Applied Energy 145 (2015) 354–363

Contents lists available at ScienceDirect

Applied Energy

journal homepage: www.elsevier.com/locate/apenergy

Parametric and dynamic studies of an iron-based 25-kW_{th} coal direct chemical looping unit using sub-bituminous coal

Samuel Bayham, Omar McGiveron, Andrew Tong, Elena Chung, Mandar Kathe, Dawei Wang, Liang Zeng [1], Liang-Shih Fan *

William G. Lowrie Department of Chemical and Biomolecular Engineering, 151 West Woodruff Avenue, Columbus, OH 43210, United States

HIGHLIGHTS

- Integrated, moving bed chemical looping reactor with iron-oxide based oxygen carrier.
- Coal carbon conversion from 84.8% to 99.9%, thermal capacity 7.4 to 27.7 kW_{th}, O_2 demand less than 1.3%.
- Dynamic temperature of moving bed reducer is established and tracked during coal injection.
- CH_4 and CO present at initial coal injection, eliminated after oxygen carrier activated.
- Lower coal injection had higher volatiles residence time and conversion.

ARTICLE INFO

Article history:
Received 19 September 2014
Received in revised form 3 February 2015
Accepted 8 February 2015
Available online 5 March 2015

Keywords:
Chemical looping combustion
Coal
CO_2 capture
Energy
Iron oxide
Moving bed

ABSTRACT

The iron-based Coal-Direct Chemical Looping (CDCL) combustion process is an alternative to conventional oxy-combustion technologies, where the oxygen used for fuel conversion in the CDCL process is provided by an iron-oxide based oxygen carrier instead of an air separation unit. The iron oxide is reduced using coal in the reducer reactor, producing highly-pure CO_2 in the flue gas, and the reduced iron oxide is regenerated in a separate combustor reactor using air. The CDCL process at Ohio State has been developed and demonstrated in a 25 kW_{th} sub-pilot unit, and it is the first chemical looping demonstration unit with a circulating moving bed reactor for solid fuel conversion. To date, the CDCL sub-pilot unit at OSU has been operated for more than 680 h, with a 200-h continuous operation, providing important data on long term operability as well as parametric optimization. This paper discusses recent parametric operational experience with sub-bituminous coal as the fuel, where dynamic changes in variables were performed to observe the effects on the unit itself. Measurements included temperature, pressure, and gas concentrations from the reducer and combustor. Furthermore, effects of different variables, such as flue gas recycle ratios (enhancer gas flow rates), feed port injection, and temperature, were observed. Tests confirmed high coal conversions with high purity of CO_2 achieved in the flue gas. Overall, the moving bed design of the reducer results in nearly full coal conversion with a high purity of CO_2, eliminating the need for additional down-stream fuel polishing and/or separation units. The combustor gas contained lean oxygen concentrations with minute amounts of carbonaceous gases detected, indicating proper regeneration of the oxygen carrier as well as good gas sealing between the reducer and combustor.

1. Introduction

It is widely known that anthropogenic carbon dioxide in the atmosphere has been linked to global warming [1], and in recent years, it has been proposed that fossil-fuel power plants should capture the carbon produced and store it underground so that it is not added to the atmosphere to contribute to global warming. However, many present post-combustion capture technologies are capital intensive, have high energy penalties, and are difficult, if not infeasible, to retrofit to many present-day power plants. Chemical looping combustion is considered a promising technological alternative to direct fuel combustion because of its inherent ability to produce electricity from carbonaceous fuels without a significant carbon dioxide separation penalty [2–6].

In recent years, there has been an interest in solid fuel systems for chemical looping processes because of the ability to convert

* Corresponding author. Tel.: +1 (614) 688 3262.
E-mail address: fan.1@osu.edu (L.-S. Fan).
[1] Current address: School of Chemical Engineering & Technology, Tianjin University, Tianjin, China.

http://dx.doi.org/10.1016/j.apenergy.2015.02.026
0306-2619/

Nomenclature

η_{CC}	the number of moles of carbon emitted from the reducer versus the total moles of carbon emitted from the CDCL reactor
η_{OO}	the ratio of oxygen used to oxidize the OC in the combustor to the total amount of oxygen used in the combustor
ϕ	the number of moles of oxygen needed to combust one mole of coal
f_{CO_2}	on a nitrogen and moisture free basis, the purity of carbon dioxide generated at the reducer outlet
F_C	the molar flow rate of carbon into the reducer from coal
$F_{C,C}$	the molar flow rate of carbon at the combustor outlet
$F_{C,R\ coal}$	the molar flow rate of carbon from coal at the reducer outlet
$F_{CO_2,C}$	the molar flow rate of carbon dioxide at the combustor outlet
$F_{CO_2,R\ coal}$	the molar flow rate of carbon dioxide from coal at the reducer outlet
$F_{i,C}$	the molar flow rate of gaseous species i at the combustor gas outlet
$F_{i,R}$	the molar flow rate of gas species i at the reducer gas outlet
$F_{O_2,C\ used}$	the molar consumption of oxygen in the combustor
$F_{N_2,R\ injected}$	the molar flow rate of nitrogen injected into the reducer
$F_{total,R}$	the total molar flow rate of gases at the reducer outlet
Ω_{OD}	the amount of oxygen needed to combust any unburnt volatile species at the reducer outlet
$X_{C,C}$	the fraction of coal carbon carried over to the combustor
$X_{C,R}$	the coal carbon conversion based on the carbon dioxide generation at the reducer outlet
$X_{C,R\ O_2\ Demand}$	the coal carbon conversion in the reducer based on the oxygen demand
$x_{i,R}$	the molar fraction of gas species i at the reducer outlet

