



Chemical looping coal gasification with calcium ferrite and barium ferrite via solid–solid reactions



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HIGHLIGHTS

- BaFe₂O₄ and CaFe₂O₄ are excellent for chemical looping coal gasification.
- BaFe₂O₄ and CaFe₂O₄ have minimal reactivity with synthesis gas.
- Steam enhances the gasification process with these oxygen carriers.
- Reaction rates of steam gasification of coal with CaFe₂O₄ was better than with gaseous oxygen.
- Coal gasification appears to be via solid–solid interaction with the oxygen carrier.

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ABSTRACT

Coal gasification to produce synthesis gas by chemical looping was investigated with two oxygen carriers, barium ferrite (BaFe₂O₄) and calcium ferrite (CaFe₂O₄). Thermo-gravimetric analysis (TGA) and fixed-bed flow reactor data indicated that a solid–solid interaction occurred between oxygen carriers and coal to produce synthesis gas. Both thermodynamic analysis and experimental data indicated that BaFe₂O₄ and CaFe₂O₄ have high reactivity with coal but have a low reactivity with synthesis gas, which makes them very attractive for the coal gasification process. Adding steam increased the production of hydrogen (H₂) and carbon monoxide (CO), but carbon dioxide (CO₂) remained low because these oxygen carriers have minimal reactivity with H₂ and CO. Therefore, the combined steam–oxygen carrier produced the highest quantity of synthesis gas. It appeared that neither the water–gas shift reaction nor the water splitting reaction promoted additional H₂ formation with the oxygen carriers when steam was present. Wyodak coal, which is a sub-bituminous coal, had the best gasification yield with oxygen carrier–steam while Illinois #6 coal had the lowest. The rate of gasification and selectivity for synthesis gas production was significantly higher when these oxygen carriers were present during steam gasification of coal. The rates and synthesis gas yields during the temperature ramps of coal–steam with oxygen carriers were better than with gaseous oxygen.

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1. Introduction

Capturing carbon dioxide (CO₂) from power plants that use fossil fuels is one of several strategies to reduce global CO₂ emissions. The task of removing CO₂ from power plant flue gas is challenging because existing methods to separate CO₂ from the gas mixture require a significant portion of power plant output. The separation task can be simplified by replacing conventional air with pure oxygen so that the products from this combustion are just CO₂ and water, which could be easily separated by condensation. However,

current commercial techniques for producing oxygen from air require very energy-intensive cryogenic processes. Chemical looping combustion (CLC) is a novel combustion technology that utilizes an oxygen carrier [1–3], such as metal oxide, to transport oxygen from air to fuel, thereby avoiding direct contact between fuel and air. The significant advantage of CLC over conventional combustion is that CLC can produce a sequestration-ready CO₂ stream—not diluted by nitrogen (N₂)—without expending any major energy required for the separation of CO₂. The overall CLC process, in which the metal oxide cycles between oxidized and reduced states, is exothermic.

Significant work has been reported on oxygen carrier development [4–13], reactor design [12–22] and thermodynamic

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efficiency [12,20,22,23] related to coal CLC. Due to these continued efforts, CLC concept has been progressed from laboratory scale to pilot-scale demonstrations [3,20]. Oxygen carrier development has been considered as one of key issues for CLC development. Several single metal oxides and bi-metallic oxides have been reported in the literature as oxygen carriers [3,12]. We have reported a promising bi-metallic oxygen carrier containing cupric oxide (CuO) and iron oxide (Fe₂O₃) for both methane (CH₄) and coal CLC [4,5]. Current research on oxygen carrier development is mainly focused on the modification of CuO, Fe₂O₃, MnO₂ and CaSO₄ materials to obtain stable and high reactivity, to lower the cost and to minimize environmental impacts. Recent economic evaluation study suggested that CLC system has very high CO₂ capture efficiencies, equivalent to a specific CO₂ release of 43 g/kW h which is significantly higher than that of current commercial processes used in CO₂ capture such as amine and physical adsorption processes [24,25].

Beside the combustion reaction, chemical looping concepts have been proposed to produce hydrogen or synthesis gas from methane, coal and biomass [13,26–58].

Preliminary energy/economic evaluation based on H₂ production from chemical looping reforming (CLR) of methane indicated that positive environmental impact compared to traditional methane reforming-water gas shifting scheme [26,27]. Our previous study on CLC of methane integrated with methane decomposition/carbon steam gasification reaction [26] showed a unique way of using Cu–Fe oxides as both an oxygen carrier in chemical looping combustion and a catalyst for methane decomposition reaction to produce H₂ and synthesis gas. Various metal (Cu, Fe, Ni) oxides and calcium sulfate (CaSO₄) have been tested and simulated in a CLR system for hydrogen/syngas production. In most of these studies oxygen carriers were used for partial oxidation of methane to produce synthesis gas and reduced oxygen carrier was oxidized with steam to produce H₂ [28,29]. Oxygen carriers based on cerium oxide [29–31] and perovskites containing lanthanum [32–34] have been used for methane partial oxidation to produce only synthesis gas. In addition, direct methane reforming using steam and oxygen carriers, CuO, Mn₂O₃, NiO and Fe₂O₃ supported on SiO₂ to produce synthesis gas has been reported by Zafar et al. [35]. Methane reforming with steam using Ni based oxygen carriers has been reported by De-diego et al. [36]. Ryden et al. [37] reported an inter-connecting fluid bed reactor with NiO/MgAl₂O₄ for methane reforming to form synthesis gas.

