substitution for N_2 weakened heat transfer, mass transfer, and O_2 diffusion, while increasing the overall activation energy. Iso-conversional methods estimate the apparent activation energy at selected conversion degrees without requiring a predefined reaction model. This advantage makes them well suited to analyzing the staged thermal conversion of solid fuels such as oil shale. Detailed kinetic studies under air and inert atmospheres have also shown that oil shale thermal conversion cannot be represented by a single reaction step. Ifticene et al. [9] investigated the conversion/combustion behavior of oil shale and its components under an air atmosphere and reported that the reaction behavior was strongly dependent on the organic and mineral fractions of oil shale. Bai et al. [10] studied the pyrolysis and combustion kinetics of Huadian, Fushun, and Nongan oil shales by non-isothermal thermogravimetric analysis and found that the thermal decomposition of oil shale involved multiple reaction processes, especially during combustion.

For inert-atmosphere pyrolysis, Wang et al. [17] and Jaber and Probert [18] also reported staged decomposition behavior and conversion-dependent kinetic responses. These studies indicate that the apparent kinetic parameters of oil shale are strongly affected by kerogen structure, mineral composition, heating history, and reaction atmosphere. Therefore, comparison with these studies provides an important basis for interpreting the apparent activation energies obtained under O₂/CO₂ atmospheres in the present work.

Iso-conversional approaches are commonly grouped into differential and integral methods, including the Friedman differential method [19] and integral methods such as FWO [20,21], KAS [22,23], and Starink [24]. The Friedman method does not rely on temperature integral approximation. In contrast, linear integral methods require approximate treatment of the temperature integral during calculation, which may introduce errors into the estimated activation energy [25]. To address this issue, Vyazovkin [26–28] proposed a nonlinear integral iso-conversional method. Its main advantage lies in replacing the temperature integral approximation with time integration, thereby improving calculation accuracy. Owing to this advantage, this nonlinear integral method has gained broad acceptance and has been applied to kinetic studies of solid fuel thermal conversion [16,29–31]. However, existing studies have mainly focused on comparisons of combustion behavior under a limited number of typical atmospheres. A systematic understanding is still lacking regarding the staged combustion responses induced by continuous changes in O₂ concentration under O₂/CO₂ conditions. In particular, how O₂ concentration acts across different combustion stages remains insufficiently understood. This knowledge gap restricts mechanistic interpretation of oil shale oxy-fuel combustion and limits the rational optimization of operating conditions.

Based on the above analysis, Changji and Fushun oil shales were selected as the research objects in this study. Four O₂/CO₂ oxy-fuel atmospheres with varied O₂ concentrations were established. Coupled TGA–DSC–MS analysis was used to track mass variation, heat release, and gaseous product evolution in parallel. Characteristic parameters, including ignition temperature, peak temperature, burnout temperature, maximum mass-loss rate, and the comprehensive combustion characteristic index, were extracted to compare how O₂ concentration affects the staged combustion behavior and heat-release intensity of oil shale. MS signals were further analyzed to clarify the release patterns of major gaseous products and to identify the responses of organic matter oxidation and mineral decomposition under oxygen-enriched atmospheres. For kinetic analysis, the Vyazovkin nonlinear integral iso-conversional method was applied to estimate the apparent activation energy at selected conversion degrees. The obtained conversion-dependent apparent activation energies were then interpreted together with TG–DTG, DSC, and MS results to identify the dominant reaction stages and to assess how O₂ concentration changes the apparent kinetic response of oil shale combustion. These results can guide the selection of appropriate oxy-fuel combustion parameters and contribute to the cleaner and more efficient utilization of oil shale.

2. Materials and Methods

2.1. Materials

In this study, Changji oil shale from Xinjiang (CJ) and Fushun oil shale from Liaoning (FS) were selected as representative oil shale samples from China. Changji oil shale has proven reserves of 4.6×10^8 t [32] and contains type II kerogen [33], whereas Fushun oil shale has recoverable reserves of approximately 11×10^8 t [3] and is characterized by type I–II kerogen [2]. Both oil shales are characterized by abundant reserves, coexistence with coal seams, and the potential for low-cost extraction during open-pit coal mining. They

also have an established basis for large-scale development and utilization. Therefore, these two samples have good regional representativeness and research value.

Before the experiments, the raw samples were crushed and ground to pass through a 100-mesh sieve. The resulting powders were then dried in a constant-temperature oven at 40 °C to constant weight to remove surface moisture and externally adsorbed water. The dried samples were sealed and stored in a desiccator at room temperature for subsequent testing and analysis.

The elemental composition, proximate characteristics, and ash composition of Changji and Fushun oil shales were reported in our previous study, with the detailed data listed in Tables 1 and 2 [16]. The proximate analysis shows that both samples contain more than 77% ash, approximately 17% volatile matter, and nearly 2% fixed carbon. These results are consistent with the typical characteristics of oil shale, namely high ash content and low fixed carbon content. Owing to the high ash content and limited combustible components, both samples exhibit relatively low higher heating values. The higher heating value of CJ oil shale is 5223 kJ/kg, exceeding that of FS oil shale at 4661 kJ/kg. Elemental analysis further shows that the sulfur contents of both oil shales are below 1%, indicating relatively low sulfur abundance.

Table 1. Proximate analysis and ultimate analysis of CJ oil shale and FS oil shale ($w_{ad}\%$) [16].

Oil Shale	Proximate Analysis				Ultimate Analysis					HHV ^c
	M	A	V	FC	C	H	N	O ^a	S ^b	
CJ	1.42	79.15	17.61	1.82	14.41	1.98	0.96	1.43	0.66	5223
FS	2.15	77.26	17.93	2.66	12.35	2.37	0.82	4.52	0.53	4661

_{ad}: air-dried basis; ^a: by difference; ^b: total sulfur; ^c: higher heating value, kJ/kg. M: Moisture; A: Ash; V: Volatiles; FC: Fixed Carbon.

Table 2. Compositional analysis of Fushun oil shale and Changji oil shale ashes (wt.%) [16].

Ash	SiO ₂	Al ₂ O ₃	Fe ₂ O ₃	CaO	MgO	SO ₃	TiO ₂	K ₂ O	Na ₂ O	P ₂ O ₅
CJ	55.70	12.20	6.99	6.14	2.66	1.23	0.54	2.59	2.22	0.52
FS	55.30	22.60	10.90	0.72	1.25	0.77	1.07	1.20	1.14	0.21

The ash composition results show that the mineral components of both oil shales are mainly composed of oxides of Si, Al, and Fe, with their total contents exceeding 70%. This indicates that silicate-, alumina-, and iron-bearing minerals constitute the major fraction of the ash in both samples. In addition, Ca, Mg, K, and Na were also detected. In comparison, FS oil shale contains a higher Al content, whereas CJ oil shale shows a relatively higher Ca content, indicating certain differences in mineral composition between the two samples. Except for Al, Fe, and Ca, the contents of other ash components are relatively similar in the two oil shales.

2.2. Experimental Apparatus and Test Conditions

Thermogravimetric–differential scanning calorimetry analysis is an effective method for investigating fuel combustion characteristics [34,35]. The instrument simultaneously records sample mass variation, heat flow signals, reaction time, and temperature, from which TG, DTG, and DSC curves are obtained. In this study, TG–DSC experiments were conducted on a Mettler Toledo TGA/DSC 1 thermal analyzer. The sample mass was controlled at 10 ± 0.1 mg. During each test, the sample was heated from 30 to 1000 °C at heating rates of 5, 10, 20, and 40 °C·min^{−1}, while the total gas flow rate was maintained at 50 mL·min^{−1}. Additional combustion experiments were carried out under four atmospheres: 35% O₂/65% CO₂, 55% O₂/45% CO₂, 75% O₂/25% CO₂, and 100% O₂. The

21% O₂/79% CO₂ dataset was obtained from our previous study [16] and was used here as the low-O₂ reference atmosphere. The same CJ and FS oil shale samples, sample pre-treatment procedure, particle-size range, sample mass, heating-rate program, gas flow rate, thermal analyzer, MS detection system, baseline correction, and data-processing procedure were used. Therefore, the 21% O₂/79% CO₂ data are directly comparable with the newly obtained 35%, 55%, 75%, and 100% O₂ datasets. This combination allows the influence of O₂ concentration on oil shale oxy-fuel combustion behavior to be evaluated over a wider oxygen-enrichment range.

During the experiments, the thermal analyzer was connected online to a Pfeiffer ThermoStar mass spectrometer to detect gaseous products released during combustion. The mass spectrometer was operated in multiple ion detection (MID) mode. Ion current signals for CO₂ (m/z 44), H₂O (m/z 18), NO₂ (m/z 46), and SO₂ (m/z 64) were recorded continuously from 30 to 1000 °C, enabling real-time tracking of the main gaseous products during combustion.

2.3. Method of Determining Combustion Characteristic Parameters

TG and DTG curves yield several parameters that describe the combustion process, including the ignition temperature (T_i), burnout temperature (T_b), and the peak temperature corresponding to the maximum mass-loss rate (T_{max}). These parameters capture the thermal conversion of organic matter in oil shale during programmed combustion and help evaluate its combustion behavior. In this study, the ignition temperature was determined using the TG–DTG tangent method, following the procedure described in Ref. [36]. As oil shale combustion generally produces multiple DTG mass-loss peaks, the ignition temperature was determined from the first major peak in the low-temperature region.

For solid fuels such as coal, T_b is commonly determined from thermogravimetric results. Typical criteria include a mass-loss rate lower than 1%·min^{−1} or a cumulative mass loss reaching 98% [36–38]. However, oil shale generally contains carbonate minerals, whose decomposition in the high-temperature region causes additional inorganic mass loss. This can interfere with the direct determination of the burnout temperature of organic matter from TG curves. Therefore, high-temperature mineral decomposition should be taken into account when determining the burnout temperature of oil shale organic matter. In this study, the burnout temperature was determined using a conversion-based criterion. Integral area analysis of the TG–DTG mass-loss peaks showed that high-temperature decomposable minerals, such as carbonates, contributed approximately 7% and 21% of the total mass loss for Fushun and Changji oil shales, respectively. Accordingly, the conversion corresponding to organic matter burnout was set as 0.93 for Fushun oil shale and 0.79 for Changji oil shale. This difference reflects the distinct contents of high-temperature decomposable minerals in the two oil shales.

To comprehensively evaluate the combustion performance of oil shale, the comprehensive combustion characteristic index S was introduced in this study [39], as calculated using Equations (1) and (2). This index has been applied in analyses of oxy-fuel combustion behavior and can comprehensively characterize fuel combustion performance under different reaction conditions in terms of ignition behavior, combustion intensity, and burnout performance [40–42].

$$S = \frac{(dw/dt)_{\max}(dw/dt)_{\text{mean}}}{T_i^2 T_b} \quad (1)$$

$$(dw/dt)_{\text{mean}} = (\alpha_{T_b} - \alpha_{T_i}) / [(T_b - T_i) / \beta] \quad (2)$$

Here, $(dw/dt)_{\max}$ denotes the maximum combustion rate ($\% \cdot \text{min}^{-1}$), whereas $(dw/dt)_{\text{mean}}$ denotes the average combustion rate from T_i to T_b (min^{-1}), equivalent to the mean conversion rate between ignition and burnout. β is the heating rate ($\text{K} \cdot \text{min}^{-1}$), and T_b and T_i are the burnout and ignition temperatures (K), respectively.