fuel directly without a need for external gasification or air separation [7–14]. As a result, the Ohio State University has developed the iron-based Coal Direct Chemical Looping (CDCL) process, shown in Fig. 1. The iron-based CDCL process converts solid fuels into electricity with in-situ carbon capture by reducing and oxidizing iron oxide based oxygen carrier particles in separate reactors without using a traditional gasifier and an energy-intensive air separation unit. Like most chemical looping combustion processes, the system consists of a reducer reactor, which converts the fuel into carbon dioxide and reduces the oxygen carrier, and a combustor reactor, which reoxidizes the oxygen carrier with air. The reaction in the combustor is exothermic, and the energy from the combustor as well as the both flue gas streams is recovered for the steam cycle for electricity generation.

Many chemical looping processes use a fluidized bed for the reducer reactor. Two integrated, circulating fluidized bed units with a designed fuel capacity of 10 and 100 kW_{th} for solid fuels have been designed and constructed at Chalmers University in Gothenburg, Sweden, with initial demonstrations performed on the 10 kW_{th} unit using fuels such as petroleum coke and a South African coal [15]. Oxygen carrier materials tested in the 10 kW_{th} unit include ilmenite, a manganese ore [16], ilmenite ore with lime, and manganese ore with lime mixtures [17]. Further work with the 100 kW_{th} unit includes tests with an ilmenite oxygen carrier and fuels such as Mexican petroleum coke and a Columbian bituminous coal [9,13,18–20]. The fate of pollutants such as sulfurous and nitrous species was also studied in the 100 kW unit at Chalmers University [21]. Hamburg University of Technology has developed and commissioned a 25 kW_{th} solid fuel CLC unit. To allow for a better fuel conversion, particularly for the volatiles, the fuel reactor was designed as a two-stage fluidized bed [12]. Tests include work with oxygen carriers such as Australian ilmenite and a synthesized CuO/Al_2O_3 oxygen-uncoupling material [12]. A 10 kW_{th} integrated chemical looping combustion unit was designed and constructed at Southeast University, China, for the purpose of converting biomass and coal using both iron oxide [22] and nickel oxide [23] as oxygen carriers. The fuel reactor consists of a spouted fluidized bed, which has the advantage of a longer solids residence time. As opposed to the 10 kW_{th} Chalmers University process, the solid fuel in the Southeast University reactor is conveyed into the bottom of the reducing reactor with carbon dioxide and steam instead of at the top. Southeast University has also studied using iron and calcium mixtures as an oxygen carrier for chemical looping in a fixed bed reactor [24]. A 1.5 kW_{th} chemical looping oxygen uncoupling (CLOU) demonstration reactor has been built and operated at the Instituto de Carboquímica in Zaragoza, Spain, with chemical looping oxygen uncoupling and ilmenite oxygen carriers [25], with further studies including work on the fate of sulfur with lignite coal using a 60% CuO and $MgAl_2O_4$ spinel oxygen carrier at temperatures around 930 °C [26]. Although promising new mixed-metal perovskite oxygen carriers have been mostly tested with gaseous fuels such as methane [27–30], perovskite oxygen carriers have also been tested with Mexican petroleum coke and Columbian coal in a batch fluidized bed [31]. It was found that gaseous sulfur species lowers the reactivity of the perovskite, most likely due to calcium sulfate formation [31].

The iron-based CDCL process developed at Ohio State uses a moving bed configuration, unlike any of the previously mentioned works. In the moving bed reducer, the oxygen carrier particles, solid fuels, and enhancing gas are introduced from the top, middle and

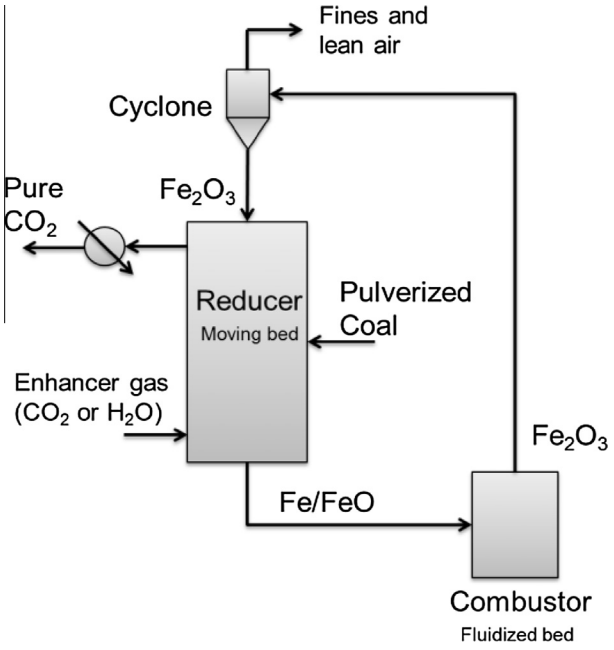

Fig. 1. Diagram of the Ohio State coal direct chemical looping process.