Biomass gasification using oxygen carriers have also been reported. Iron based oxygen carriers have been used to increase synthesis gas production rate and this rate improvement has been attributed to tar reforming and tar-cracking process by the oxygen carrier during biomass gasification [38–43]. Similarly, tar cracking and improved biomass gasification have been reported with Ni based oxygen carriers [44–47]. Ilmenite and Mn based oxygen carriers have also been used for biomass gasification [46,47]. CaO [48] has also been used in biomass chemical looping gasification to promote CO₂ sorption and tar cracking.

A method [49–54] to produce H₂ from coal using a chemical looping process has also been reported. In this process, oxygen carriers such as iron oxide were reduced with coal derived synthesis gas and reduced oxygen carrier was oxidized with steam to produce H₂.

There are only limited studies [13,55–58] in the literature on using oxygen carriers to produce synthesis gas via coal gasification. Direct coal gasification using steam and oxygen carriers is difficult since the oxygen carrier can further oxidize the synthesis gas produced by steam gasification to form CO₂ and water (H₂O) making it difficult to control the reaction to selectively produce synthesis gas.

In the present study, we are reporting coal gasification using novel oxygen carriers, barium ferrite (BaFe₂O₄) and calcium ferrite

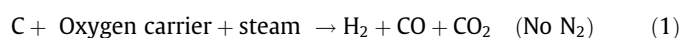
(CaFe₂O₄). These materials have unique properties: they can react with coal directly via solid–solid reactions to produce synthesis gas and the materials have minimal reactivity with synthesis gas. This makes it very favorable for the coal gasification process because gas produced during coal gasification remains as synthesis gas without getting further oxidized to CO₂ and H₂O. These materials also perform well in the presence of steam.

Guo et al. [55] reported synthesis gas generation by coal chemical looping gasification using surface Ca-doped iron based oxygen carriers in a fluidized-bed reactor. They reported that Fe₂O₃ was partially reduced to FeO during coal/steam gasification, and a H₂/CO ratio of 12:1 was observed. When Fe₂O₃ was used as the oxygen carrier, the volume concentration of the synthesis gas was lower than that without the oxygen carrier since iron oxide reacts with the synthesis gas produced by coal–steam gasification. When CaO was present with Fe₂O₃ the H₂ volume concentration and carbon conversion increased and authors have reported that this is due the catalytic effects of CaO. The reaction sequence in their work is different from the present work with barium ferrite and calcium ferrite since their experiments were performed in a fluidized bed reactor and hence the solid–solid interactions were minimal. In addition, barium ferrite and calcium ferrite directly participated in the gasification reaction increasing the synthesis gas production from coal/steam without consuming the synthesis gas produced by coal/steam gasification.

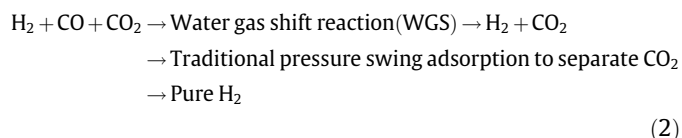
Liu and Guo [56] investigated coal gasification using calcium sulfate (CaSO₄) in a fixed-bed reactor and the syngas had a H₂/CO ratio of 1.6:1. Their thermodynamic analysis indicated that for an auto-thermal system, the CaSO₄ to C ratio should be higher than 0.2. They also observed that the syngas yield with the oxygen carrier was less than that without the oxygen carrier due to the reaction of syngas with CaSO₄ which is different from the observations with barium ferrite and calcium ferrite in our present study. Liu et al. [57] also showed that CO₂ can promote the reaction between coal and CaSO₄.

White et al. [58] described a dual fluidized bed reactor for coal gasification using various oxygen carriers and they indicated that Fe₂O₃, Fe₃O₄, MnOx, CoOx, NiOx, FeTiO₃, CaCO₃, CaO and Mn_{1-x}Cu_xO_y and Mn_{1-x}Fe_xO_y may be suitable oxygen carriers for coal gasification. Andrus Jr. et al. [13] described a coal gasification reactor system to produce synthesis gas and hydrogen (H₂) based on CaSO₄ oxygen carrier. It should be noted that most of these oxygen carriers can react with synthesis gas which is different from the barium ferrite and calcium ferrite reported in the present study.

Synthesis gas produced by coal gasification with steam and oxygen carrier as shown in reaction (1) can be used for many important applications since the gas stream is free of N₂ unlike the synthesis gas produced from traditional gasification using gaseous O₂ in air.



This N₂-free synthesis gas can be used to produce pure H₂ as shown in reaction Scheme (2).



A synthesis gas stream, without N₂, with catalysts can also be used to produce useful chemicals as shown in reaction Scheme (3) and (4).



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