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Experimental study of low-temperature combustion characteristics of shale rocks

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ABSTRACT

Relatively low temperature (500 °C) combustion has been applied to shale rocks collected from Lianmuqing, Xinjiang Province, China, to improve the permeability of shale without pore structure change caused by mineral decomposition. The shale rocks were firstly grinded into small particles, then burned in a furnace at a constant temperature of 500 °C for 5 min, 15 min, and 30 min, respectively. A cylindrical shale sample was also subjected to the combustion experiment. It was found that thermal cracking occurred along the height of the shale as combustion propagated from bottom to top. From the low-temperature nitrogen adsorption test, it was found that the pore diameters of shale samples were in the range of 2–50 nm, which were less than the mean free path of an oxygen molecule. Thus, the diffusion of gas inside the shale was Knudsen diffusion and the Knudsen number (K_n) was between 8 and 25. Moreover, the mean diameter of shale pores and the effective diffusion coefficient increased with increasing oxidization time. Whereas the surface area decreased after combustion, the diameter of the shale particles remained constant. So the density of the shale decreased with increase of combustion time. According to the porous media combustion model, the oxidization of shale particles was considered to be in Regime I, which is under kinetic control at isothermal combustion condition (500 °C). Furthermore, the effective diffusion coefficient was in a range of 3×10^{-6}–6×10^{-6} m^2/s. It increased with increasing combustion duration, especially during the first five minutes. The experiment results showed that low temperature combustion can effectively improve shale permeability to facilitate gas extraction from shale reservoir.

1. Introduction

As an unconventional gas, shale gas has attracted increasing attention due to its large reservoir globally, especially in China [2,3]. Shale gas accounts for a large portion of the total gas production in the United States and its use is increasing. Organic rich mudstone/siltstone (i.e., shale) contains retained hydrocarbons generated over a long geologic time with total organic matter (TOM) stored inside the matrix [4,5]. The soluble part of the TOM is classified as bitumen, and the insoluble part is kerogen [4]. The organic rich shale was considered to be fine-grained sedimentary deposits with large compositional heterogeneity, and it was recognized as complex and heterogeneous porous media [1,6]. Shale normally has intricate pore systems, with various pore types and geometries [7]. Gas in the shale matrix can be classified into three categories [6]: (1) a free state in pores and fractures; (2) an adsorbed state on the surface or inside organic matter and minerals; and (3) a dissolved state in organic matter and water. Depending on the depth of burial, shale permeability varies between micro-Darcy range and nano-Darcy range [4,8]. A shale matrix has predominantly micro-pores (diameter < 2 nm) and meso–pores (diameter of 2–50 nm) [9]. Recently, hydraulic fracturing and supercritical CO_2 technologies have made the recovery of natural gas from shale more economically viable [10]. However, the low matrix permeability of shale in China and the lack of water resources are the main challenges for large-scale gas extraction. Moreover, hydraulic fracturing has negative effects on environment, such as underground water contamination which threatens ecological balance [1]. To find an alternative to hydraulic fracturing, researchers started using combustion to remove the organic matter in shale to increase rock permeability [11]. The TOM in shale was considered to be a reactive porous media [12], and its weight percentage was found to range from poor to excellent ((poor (less than 0.5%),

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Nomenclature

BET	Brunauer–Emmett–Teller
B_v	Pre-exponential factor
D_{eff}	Effective diffusion coefficient
D_k	Diffusion coefficient
d_p	The diameter of shale pore
d_s	The diameter of shale particle
FLIR	Forward Looking Infrared
K_n	Knudsen number
k_v	The specific reaction rate constant for volatile release
m_c	The mass of fixed carbon
$m_{og,0}$	Initial organic matter
m_v	The mass of volatile species
$\dot{m}'''$	Mass consumption rate
$\dot{m}_c$	Fixed carbon combustion rate
$\dot{m}_{v,g}$	Gaseous combustion rate
$\dot{m}_{v,s}$	Remaining volatile combustion rate
R_h	Characteristic pore diameters
R_o	Vitrinite reflectance
S_v	Surface area per unit volume
TOM	Total organic matter
ν_{o_2}	Stoichiometric coefficient
XRD	X-ray diffraction
Y	The mass fraction of species
Y_{o_2}	The mass fraction of oxygen in free stream
$Y_{produces}$	The mass fraction of product
Y_w	The mass fraction of oxygen at ambient at wall
Y_∞	The mass fraction of oxygen at ambient
α	The percentage of organic matter released as vapor
ε	Porosity
η_{eff}	Effective factor
λ	Mean free path
ρ	The density of shale particles
ρ_p	The density of shale at time t
τ	Tortuosity