2.4. Kinetic Analysis

Based on the thermogravimetric data, the kinetic characteristics of oil shale combustion under different O_2 concentrations were further investigated. The experiments covered five reaction atmospheres with O_2 concentrations of 21%, 35%, 55%, 75%, and 100%. Kinetic parameters obtained under different atmospheres were compared to evaluate how O_2 concentration affects the combustion reactivity of oil shale. The non-isothermal heterogeneous reaction process can be expressed using the following basic rate equation:

$$\frac{d\alpha}{dt} = k(T)f(\alpha) \quad (3)$$

where α denotes the conversion degree of the sample, t is the reaction time (min), T is the reaction temperature (K), $k(T)$ is the temperature-dependent rate constant, and $f(\alpha)$ represents the reaction model function. The conversion degree α is calculated as follows:

$$\alpha = \frac{m_0 - m_t}{m_0 - m_f} \quad (4)$$

where m_0 and m_f denote the initial and final sample masses, respectively, and m_t is the sample mass at time t . All masses are given in mg. Because the conversion degree α was calculated from the total TG mass loss, the E_α values obtained in this study should be regarded as apparent activation energies of the overall mass-loss process. For oil shale, this overall process includes organic matter decomposition and oxidation, residual carbon conversion, and, especially in the high-temperature region, possible mineral decomposition. Therefore, the calculated E_α values should not be interpreted as intrinsic activation energies of organic matter combustion alone. The Arrhenius expression for $k(T)$ is:

$$k(T) = A \exp\left(-\frac{E}{RT}\right) \quad (5)$$

Substitution of Equation (5) into Equation (3) gives Equation (6):

$$\frac{d\alpha}{dt} = A \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (6)$$

where A , E , and R in the Arrhenius equation denote the pre-exponential factor (s^{-1}), activation energy ($\text{kJ} \cdot \text{mol}^{-1}$), and universal gas constant ($8.314 \text{ J} \cdot \text{mol}^{-1} \cdot \text{K}^{-1}$), respectively.

In non-isothermal thermogravimetric analysis, oil shale is heated at a constant heating rate, $\beta = dT/dt$ ($\text{K} \cdot \text{min}^{-1}$). Thus, Equation (6) can be rearranged into Equation (7):

$$\frac{d\alpha}{dT} = \left(\frac{A}{\beta}\right) \exp\left(-\frac{E}{RT}\right) f(\alpha) \quad (7)$$

Equation (7) provides the basic framework for the kinetic analysis of oil shale combustion. In general, thermogravimetric experiments conducted at multiple heating rates, combined with iso-conversional analysis, are an important approach for determining the apparent activation energy of solid fuel thermal conversion. Iso-conversional methods can calculate the activation energy at each conversion degree from thermogravimetric data obtained at different heating rates without assuming a specific reaction model function.

They are therefore suitable for complex multistage heterogeneous reaction systems such as oil shale. Based on their mathematical formulation, iso-conversional methods are generally grouped into differential and integral approaches, with the integral approaches further separated into linear and nonlinear forms. Conventional linear integral methods, including FWO, KAS, and Starink, generally use approximations of the temperature integral. Such approximations can affect the estimated apparent activation energy, particularly when activation energy changes markedly with conversion.

$$J[E_\alpha, T_i(t_\alpha)] = \int_{t_{\alpha-\Delta\alpha}}^{t_\alpha} \exp\left(-\frac{E_\alpha}{RT_i(t)}\right) dt \quad (8)$$

$$\Phi(E_\alpha) = \sum_{i=1}^n \sum_{j \neq i}^n \frac{J[E_\alpha, T_i(t_\alpha)]}{J[E_\alpha, T_j(t_\alpha)]} \quad (9)$$

To reduce the systematic error caused by temperature integral approximation in conventional linear integral iso-conversional methods, Vyazovkin proposed a nonlinear integral iso-conversional method [26–28]. In this method, E_α is regarded as nearly unchanged over a small conversion range. The kinetic equation is then integrated over this finite interval, as shown in Equation (8). For n sets of non-isothermal data collected at different heating rates, the E_α value for each conversion interval is obtained by minimizing the objective function $\Phi(E_\alpha)$ defined in Equation (9). This optimization procedure is then repeated at different conversion degrees, α , to establish the relationship between E_α and α . Compared with conventional linear integral methods, the Vyazovkin method uses segmented time integration to describe non-isothermal processes and avoids reliance on approximate solutions of the temperature integral. It can therefore effectively reduce systematic errors in activation energy calculation [43].

It should be emphasized that the kinetic analysis in this study was not intended to establish a single lumped reaction model for the entire oil shale sample. Oil shale combustion involves several overlapping physicochemical processes, including kerogen decomposition, volatile release and oxidation, semi-char combustion, residual carbon oxidation, and mineral transformation. Therefore, the E_α values calculated by the Vyazovkin method should be regarded as conversion-dependent apparent activation energies. They describe the apparent kinetic response of different conversion intervals under the specified experimental conditions rather than intrinsic kinetic parameters of a single elementary or global reaction.

3. Results and Discussion

3.1. Effects of O₂ Concentration on Thermophysical and Transport Properties of the Combustion Atmosphere

To clearly illustrate the differences in thermophysical and transport properties between different O₂/CO₂ oxy-fuel atmospheres and air, the ratios of atmospheric parameters under different O₂ concentrations to those under air were calculated in this study. Figure 1 shows the variations in thermodynamic, heat-transfer, and mass-transfer parameters of different O₂/CO₂ atmospheres relative to the 21% O₂/79% N₂ air atmosphere at 1 atm. The results show that replacing N₂ with CO₂ leads to marked changes in the heat capacity, viscosity, thermal conductivity, thermal diffusivity, and O₂ diffusion coefficient of the reaction atmosphere. This indicates that the O₂/CO₂ atmosphere changes not only the oxidant concentration but also the heat- and mass-transfer environment in which combustion occurs. These changes can affect heat accumulation around fuel particles, oxygen transport, and the initial oxidation process, thereby playing an important role in oil shale ignition, volatile release, and the staged evolution of combustion.

As shown in Figure 1a,b, the ratios of C_p and C_v gradually increase with temperature and tend to stabilize in the medium- and high-temperature regions. In general, a higher CO_2 content corresponds to a larger heat capacity ratio. This indicates that CO_2 -enriched atmospheres have a stronger heat absorption capacity. This behavior is mainly because CO_2 is a linear polyatomic molecule, and more molecular degrees of freedom can be activated as temperature increases. A higher heat capacity absorbs more reaction heat and reduces the local heating rate. Therefore, in the initial combustion stage, the presence of CO_2 may delay fuel heating, weak-bond cleavage, and low-temperature oxidation reactions.

The variation in viscosity is shown in Figure 1c,d. The dynamic viscosity μ increases with temperature, whereas the kinematic viscosity ν in O_2/CO_2 atmospheres is generally lower than that in air. This phenomenon is mainly related to the higher molecular weight of CO_2 . The addition of CO_2 increases the density of the gas mixture, while kinematic viscosity is determined jointly by dynamic viscosity and gas density. Therefore, even if the dynamic viscosity increases, the higher gas density keeps the kinematic viscosity at a relatively low level. A lower kinematic viscosity indicates weaker gas-phase momentum diffusion and mixing ability, which is unfavorable for the transport of reactants to the fuel surface and reactive regions.

Figure 1e,f further show the changes in the heat-transfer capacity of the combustion atmospheres. In the low- and medium-temperature regions, the thermal conductivity, k , of the O_2/CO_2 atmospheres is lower than that of air. As the temperature increases, the differences among the atmospheres gradually decrease. By comparison, the reduction in thermal diffusivity, α , is more pronounced, and this decrease becomes greater at higher CO_2 contents. Thermal diffusivity is jointly governed by thermal conductivity, gas density, and heat capacity. CO_2 -enriched atmospheres have higher density and heat capacity, which weakens heat diffusion in the gas phase. These results indicate that CO_2 not only acts as a thermal diluent but also reduces the efficiency of heat transfer to fuel particles and reactive sites.

The change in O_2 diffusion capacity is shown in Figure 1g. Over the entire temperature range, the diffusion coefficient of O_2 in CO_2 is lower than that of O_2 in N_2 . This indicates that a CO_2 atmosphere weakens the mass-transfer ability of O_2 . For oil shale kerogen, low-temperature oxidation depends on the contact between O_2 and active sites, such as aliphatic side chains, aromatic edge structures, and heteroatom-containing functional groups. When O_2 diffusion is restricted, oxidation reactions and radical generation are suppressed, causing the initial reaction to shift toward higher temperatures.

Compared with the above parameters, the Prandtl number Pr in Figure 1h changes only slightly. Under most atmospheres, the Pr ratio remains close to 1, indicating that the relative relationship between momentum diffusion and thermal diffusion changes only to a limited extent. Therefore, within the atmospheric range investigated in this study, Pr is not the main factor responsible for the differences in combustion behavior. In contrast, changes in heat capacity, thermal diffusivity, and the O_2 diffusion coefficient more directly reflect the influence of the O_2/CO_2 atmosphere on the combustion process.

