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Oxyfuel technology: Oil shale desulfurization behavior during staged combustion

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HIGHLIGHTS

- First investigation on oil shale desulfurization under staged firing.
- Significant reduction in SO_2 emissions is obtained by limestone injection.
- A significant difference exists in sulfation during staged and unstaged combustion.
- Desulfurization efficiency is affected by oxidant-stage level.
- Oxyfuel technology is highly recommended for oil shale combustion.

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ABSTRACT

A high sulfur content in Jordanian oil shale is considered one of the biggest challenges preventing its full utilization. To resolve this issue, direct limestone injection during staged combustion has been investigated for the simultaneous control of NO and SO_2 emissions. Staged El-Lajjun oil shale combustion under oxyfuel conditions and conventional air-firing conditions was performed at 1200 °C in a 20-kW vertical reactor. Limestone was mixed with oil shale before combustion. Three different molar ratios of Ca/S, three different burner oxygen ratios (0.75, 0.85 and 0.95) and different positions of the burnout oxidant probe were tested in both firing conditions to determine the optimum conditions for the lowest SO_2 and NO emissions. The SO_2 emissions were significantly lowered by adding limestone during staged air-firing and OF27 (27% O_2/73% CO_2 environment) combustion. The desulfurization efficiencies ranged from 32 to 61% and from 25 to 60% during the staged air-firing and staged OF27 combustion, respectively. The staging level, the Ca/S molar ratio and the position of the secondary oxidant are important parameters that affect the desulfurization efficiency. Higher desulfurization efficiencies were obtained during OF27 combustion compared with air-firing at burner oxygen ratios of 0.85 and 0.95. At a burner oxygen ratio of 0.75, the opposite trend was observed. The SO_2 emissions during staged combustion were significantly higher than those during unstaged combustion in air and during OF27 combustion. This was due to high competition among many reactions, which minimized the desulfurization efficiency. The maximum desulfurization efficiency during staged OF27 combustion was 60% with $\lambda = 0.85$ and Ca/S = 2 at 1 m from the burner. During air-firing combustion, the maximum desulfurization efficiency was 61% with $\lambda = 0.85$ and Ca/S = 3 at 1.5 m from the burner. Based on the current and previous studies, the authors recommend that oxyfuel technology be used for oil shale combustion so that CO_2, SO_2 and NO_x emissions can be simultaneously controlled.

1. Introduction

Oil shale is a future energy source of Jordan. However, oil shale combustion causes serious air pollution due to the high sulfur content in oil shale. This is considered a significant challenge that prevents the full utilization of the resource. The presence of sulfur in

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fuel and its subsequent release as gaseous compounds are associated with high temperature corrosion of furnace walls and heat exchangers and low temperature corrosion in economizers and pre-heaters [1]. Sulfur exists as organic and inorganic compounds in oil shale [2]. Inorganic sulfur is mostly present as pyrite or marcasite and may also be present as small amounts of sulfates depending on the oil shale grade [3]. Organic sulfur exists in aromatic rings or in aliphatic functional groups, e.g., mercaptans, aliphatic and aryl sulfides, disulfides and pyritic sulfur, depending on the rank and total sulfur content of the oil shale [4].

Carbon dioxide released from fossil fuel combustion has been implicated as a major cause of climate change. The oxyfuel process has emerged as a promising option for combination with carbon capture and storage (CCS) technologies. During the oxyfuel process, more than 95 vol.% pure oxygen diluted with CO_2 recycled flue gas with or without H_2O is used for fossil fuel combustion. Part of the CO_2 flue gas is recycled back to the furnace to maintain the temperature and heat flux profiles and to entrain the pulverized fuel. As a result, the concentration of carbon dioxide in the exhaust gas is significantly increased, and the recovery of CO_2 becomes feasible with a lower-efficiency penalty [5]. Oxyfuel combustion impacts the combustion process and other processes, such as heat transfer, by varying the oxidant and consequently the in-furnace gas environment (compare with conventional air-firing). Accordingly, the gas compositions and flame characteristics during fossil fuel combustion under oxyfuel conditions are expected to influence the emission behavior and associated formation mechanisms of SO_x species [1]. An oxyfuel process that uses recycled flue gas typically yields higher concentrations of SO_2 (ppm) but lower emission rates of SO_2 (mg/MJ) than conventional pulverized coal combustion [6–10].