fair (0.5–1%), good (1–2%), very good (2–4%) and excellent (more than 4%)) [4]. In contrast, oil shale normally contains 20%–50% organic matter [13]. It is organic rich sedimentary rock containing various amounts of insoluble organic substance (eg., kerogen). When heated, liquid hydrocarbons (shale oil) can be released from the oil shale. As a result, liquid hydrocarbons are the main products of oil shale. However, shale is usually mature rock formation in the thermogenic gas window. By applying the fracturing technology, the trapped gas can be extracted from the shale. So the product from the exposition of shale is nature gas (mainly CH_4). The TOM has large surface area and is permeable to a variety of fluids, such as air and water. The organic matter becomes combustible if an oxidizer is supplied under high temperature [14]. The diameter of the pores significantly affects the O_2 diffusion inside the shale. According to Loucks et al., shale pores mainly consist of three basic types: (1) organic pores inside organic matter; (2) interparticle pores between grains and crystals; and (3) intraparticle pores inside mineral particles [15,16]. At low-temperature combustion (400–500 °C), the organic pores could be removed through the oxidization of the organic matter [1]. At relatively high temperature (> 600 °C), both the volume and diameter of the intraparticle pores were reported to increase because of the decarbonation and organic oxidization inside the shale [17]. Thus high-temperature combustion can significantly increase pore connectivity [18].

Regarding porous media combustion, extensive research studies have considered porous combustion of coal and biomass particles in the past several decades. The combustion of char was classified into three regimes (Regime I, II, and III), depending on the penetration depth of the reactants into a porous solid [19,20]. In Regime I, particle mass reduction occurs at low temperature. Mass loss rates are determined by chemical reaction rates, and each particle reacts quite uniformly throughout its volume. Particle mass loss would not change its diameter while particle density decreased due to chemical reaction [21]. Different from char, the weight percentage of fixed carbon in shale is very low, usually less than 5%. Interparticle pores mainly exist in inorganic matters. To date, little work has been performed to understand the behavior of shale combustion. Early work and most of the current work focused on oil shale combustion process as well as the ignition and self-heating behavior of oil shale [12]. For porous oil shale, the combustion process generally includes five steps: (1) moisture evaporation, (2) release of volatile matter, (3) low-temperature oxidation of organic matter, (4) high-temperature oxidation of fixed carbon and remaining volatile matter, and (5) decomposition of carbonate minerals [22]. Homogeneous combustion occurs during low-temperature stage (gaseous volatile oxidization) while in high-temperature stage, homogeneous combustion gradually shifts to heterogeneous combustion (fixed carbon and residual volatile oxidization) [13]. The oxidation of the organic matter inside oil shale provided energy for the combustion front propagation inside the oil shale [23]. In addition, the pyrolysis of large amount of volatile increased pressure inside the particles, causing the pore mouths to open in the main combustion stage [24]. Moreover, inorganic minerals not only had catalytic effect to further oxidize organic matter but also created additional porosity (the presence of inorganic framework) after oxidation, which significantly decreased the resistance of oxygen diffusion into the inner of oil shale [25].

However, few studies have been conducted on shale combustion. The combustion behaviors inside the shale, such as gas flow diffusion, reaction kinetics, and internal pressure variation during combustion are to be understood. The main purpose of shale combustion is to improve the permeability (eg., interconnectivity of pore and fracture system) inside shale reservoir to promote the gas transportation condition for large scale gas extraction by removing organic matter and producing micro fractures. In this study, low-temperature combustion characteristics of shale from Lianmuqing, Xinjiang, China were investigated. The fundamental combustion behaviors of small size shale particles and a cylinder-shaped shale sample were studied. The effect of combustion time on gas shale microstructure changes and Brunauer–Emmett–Teller (BET) surface areas was investigated. Moreover, the changes in the shale particle size before and after combustion were also analyzed. Effective diffusion coefficients were calculated based on the experimental data.

2. Fuel properties and preparation

In this study, the raw shale samples (Fig. 1) were collected from Xingjiang Province, China. This area has large desert areas with very limited water sources. The rocks in this area are mainly composed of mudstone and siltstone. The stratum of shale samples belongs to the Lianmuqin formation. The lithology of the shale is purple sandy mudstone and mudstone, which are seriously eroded and have weak cementation and poor diagnosis. After being grinded into small particles (Fig. 1), the samples were sent to a commercial laboratory for proximate analysis, thermal conductivity measurement, and other geochemical tests. The proximate analysis and other physical properties of the shale are given in Table 1.

2.1. Mineral composition

For shale rocks, the main inorganic matter species are quartz, clay, carbonate, feldspar, and apatite [26]. The porosity of shale