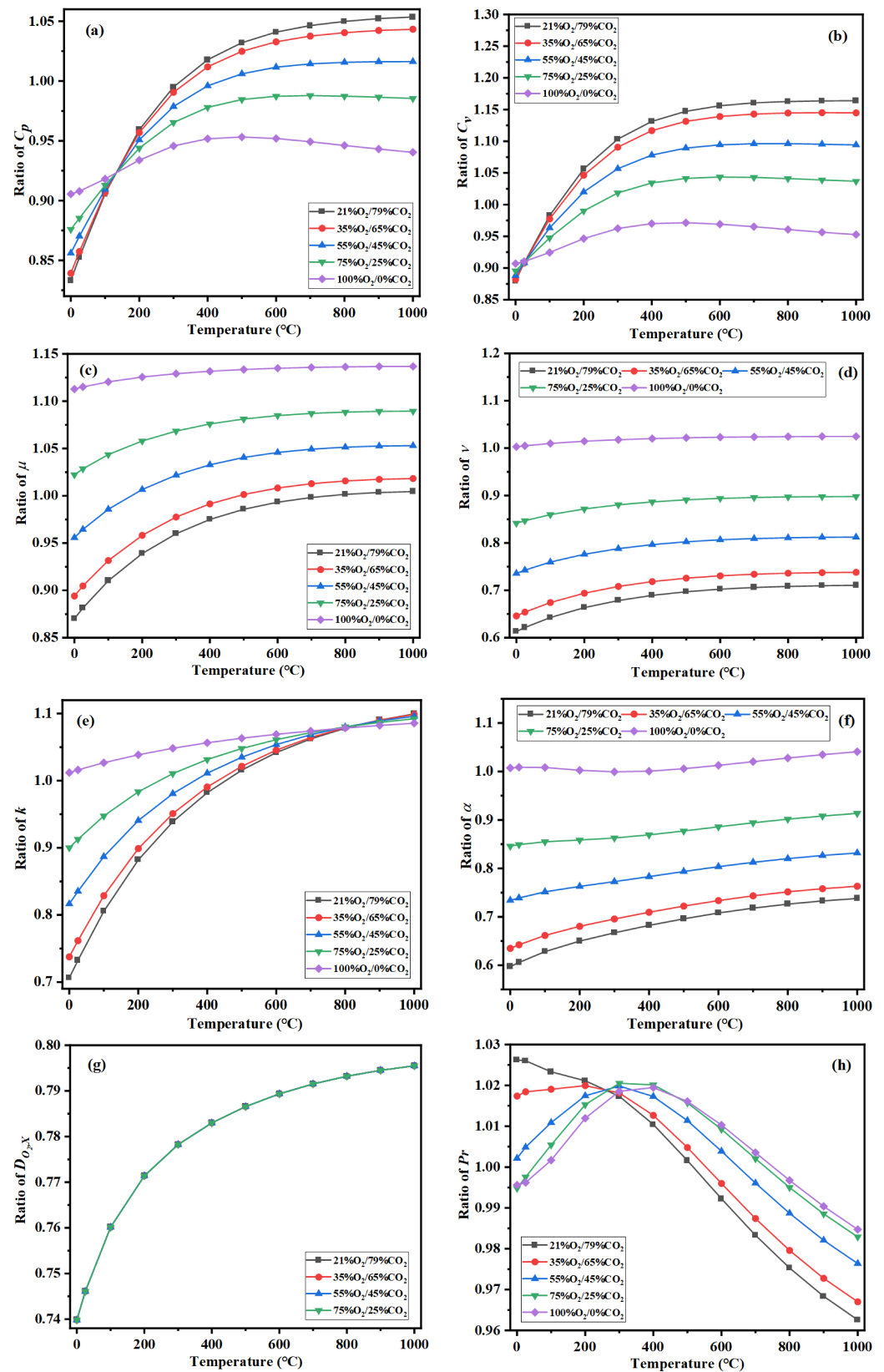


Figure 1. Ratios of thermophysical and transport properties of O_2/CO_2 atmospheres to those of the reference air atmosphere $21\%\text{O}_2/79\%\text{N}_2$ as a function of temperature at 1 atm: (a) C_p ; (b) C_v ; (c) μ ; (d) ν ; (e) k ; (f) α ; (g) $D_{\text{O}_2,X}$; (h) Pr .

Overall, CO_2 exerts a pronounced inhibitory effect during the initial stage of oxy-fuel combustion. Its higher heat capacity enhances the thermal dilution effect, its lower

thermal diffusivity weakens heat transfer, and its lower O_2 diffusion coefficient restricts oxygen transport. These factors jointly delay kerogen heating, structural cleavage, and initial oxidation. As the O_2 concentration increases, the amount of available oxygen in the system rises, partially offsetting the dilution and diffusion limitation effects of CO_2 . Therefore, increasing the O_2 concentration helps strengthen subsequent oxidation reactions and improve the combustion intensity under O_2/CO_2 atmospheres. These results provide a thermophysical basis for explaining the differences in oil shale combustion behavior under different oxy-fuel atmospheres.

3.2. Effects of O_2 Concentration on the Combustion Characteristics

3.2.1. Overall Combustion Process Based on TG-DTG Curves

Figures 2 and 3 show the TG–DTG profiles of CJ and FS oil shales, respectively, under different O_2/CO_2 atmospheres and heating rates. The peak temperatures and corresponding mass-loss rates derived from the DTG curves are summarized in Tables 3 and 4. The combustion-induced mass loss of both oil shales proceeds through three stages. In the low-temperature range of 30–200 °C, the TG curves change only slightly, mainly due to moisture removal and the release of a small amount of light components [17,18]. After the temperature increases to approximately 300 °C, the sample mass decreases rapidly, and obvious mass-loss peaks appear in the DTG curves. This suggests that kerogen thermal cracking, volatile release, and subsequent oxidation reactions are rapidly activated at this stage. With a further increase in temperature, the TG curves gradually become smoother, suggesting that combustible organic matter is continuously consumed and the system enters a later stage dominated by residual carbon oxidation and mineral transformation.

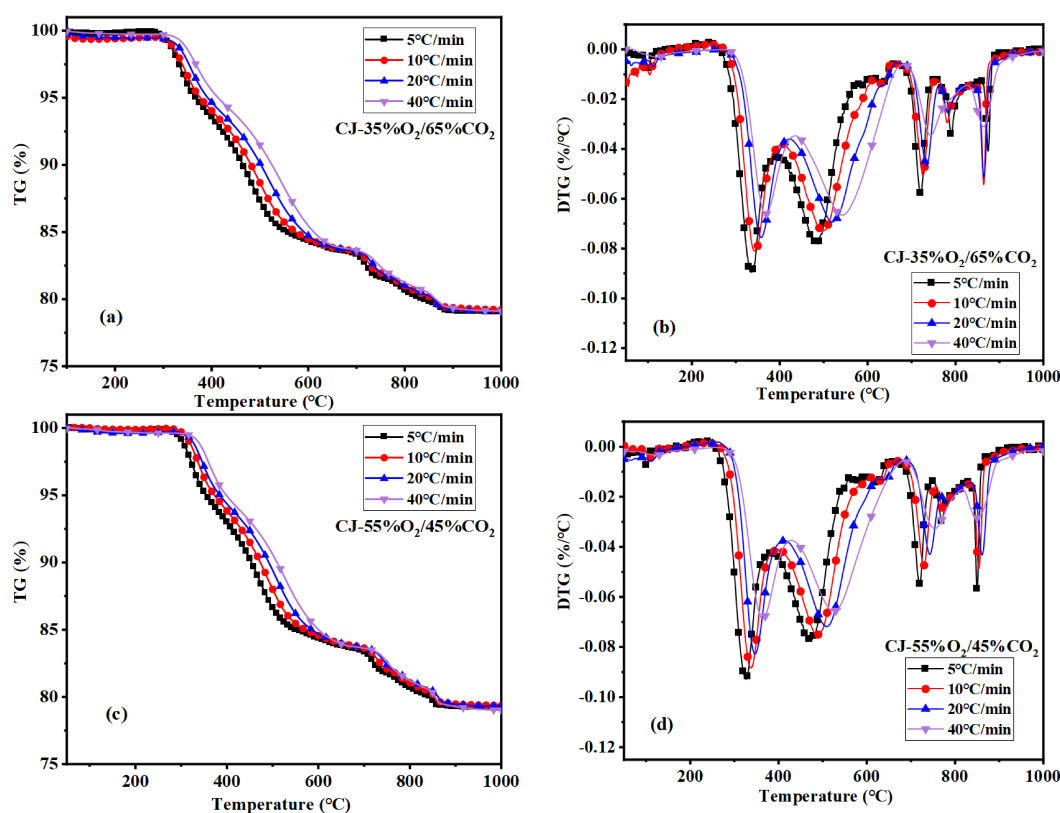


Figure 2. Cont.

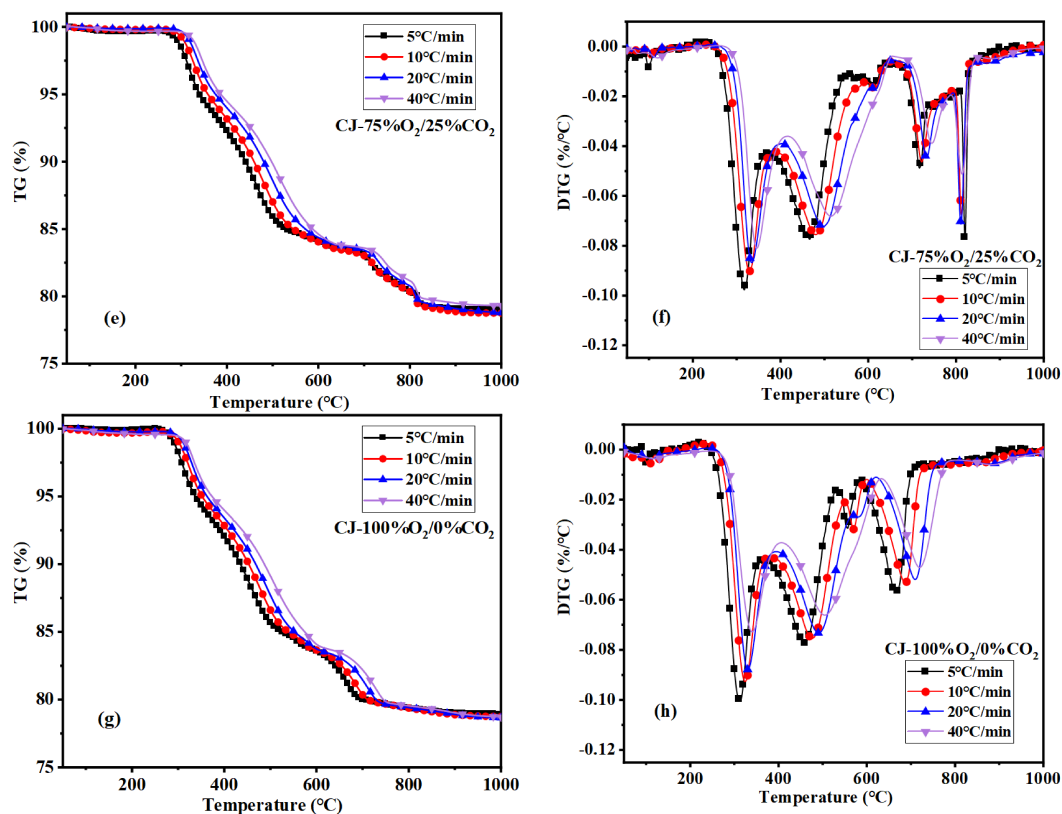


Figure 2. TG and DTG curves of CJ oil shale under different oxy-fuel atmospheres and heating rates: (a) TG of CJ-35% O₂/65% CO₂; (b) DTG of CJ-35% O₂/65% CO₂; (c) TG of CJ-55% O₂/45% CO₂; (d) DTG of CJ-55% O₂/45% CO₂; (e) TG of CJ-75% O₂/25% CO₂; (f) DTG of CJ-75% O₂/25% CO₂; (g) TG of CJ-100% O₂/0% CO₂; (h) DTG of CJ-100% O₂/0% CO₂.