Among the various types of desulfurization technologies, sulfur removal in furnaces is an attractive option for controlling SO_x pollutants due to low capital and operating costs. Sulfur absorbents include coal calcium, which may be present as minerals such as calcite, as calcium ions in the coal matrix, or as calcium stones, such as limestone and dolomite, which may be injected in post-flame regions of furnaces [11]. A detailed desulfurization background during unstaged combustion has been presented [12]. The inhibitory influence of high CO_2 and SO_2 partial pressures on the calcination of limestone has been confirmed [13,14]. Al-makhadmeh et al. [12] studied direct limestone injections during unstaged combustion under oxyfuel and air-firing conditions for Jordanian oil shale. They found that the conversion rates of sulfur in oil shale to SO_2 were lower during unstaged oxyfuel combustion than during air-firing. The conversion rates were 61%, 49%, and 58% for air-firing, OF27, and OF35 combustion, respectively. Significant reductions in SO_2 emissions were obtained by adding limestone in both combustion modes. At a Ca/S molar ratio of 3, the desulfurization efficiencies were increased to 95%, 100% and 93% for air-firing, OF27, and OF35 combustion, respectively.

Air-staged combustion as a means to reduce NO_x emissions has been widely investigated. Air-staged combustion involves the supply of the total combustion air weight in two stages. The combustion occurs in two zones. In a first combustion zone (primary combustion zone) where the burner oxygen ratio is less than 1, the oxygen availability and flame temperature are reduced, resulting in low thermal-NO_x and fuel-NO_x formations. In a second combustion zone (burnout zone), combustion occurs in an oxidant-rich atmosphere, and unburned fuel and CO formed in the primary combustion zone are combusted. A staged calcium-based absorbent injection process has recently been proposed to control SO_x emissions [15–17]. During staged combustion, CaS is formed in the high temperature and reducing primary combustion zone. Then, CaS is further converted to $CaSO_4$ or SO_2 in the low temperature and oxidizing burnout zone [11,15]. Torres-Ordonez and Klein [2] performed thermodynamic calculations on the retention of sulfur by calcium for the combustion of Illinois No. 6 and Wyoming coals. They reported that CaS was the favorable form of the calcium solid product at fuel-rich conditions and high temperatures (T = 2000 K), while $CaSO_4$ was the favorable form at fuel-lean conditions and low temperatures (T = 1500 K). This method enhanced in-furnace desulfurization efficiencies to 80–85% [2,11]. Unfortunately, few studies have examined the reduction of SO_2 emissions by limestone in pulverized coal staged combustion. More research is required to confirm the mechanism of SO_2 reduction under staged combustion conditions [18]. No studies have examined SO_2 reduction for oil shale combustion.

This work aims to determine the optimum conditions for lowered NO and SO_2 emissions from high-sulfur content Jordanian oil shale combustion under air and oxyfuel conditions. Direct limestone injection was investigated during staged combustion with different parameters in a 20-kW vertical furnace. Simulations could not be used to model actual oxyfuel conditions with SO_2 injection due to the analysis limitations at the high SO_2 concentration range. The SO_2 concentration in the furnace during 27% O_2/73% CO_2 combustion did not represent the SO_2 concentration of an actual oxyfuel plant with flue gas recirculation because there was no accumulation of SO_2 in the furnace.

2. Experimental

2.1. Materials

The oil shale sample used in this study was obtained from the El-Lajjun area in Jordan. Proximate and ultimate analyses, heating value, ash major and minor elements and size distribution measurements were made, and the results are shown in Tables 1 and 2. The particle size was D_{90} = 35.3 μm (D_{90}: represents the diameter at which 90% by volume of the particles have a diameter equal to or less than D_{90}). Limestone samples with 96 wt.% $CaCO_3$ were ordered from Kalk-Laden & Kalk-Schule. The chemical compositions of the samples were determined using RTG fluorescence as previously presented [12].

2.2. Experimental parameters and approach

The combustion of the El-Lajjun oil shale was performed in a 20-kW vertical furnace as shown in Fig. 1. Details of the furnace

Table 1
Proximate and ultimate analyses of El-Lajjun oil shale.

Proximate analysis	
Water (ar, %)[a]	1.08
Ash (wf, %)[b]	54.20
Volatile (waf, %)[c]	99.06
Fixed carbon (waf, %)[d]	0.85
Ultimate analysis	
C (waf, %)	55.68
H (waf, %)	4.27
N (waf, %)	0.87
S (waf, %)	8.30
O (diff, %)[d]	30.88
LHV (waf, kJ/kg)	19585.15
Size distribution	
D_{10} (μm)[e]	1.25
D_{50} (μm)	9.86
D_{90} (μm)	35.3

[a] As received.
[b] Water free.
[c] Water ash free.
[d] By difference.
[e] Di: represent that i% by volume of the particles that have a diameter equal to or less than Di.