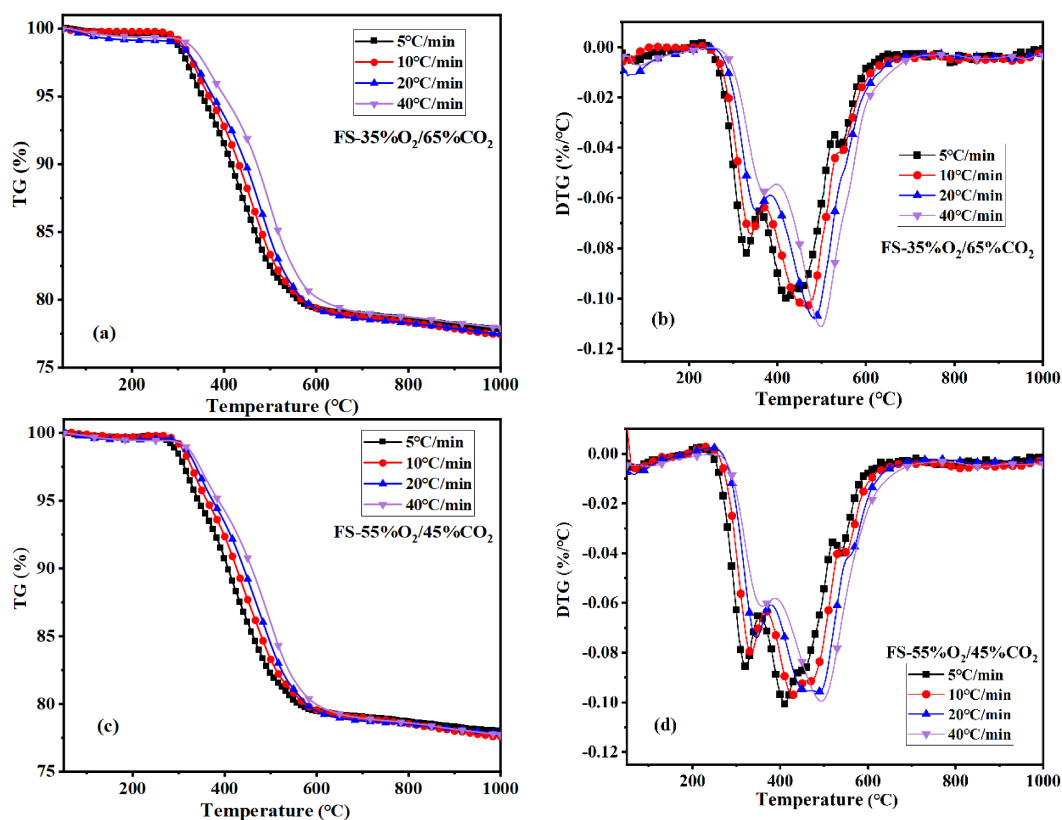


Figure 3. Cont.

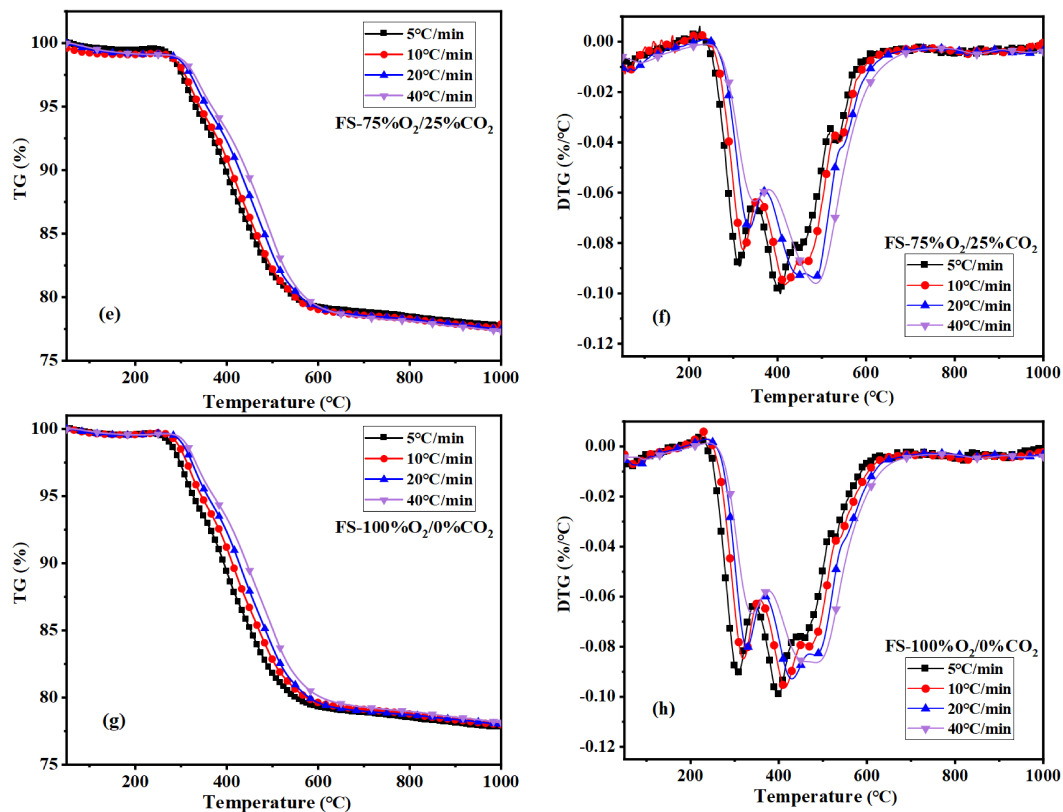


Figure 3. TG and DTG curves of FS oil shale under different oxy-fuel atmospheres and heating rates: (a) TG of FS-35% O₂/65% CO₂; (b) DTG of FS-35% O₂/65% CO₂; (c) TG of FS-55% O₂/45% CO₂; (d) DTG of FS-55% O₂/45% CO₂; (e) TG of FS-75% O₂/25% CO₂; (f) DTG of FS-75% O₂/25% CO₂; (g) TG of FS-100% O₂/0% CO₂; (h) DTG of FS-100% O₂/0% CO₂.

Table 3. The peak characteristic parameters of CJ oil shale under different oxy-fuel atmospheres and heating rates.

Atmosphere	Heating Rate °C/min	T_{p1} °C	$(dw/dT)_{p1}$ %/°C	T_{p2} °C	$(dw/dT)_{p2}$ %/°C
35%O ₂ /65%CO ₂	5	335.1	−0.090	487.1	−0.078
	10	343.5	−0.081	497.3	−0.073
	20	357.3	−0.076	519.7	−0.069
	40	368.3	−0.066	542.2	−0.067
55%O ₂ /45%CO ₂	5	326.1	−0.093	471.9	−0.077
	10	337.5	−0.083	486.5	−0.075
	20	346.3	−0.083	509.1	−0.072
	40	364.1	−0.069	525.3	−0.066
75%O ₂ /25%CO ₂	5	317.6	−0.098	466.1	−0.077
	10	329.5	−0.090	480.3	−0.076
	20	334.3	−0.087	496.7	−0.072
	40	346.5	−0.081	514.7	−0.068
100%O ₂ /0%CO ₂	5	313.3	−0.100	456.8	−0.078
	10	324.3	−0.093	476.2	−0.075
	20	331.2	−0.088	491.5	−0.073
	40	341.3	−0.073	504.7	−0.066

Table 4. The peak characteristic parameters of FS oil shale under different oxy-fuel atmospheres and heating rates.

Atmosphere	Heating Rate °C/min	T_{p1} °C	$(dw/dT)_{p1}$ %/°C	T_{p2} °C	$(dw/dT)_{p2}$ %/°C
35%O ₂ /65%CO ₂	5	329.0	−0.082	419.9	−0.100
	10	339.8	−0.074	460.3	−0.103
	20	352.3	−0.065	484.0	−0.108
	40	369.3	−0.057	498.7	−0.111
55%O ₂ /45%CO ₂	5	320.5	−0.085	410.8	−0.101
	10	333.3	−0.080	429.0	−0.097
	20	346.3	−0.074	459.0	−0.095
	40	359.3	−0.061	493.3	−0.099
75%O ₂ /25%CO ₂	5	313.5	−0.089	405.8	−0.100
	10	322.8	−0.082	418.2	−0.096
	20	335.7	−0.074	448.0	−0.093
	40	348.0	−0.063	486.0	−0.096
100%O ₂ /0%CO ₂	5	307.2	−0.091	400.2	−0.099
	10	318.4	−0.085	413.5	−0.096
	20	326.6	−0.080	429.7	−0.093
	40	339.3	−0.067	457.0	−0.086

The heating rate noticeably shifts the TG–DTG profiles. Under a fixed atmosphere, increasing the heating rate from 5 to 40 °C·min^{−1} displaces the TG curves toward higher temperatures and shifts the DTG mass-loss peaks to later temperature regions. The peak temperatures summarized in Tables 3 and 4 follow this pattern. For CJ oil shale under 35% O₂/65% CO₂, the first mass-loss peak moves from 335.1 to 368.3 °C, while the second peak moves from 487.1 to 542.2 °C. FS oil shale exhibits a similar response under the same atmosphere, with the first peak temperature increasing from 329.0 to 369.3 °C and the second peak temperature increasing from 419.9 to 498.7 °C. This temperature displacement is mainly attributed to thermal lag. At higher heating rates, the temperature gradient between the furnace and the sample interior becomes more pronounced. Heat transfer into the particles requires sufficient time, while volatile release and oxygen diffusion are also constrained. As a result, thermal decomposition and oxidation reactions occur effectively only when the apparent temperature becomes higher.

CJ and FS oil shales show distinct combustion behaviors. The DTG curves of CJ oil shale contain multiple peaks, with several secondary peaks appearing in the high-temperature region. This indicates that CJ oil shale combustion involves several overlapping reaction stages. The peaks in the low- to medium-temperature regions mainly correspond to kerogen cracking, volatile release, and oxidation. The secondary peaks in the high-temperature region are attributed to the thermal decomposition of carbonate minerals, which has been analyzed and confirmed in detail in previous work [16]. Similar behavior has also been reported for Estonian oil shale under oxy-fuel atmospheres, where high-temperature DTG mass-loss peaks were assigned to the decomposition of carbonate minerals, mainly dolomite and calcite [11].

In contrast, the main mass-loss interval of FS oil shale is more concentrated. Its TG curve decreases rapidly within approximately 300–600 °C and then gradually levels off. The high-temperature secondary peaks in the DTG curve are not obvious. This suggests that organic matter decomposition and oxidation in the FS sample are mainly completed in the medium-temperature region, while residual reactions at high temperatures are relatively weak. Compared with CJ oil shale, FS oil shale generally shows a lower second peak temperature. For instance, under 35% O₂/65% CO₂ at 5 °C·min^{−1}, the second peak temperature of FS oil shale is 419.9 °C, which is much lower than that of CJ oil shale,

487.1 °C. This indicates that the combustible components in FS oil shale have higher reactivity and that the main oxidation process occurs more readily. The DTG peak intensity also reflects differences in the reaction processes of the two samples. The first mass-loss peak of CJ oil shale is more prominent and is accompanied by several subsequent peaks in the high-temperature region, indicating that both pyrolysis–oxidation and later residual reactions are significant. In contrast, the second mass-loss peak of FS oil shale is usually stronger, suggesting that its main mass loss is concentrated in volatile oxidation and rapid organic matter combustion.

3.2.2. Effect of O₂ Concentration on TG-DTG and Heat-Flow Curve

To eliminate the influence of different heating rates, Figures 4 and 5 further compare the effects of O₂ concentration on the combustion behavior of CJ and FS oil shales at 20 °C·min^{−1}, including the TG–DTG curves and heat flow curves. The data obtained under the 21% O₂/79% CO₂ atmosphere were taken from our previous work [16]. As the O₂ concentration increases, the main mass-loss regions and heat release peaks of both samples shift toward lower temperatures. This indicates that oxygen-enriched conditions promote volatile oxidation and semi-char combustion. This trend is consistent with the changes in characteristic temperatures discussed above. It also suggests that the dilution and mass-transfer limitations caused by CO₂ are gradually weakened as the O₂ proportion increases.

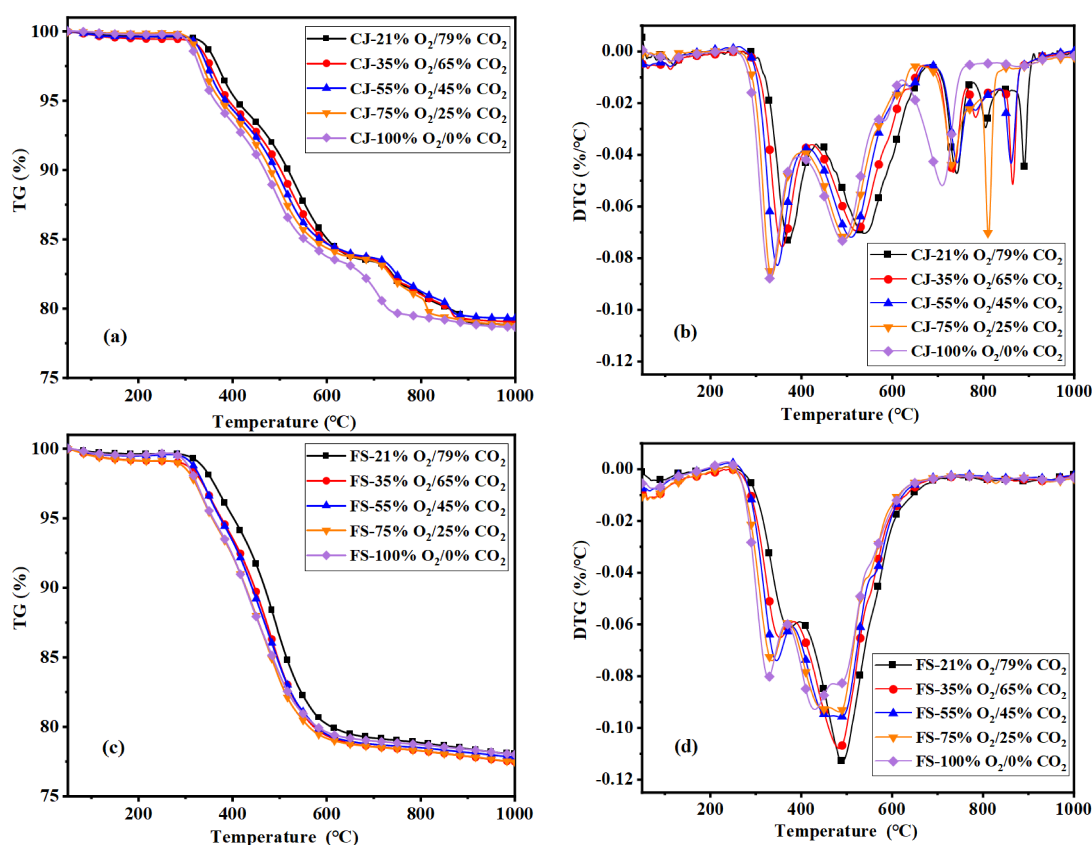


Figure 4. TG and DTG curves of CJ and FS oil shale during oxy-fuel combustion at different O₂ concentrations under a heating rate of 20 °C/min: (a) TG of CJ; (b) DTG of CJ; (c) TG of FS; (d) DTG of FS.

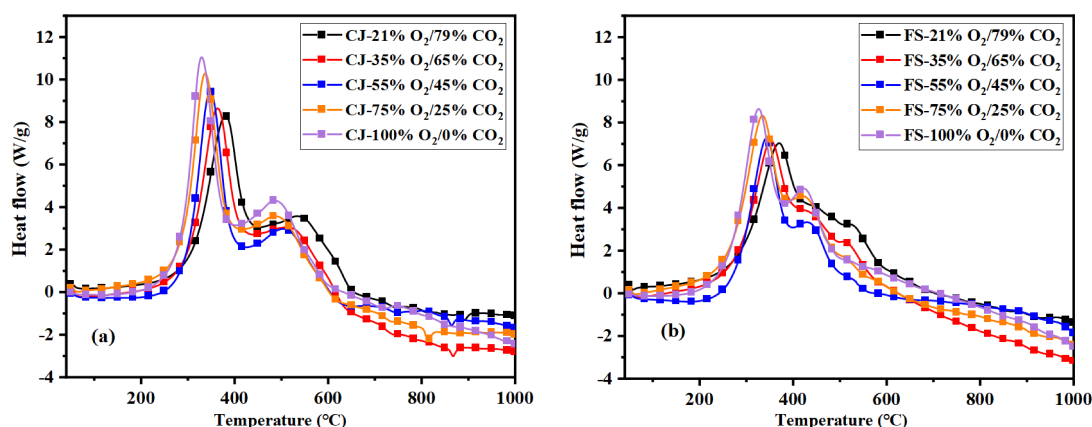


Figure 5. Heat flow curves of CJ and FS oil shale during oxy-fuel combustion at different O_2 concentrations under a heating rate of $20\text{ }^{\circ}\text{C}/\text{min}$: (a) Heat flow of CJ; (b) Heat flow of FS.

As shown by the TG and DTG curves in Figure 4, the main mass-loss peaks of both oil shales shift toward lower temperatures with increasing O_2 concentration. This demonstrates that higher O_2 concentrations promote initial oxidation and subsequent combustion reactions. For the CJ sample at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, the first peak temperature decreases from $357.3\text{ }^{\circ}\text{C}$ under $35\%\text{ }O_2/65\%\text{ }CO_2$ to $331.2\text{ }^{\circ}\text{C}$ under pure O_2 . The second peak temperature decreases from 519.7 to $491.5\text{ }^{\circ}\text{C}$. A similar trend is observed for the FS sample. Its first peak temperature decreases from 352.3 to $326.6\text{ }^{\circ}\text{C}$, while the second peak temperature decreases from 484.0 to $429.7\text{ }^{\circ}\text{C}$. These results indicate that increasing the O_2 concentration improves oxygen supply, weakens the dilution effect of CO_2 , and enhances the oxidation rates of volatiles and residual carbon.

According to the thermophysical analysis of different oxy-fuel atmospheres in Section 3.1, atmospheres with higher CO_2 contents have larger heat capacities, lower thermal diffusivities, and lower O_2 diffusion coefficients. These characteristics restrict heat and mass transfer during the initial stage. Therefore, under the $35\%\text{ }O_2/65\%\text{ }CO_2$ atmosphere, sample heating, volatile release, and oxidation reactions are relatively delayed. As the O_2 proportion increases, the higher O_2 partial pressure enhances oxygen diffusion toward the particle surface and into internal pores. This makes volatile oxidation and residual carbon combustion easier to initiate. Consequently, the rapid mass-loss region in the TG curves moves to lower temperatures, and the DTG peaks shift accordingly to earlier positions.

Based on the heat flow curves under different O_2 concentrations shown in Figure 5, both oil shales exhibit distinct exothermic peaks. The main heat-release region is concentrated at $300\text{--}600\text{ }^{\circ}\text{C}$, broadly corresponding to the rapid mass-loss stage observed in the TG and DTG curves. This indicates that this temperature range corresponds to the main reaction stage of volatile oxidation and semi-char combustion.

For CJ oil shale, the main exothermic peak becomes stronger and shifts toward lower temperatures as the O_2 concentration increases. This suggests that a higher O_2 partial pressure promotes the oxidation of cracking products, volatiles, and semi-char. Under the $21\%\text{ }O_2/79\%\text{ }CO_2$ atmosphere, the exothermic peak is weaker and appears at a relatively higher temperature, indicating that CO_2 enrichment delays initial oxidation through thermal dilution and mass-transfer inhibition. A small endothermic peak is observed after the main exothermic peak for the CJ sample, indicating the occurrence of endothermic reactions in the high-temperature region. This behavior is consistent with the endothermic decomposition of carbonate minerals and further confirms that the high-temperature mass-loss peak is associated with carbonate mineral decomposition.

The heat flow curves of FS oil shale show a similar trend to those of CJ oil shale, but the heat release process is more concentrated. Its main exothermic peak appears within the 300–550 °C range, followed by a rapid decline in heat flow. The thermal response in the high-temperature region is relatively weak, suggesting that the main combustible components in the FS sample are largely oxidized in the medium-temperature region. As the O₂ concentration increases, the main exothermic peak of FS oil shale also becomes stronger and shifts to lower temperatures, further confirming that increasing O₂ concentration enhances the combustion reaction.

3.2.3. Ignition, Burnout and Comprehensive Combustion Indices

Figure 6 summarizes the ignition temperature (T_i) and burnout temperature (T_b) of CJ and FS oil shales under different O₂/CO₂ atmospheres and heating rates. T_i reflects the ease with which the sample shifts from slow mass loss to rapid oxidation, whereas T_b is related to the complete oxidation of residual organic matter and semi-char. These two parameters therefore provide direct indicators of oil shale combustion reactivity under oxy-fuel atmospheres.

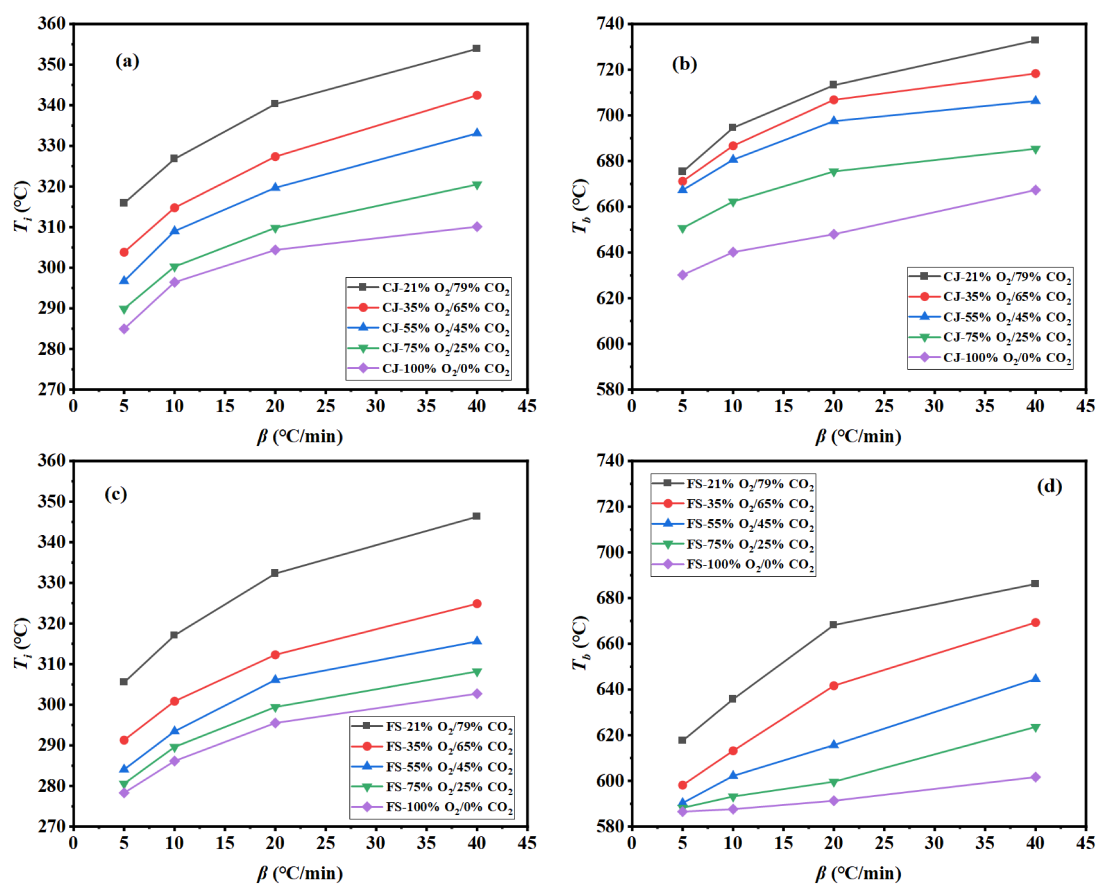


Figure 6. Ignition temperature and burnout temperature of CJ and FS oil shale under different oxy-fuel atmospheres and heating rates: (a) T_i of CJ; (b) T_b of CJ; (c) T_i of FS; (d) T_b of FS.

Figure 6 shows that the heating rate influences both T_i and T_b . For CJ and FS oil shales, both temperatures rise progressively as the heating rate increases from 5 to 40 °C·min^{−1}, indicating that ignition and burnout are shifted to higher temperature regions at higher heating rates. This behavior is mainly caused by an enhanced thermal hysteresis effect. Under rapid heating, the furnace temperature increases quickly, whereas heat transfer within the sample, volatile release, oxygen diffusion, and surface oxidation reactions all require time. Therefore, at the same apparent temperature, the actual reaction degree

inside the sample is relatively insufficient. The sample can enter the rapid combustion stage only after a higher temperature is reached. Similarly, the continued oxidation of residual semi-char and stable organic structures is delayed, resulting in an increase in the burnout temperature.

The atmosphere composition also has a clear influence on oil shale combustion characteristics. At the same heating rate, T_i of both CJ and FS oil shales gradually decreases as the O_2 concentration increases. The highest ignition temperature is observed under the 21% O_2 /79% CO_2 atmosphere, whereas the lowest value appears under the 100% O_2 atmosphere. This indicates that increasing the O_2 concentration promotes the initial oxidation of oil shale. A higher O_2 partial pressure increases the driving force for oxygen diffusion toward the particle surface and into internal pores. It also enhances the probability of contact between O_2 and volatiles, radicals, and active sites in semi-char. Once the initial oxidation reaction is strengthened, local heat release increases. This further promotes organic matter cracking and volatile release, forming a positive feedback effect that makes the sample easier to ignite.

T_b also decreases as the O_2 concentration increases, indicating that a high O_2 concentration promotes not only ignition but also later-stage burnout. The later stage of oil shale combustion mainly involves semi-char oxidation, decomposition of residual organic matter, and reactions related to carbonate mineral decomposition. When the CO_2 content is high, the atmosphere has a higher heat capacity, lower thermal diffusivity, and a lower O_2 diffusion coefficient. These factors restrict the oxidation of residual carbon to some extent. As a result, the burnout temperature is higher under the 21% O_2 /79% CO_2 atmosphere. With increasing O_2 proportion, the thermal dilution and mass-transfer inhibition effects of CO_2 are weakened. Residual semi-char can then be oxidized more completely at lower temperatures, leading to a decrease in T_b .

Differences are also observed between CJ and FS samples. Overall, T_i and T_b of FS oil shale are lower than those of CJ oil shale, indicating that FS is easier to ignite and burn out. This is consistent with the TG-DTG and heat flow analyses discussed above. The main mass-loss region of FS is more concentrated, and its main heat release process is completed earlier. This suggests that its combustible components have higher reactivity in the medium-temperature region. In contrast, the DTG curves of CJ show more obvious multi-peak characteristics, with subsequent mass loss and thermal effects still present in the high-temperature region.

In terms of variation magnitude, the effect of O_2 concentration on T_b is generally more pronounced than that on T_i , especially for the FS sample. This suggests that oxy-fuel conditions have a stronger promoting effect on later-stage semi-char oxidation and burnout. Ignition is jointly controlled by volatile release, initial oxidation, and local heat release, whereas burnout depends more strongly on continuous oxygen supply. When the O_2 concentration increases, the diffusion limitation of residual carbon oxidation is weakened, and the later oxidation process is significantly accelerated. Therefore, the decrease in T_b is more evident.

Overall, a higher heating rate postpones the ignition and burnout of both CJ and FS oil shales, whereas a higher O_2 concentration promotes their occurrence at lower temperatures. A higher heating rate enhances thermal hysteresis and transport limitations, causing the characteristic temperatures to increase. A higher O_2 concentration improves oxygen supply and weakens the dilution effect of CO_2 , allowing initial oxidation and later-stage burnout to occur earlier. These two effects jointly determine the combustion characteristics of oil shale under O_2/CO_2 atmospheres. The differences in characteristic temperatures between CJ and FS further indicate that oil shale combustion behavior is controlled not only by

the external atmosphere but also by organic matter structure, semi-char reactivity, and mineral composition.

Figure 7 summarizes the comprehensive combustion characteristic index, S , of CJ and FS oil shales under different O_2/CO_2 atmospheres and heating rates. A larger S value usually corresponds to more favorable combustion behavior, including a higher mass-loss rate, a lower ignition temperature, and improved burnout performance. For both CJ and FS oil shales, S increases with heating rate, and this increase becomes especially evident between 20 and 40 °C·min^{−1}. This trend is mainly related to the heating-rate-induced enhancement of mass loss per unit time, which leads to larger DTG peak values and higher average mass-loss rates. Although higher heating rates also raise the ignition and burnout temperatures, the increase in mass-loss rate makes a greater contribution to S . As a result, the comprehensive combustion characteristic index increases with heating rate. It should be noted, however, that this change contains a clear heating-rate effect and should not be directly regarded as an improvement in the intrinsic reactivity of the oil shale samples.

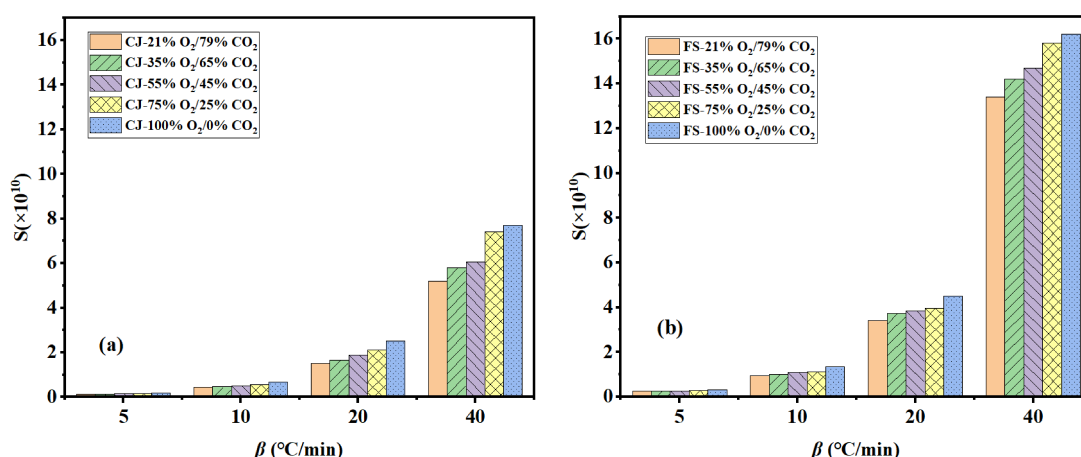


Figure 7. Composite combustion characteristic index of CJ and FS oil shale under different oxy-fuel atmospheres and heating rates: (a) S of CJ; (b) S of FS.

At the same heating rate, increasing the O_2 concentration leads to a gradual increase in S . The lowest S value is observed under the 21% $O_2/79\%$ CO_2 atmosphere, whereas the highest value appears under the 100% O_2 atmosphere. This indicates that increasing the O_2 concentration improves the overall combustion performance of oil shale. A higher O_2 partial pressure favors volatile oxidation and semi-char combustion. It reduces the ignition and burnout temperatures and increases the mass-loss rate during the main reaction stage. In contrast, in atmospheres with high CO_2 contents, stronger thermal dilution and weaker O_2 diffusion suppress initial oxidation and later-stage burnout, resulting in relatively lower S values.

A comparison between the two samples shows that FS oil shale has clearly higher S values than CJ oil shale, especially at heating rates of 20 and 40 °C·min^{−1}. This difference points to stronger overall combustion reactivity for FS oil shale. Combined with the TG–DTG curves, heat flow curves, and characteristic temperature results discussed above, the main mass-loss and heat-release processes of FS are more concentrated, and its ignition and burnout temperatures are generally lower than those of CJ. Therefore, the FS sample is more prone to rapid oxidation and complete burnout. CJ oil shale also shows enhanced combustion performance at higher O_2 concentrations, but its multi-stage reaction behavior remains more evident. Subsequent reactions still occur in the high-temperature region, resulting in relatively weaker overall combustion performance.

3.3. Combustion Kinetic Analysis

To clearly illustrate the effect of O_2 concentration in the combustion atmosphere on the activation energy, E_α , the relationship between E_α and the conversion degree, α , during the combustion of CJ and FS oil shales was plotted using the advanced Vyazovkin iso-conversional method, as shown in Figure 8. For both oil shales, E_α varies markedly with α rather than remaining constant. This indicates that oil shale combustion is not governed by a single-step reaction. Instead, it is controlled by several coupled processes, including kerogen cracking, volatile release and oxidation, and semi-char combustion. This conversion-dependent behavior is consistent with previous kinetic studies of oil shale under air and inert atmospheres. Bai et al. [10] showed that the pyrolysis and combustion of different Chinese oil shales exhibited multiple reaction processes, and that the diversity of organic and mineral compositions strongly affected the thermal behavior and kinetic parameters. For pyrolysis under inert conditions, Wang et al. [17] reported non-isothermal decomposition behavior with staged kinetic characteristics. These results support the present finding that E_α changes with α and that oil shale combustion under O_2/CO_2 atmospheres should be interpreted as a multistage apparent kinetic process rather than a single global reaction.

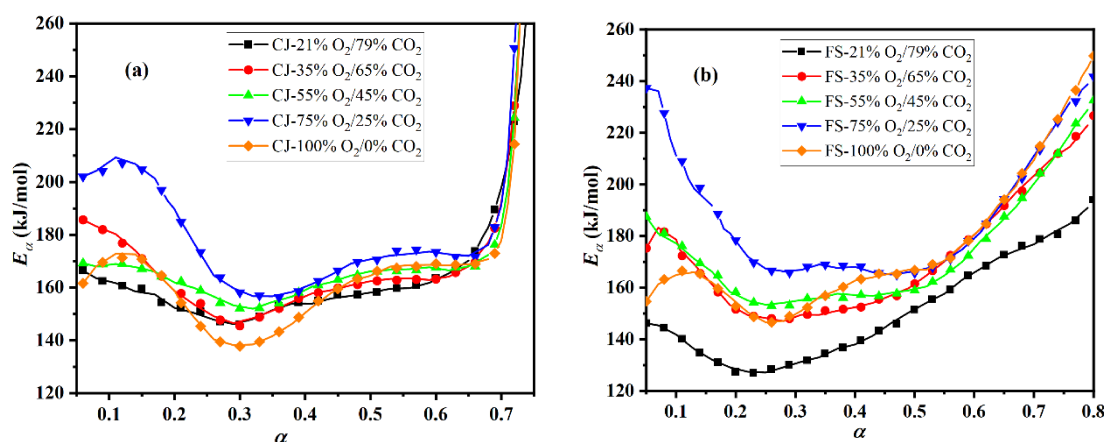


Figure 8. Activation energy as a function of conversion for CJ and FS oil shale combustion under different O_2/CO_2 atmospheres calculated by the Vyazovkin method: (a) E_α of CJ; (b) E_α of FS.

In the low-conversion region, E_α is relatively high. This region mainly corresponds to the initiation of oil shale combustion, including the cleavage of weak organic bonds, the release of light components, and the onset of oxidation. Because the reaction has not yet entered the intense mass-loss and heat-release stage, the apparent energy barrier remains relatively high. In the medium-conversion region, especially around $\alpha = 0.25\text{--}0.35$, E_α decreases to a lower level. This region overlaps with the main TG–DTG mass-loss stage and the main heat-release region. The heat-flow results show that the main exothermic region is mainly concentrated at $300\text{--}600^\circ\text{C}$, corresponding to volatile oxidation and semi-char combustion. Therefore, the lower E_α in this region can be attributed to the rapid release and oxidation of volatiles, heat feedback from oxidation reactions, and the accelerated decomposition of reactive organic structures. In the high-conversion region, E_α increases markedly. At this stage, easily reactive components have been largely consumed, and the reaction is increasingly controlled by residual semi-char oxidation, stable organic structures, and mineral-related transformations. For CJ oil shale, the increase in E_α is more pronounced, which agrees with its multipeak DTG behavior and the endothermic response associated with carbonate mineral decomposition in the high-temperature region.

CJ and FS oil shales show similar overall trends in activation energy, but their curve shapes and value ranges differ. For CJ oil shale, E_a increases more sharply at high conversion degrees, indicating a higher energy barrier for later-stage reactions. This is consistent with the pronounced high-temperature multipeak behavior observed in its DTG curves. In contrast, the main reaction region of FS oil shale is more concentrated. However, under oxy-fuel conditions, E_a also increases markedly at high conversion degrees, suggesting that its later-stage burnout is still limited by the conversion of residual semi-char and stable structures.

O₂ concentration has a marked effect on E_a for both CJ and FS oil shales. As the O₂ concentration increases from 21% to 75%, the overall E_a values for oil shale combustion gradually rise. This trend is not unique to the present study. Bai et al. found that, during the oxy-fuel combustion of Huadian oil shale, higher O₂ concentrations enhanced kerogen oxidation and intensified the reaction, while the activation energy also increased [14,15]. Comparable behavior has also been reported for coal char–straw co-combustion under O₂/CO₂ atmospheres. In that study, higher O₂ concentrations shifted the TG and DTG curves to lower-temperature regions and improved overall combustion performance, while the average activation energy also increased [44]. A similar pattern was noted during the oxy-fuel combustion of Chlorella, where both the combustion rate index and apparent activation energy increased with the O₂ concentration in the O₂/CO₂ atmosphere [45].

The overall increase in E_a with O₂ concentration suggests that oxygen-enriched conditions change the reaction-controlling steps. A higher O₂ partial pressure promotes volatile oxidation, semi-char combustion, and deep oxidation. As a result, at the same conversion degree, the reaction is more likely to be controlled by oxidation steps with higher temperature sensitivity, leading to a higher apparent activation energy. However, when the O₂ concentration further increases to 100%, the atmosphere changes from an O₂/CO₂ mixture to pure O₂. In this case, the thermal dilution effect of CO₂, O₂ diffusion limitation, and complex CO₂-involved conversion processes are largely eliminated. Oxidation reactions can then proceed more directly and more completely. Sufficient oxygen supply and stronger exothermic feedback reduce the apparent reaction resistance during the main combustion stage, causing E_a to decrease rather than continue increasing. Therefore, the non-monotonic variation in E_a reflects atmosphere-induced changes in reaction pathways and controlling mechanisms. It should not be simply interpreted as a linear change in combustion reactivity with O₂ concentration.

3.4. Combustion Product Analysis

Figures 9 and 10 present the evolution profiles of CO₂, H₂O, SO₂, and NO₂ released during CJ and FS oil shale combustion under different O₂/CO₂ atmospheres, respectively. Overall, the release of the main gaseous products is mainly concentrated within 300–600 °C. This temperature range broadly overlaps with the rapid mass-loss region in the TG–DTG curves and the main heat-release region in the heat flow curves. It indicates that kerogen cracking, volatile oxidation, and semi-char combustion occur simultaneously in this range, making it the most active stage of oil shale combustion. It should be noted that CO₂ was used as the balance gas in the O₂/CO₂ atmospheres. Therefore, the m/z 44 signal contains a strong background contribution from the carrier gas and cannot be directly interpreted as the absolute amount of CO₂ generated from oil shale combustion. In this study, the CO₂ signal was mainly used to compare peak position, peak-shape evolution, and relative changes under different O₂ concentrations. Therefore, the following discussion focuses on the temperature shift and relative variation of the CO₂ signal rather than on absolute CO₂ release intensity.

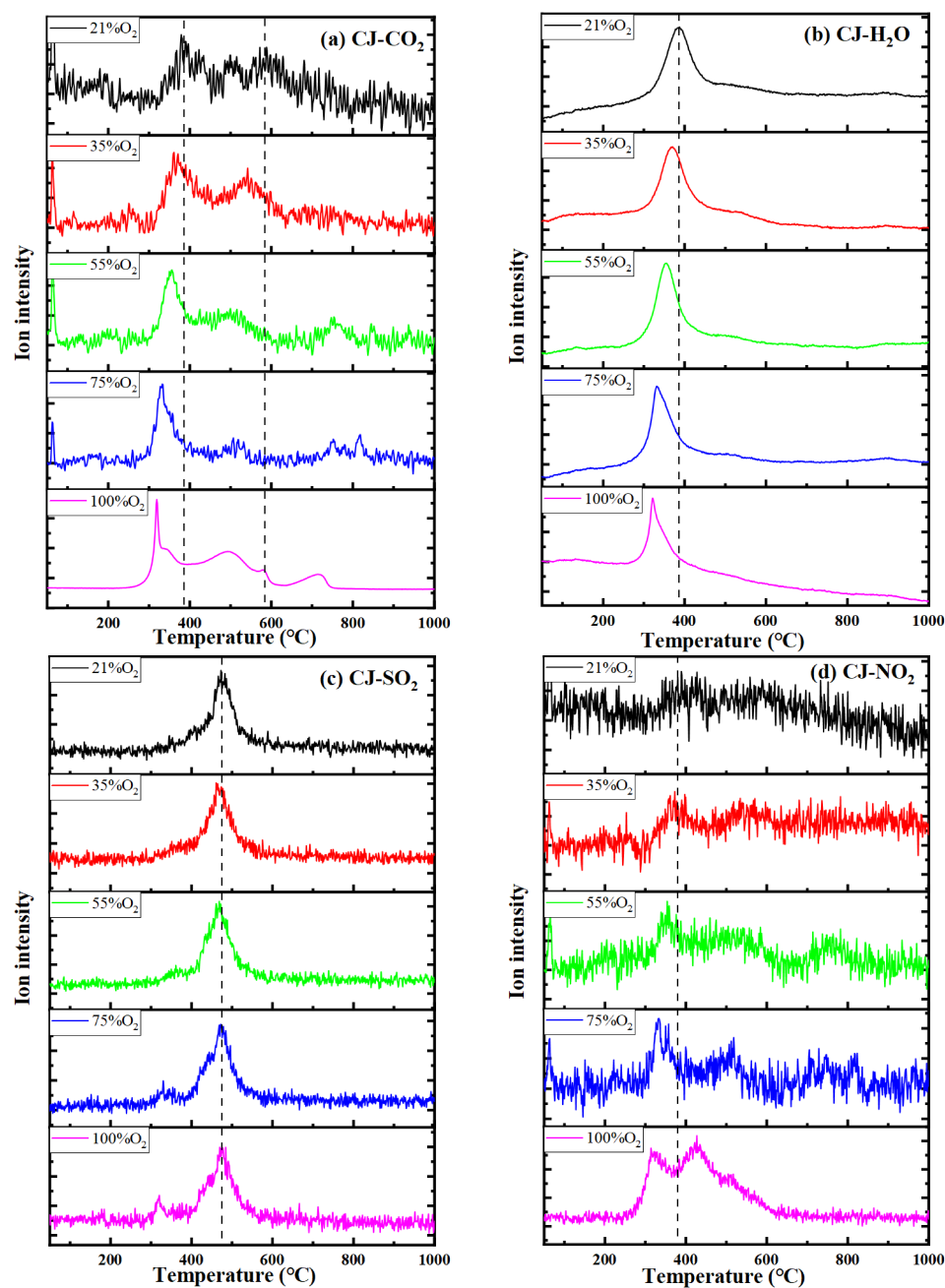


Figure 9. Evolution of CO₂, H₂O, SO₂ and NO₂ during the combustion of CJ oil shale under different oxy-fuel atmospheres.

As discussed above, the m/z 44 signal was interpreted mainly from its peak position, peak shape, and relative variation. For both CJ and FS oil shales, the CO₂ signal mainly appears in the medium-temperature region and changes clearly with O₂ concentration. As the O₂ concentration increases, the CO₂-related peak shifts toward lower temperatures, suggesting that a higher O₂ partial pressure promotes the oxidation of organic carbon and semi-char and causes carbon conversion to occur earlier. Under the 100% O₂ atmosphere, the CO₂ signal becomes more concentrated, indicating that carbonaceous components can be rapidly oxidized at lower temperatures once CO₂ dilution and diffusion limitations are removed.

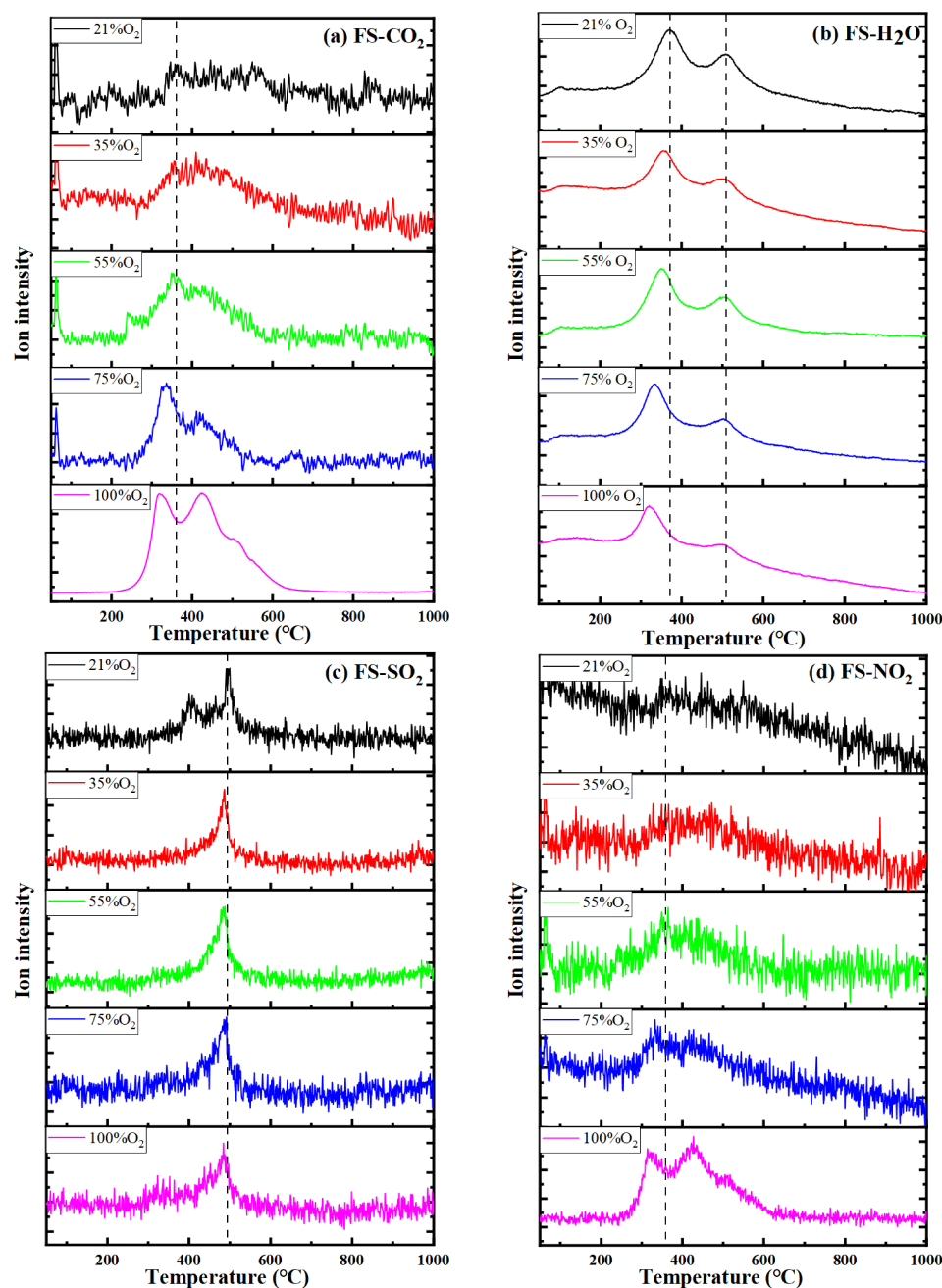


Figure 10. Evolution of CO₂, H₂O, SO₂ and NO₂ during the combustion of FS oil shale under different oxy-fuel atmospheres.

H₂O release mainly arises from the oxidation of hydrogen-containing structures, such as aliphatic side chains, hydroxyl groups, and carboxyl groups. It is also associated with the oxidation of H radicals and small hydrocarbon fragments generated during cracking. For both oil shales, the H₂O signal shows distinct peaks within 300–550 °C, which correspond well to the main mass-loss stage. As the O₂ concentration increases, the H₂O peaks move to lower-temperature regions and become more narrowly distributed. This indicates that oxygen-enriched conditions promote the oxidation of hydrogen-containing volatiles and active hydrogen species on the semi-char surface.

Compared with the CJ sample, the H₂O release curve of the FS sample exhibits two distinct peaks, suggesting a more staged conversion of hydrogen-containing structures. In contrast, the CJ sample mainly shows one prominent H₂O peak. This indicates that moisture release, volatile oxidation, and initial semi-char oxidation overlap within a

similar temperature range, without forming two clearly separated H₂O release stages. This difference reflects variations in kerogen structure, hydrogen-containing functional group distribution, and mineral composition between the two oil shales.

SO₂ release reflects the transformation of sulfur-containing structures in oil shale. As shown in the figure, the SO₂ signal is mainly concentrated in the medium- to medium-high-temperature regions. It generally appears after the main CO₂ and H₂O peaks or partially overlaps with them. This suggests that the cleavage and oxidation of sulfur-containing functional groups do not occur entirely during the initial combustion stage, but are closely related to deep kerogen decomposition and semi-char oxidation. As the O₂ concentration increases, the SO₂ peaks become progressively clearer. This indicates that a stronger oxidizing atmosphere favors the conversion of sulfur-containing structures, such as organic sulfur, thioethers, thiols, and sulfides, into SO₂. The different SO₂ peak shapes of CJ and FS oil shales further suggest differences in sulfur occurrence forms and release pathways between the two samples.

The NO₂ signal is generally weak and shows relatively large fluctuations, indicating that the release and oxidation of nitrogen-containing species are complex. Because the O₂/CO₂ atmosphere contains almost no N₂, NO₂ mainly originates from the oxidation of fuel-bound nitrogen in oil shale, rather than from thermal NO_x formation as in air combustion. During cracking, nitrogen-containing functional groups can generate NH₃, HCN, nitrogen-containing radicals, and small nitrogenous intermediates, which are subsequently converted into NO_x under oxidizing conditions. As the O₂ concentration increases, the NO₂ signal gradually strengthens and becomes more concentrated in the medium-temperature region. This suggests that oxygen-enriched conditions promote the conversion of fuel-bound nitrogen into oxidized nitrogen species. However, NO₂ formation is also jointly affected by intermediate reduction, radical reactions, and local oxygen concentration. Therefore, its evolution trend is less distinct than those of CO₂ and H₂O.

Overall, increasing the O₂ concentration promotes the earlier release of CO₂ and H₂O and enhances the oxidative formation of SO₂ and NO₂. When the CO₂ content is high, thermal dilution and restricted O₂ diffusion delay organic matter oxidation. In contrast, under high-O₂ conditions, sufficient oxygen supply facilitates the deep oxidation of volatiles, semi-char, and S- and N-containing functional groups. The evolution of gaseous products is consistent with the TG–DTG, heat flow, and combustion characteristic analyses. These results indicate that increasing the O₂ concentration shifts oil shale combustion toward lower temperatures and modifies the release and conversion pathways of carbon, hydrogen, sulfur, and nitrogen species.

4. Conclusions

This study combined TGA–DSC–MS analysis with the Vyazovkin nonlinear iso-conversional method to evaluate the combustion behavior, gaseous product evolution, and kinetic response of CJ and FS oil shales under different O₂/CO₂ atmospheres. The main findings are summarized as follows:

- (1) Replacing N₂ with CO₂ changed the thermophysical and transport properties of the combustion atmosphere. CO₂-enriched atmospheres have higher heat capacity, lower thermal diffusivity, and lower O₂ diffusion capacity. These properties weaken heat and mass transfer during the initial combustion stage and delay oil shale heating, volatile release, and initial oxidation. As the O₂ concentration increases, the thermal dilution and diffusion inhibition effects of CO₂ are gradually weakened, while oxygen supply is enhanced.
- (2) Higher O₂ concentrations enhanced the combustion behavior of both CJ and FS oil shales. As the O₂ concentration increased, the TG–DTG curves and heat flow

peaks moved to lower-temperature regions, the ignition and burnout temperatures decreased, and the comprehensive combustion characteristic index increased. Quantitatively, at $20\text{ }^{\circ}\text{C}\cdot\text{min}^{-1}$, T_{p1} and T_{p2} decreased by 26.1 and 28.2 $^{\circ}\text{C}$ for CJ oil shale and by 25.7 and 54.3 $^{\circ}\text{C}$ for FS oil shale, respectively, when the O_2 concentration increased from 35% to 100%. These changes suggest that oxygen-enriched conditions facilitated volatile oxidation and semi-char combustion. In contrast, increasing the heating rate enhanced thermal hysteresis, causing the mass-loss peaks, ignition temperature, and burnout temperature to shift toward higher temperatures.

- (3) CJ and FS oil shales show different combustion responses. The main mass-loss and heat-release processes of the FS sample are more concentrated. Its ignition and burnout temperatures are generally lower than those of CJ oil shale, and its comprehensive combustion characteristic index is higher. These results indicate that FS oil shale has better combustion reactivity. In contrast, CJ oil shale exhibits more pronounced multipeak mass-loss behavior and endothermic responses in the high-temperature region, suggesting that its later-stage reactions are more strongly affected by carbonate mineral decomposition and residual solid-phase conversion. The MS results further show that the release of CO_2 , H_2O , SO_2 , and NO_2 is mainly concentrated within 300–600 $^{\circ}\text{C}$ and shifts overall toward lower temperatures as the O_2 concentration increases. This behavior suggests that oxygen-enriched conditions facilitate the oxidative conversion of organic carbon, hydrogen-bearing structures, and S- and N-containing functional groups.
- (4) The stage-resolved apparent kinetic analysis based on the Vyazovkin method shows that E_{α} varies with conversion for both oil shales, confirming that their combustion cannot be described by a single lumped reaction. The medium-conversion region is associated with volatile release, rapid oxidation, and semi-char combustion, whereas the high-conversion region is increasingly influenced by residual semi-char, stable organic structures, and mineral transformation. Therefore, the E_{α} values obtained in this study should be interpreted as conversion-dependent apparent kinetic descriptors rather than intrinsic kinetic constants of the entire oil shale sample.

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