Fuel 231 (2018) 73–84

Contents lists available at ScienceDirect

Fuel

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

Full Length Article

Chemical looping combustion of biomass in 10- and 100-kW pilots – Analysis of conversion and lifetime using a sintered manganese ore

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ARTICLE INFO

Keywords:
Chemical looping combustion
Carbon capture and storage
Solid fuel combustion
Oxygen carriers
BECCS

ABSTRACT

Chemical looping combustion (CLC) is a type of carbon capture technology that employs metal oxide particles in a redox reaction to transport oxygen to the fuel. As opposed to first-generation carbon capture concepts, CLC does not include a gas separation step and thus offers the advantage of having no thermodynamic energy penalty in the capture process.

Manganese-containing oxygen carriers have been shown to offer a good compromise of gas conversion performance, availability, and cost. On the other hand, previously tested manganese materials have often been challenged with high attrition in continuous CLC.

By sintering the ore prior to its use as oxygen carrier, the structure of the particles can be reinforced to increase their durability in the process. In this study, a sintered manganese ore was tested for 56 h in two pilot units of different size. The oxygen carrier worked well in the process, was easily fluidized, and did not exhibit any tendency towards agglomeration. Compared to other manganese materials tested in the same units, a higher lifetime based on fines production was reached, while gas conversion performance was similar.

Different biomass fuels, mainly biochar of different sizes and black wood pellets, were employed in the study. A clear correlation between gas conversion and the fuel volatile content was detected; this is consistent with results reported in previous studies. The highest gas conversion reached in both units was ~93.5% using wood char. The highest carbon capture efficiency, 99% and 100% in the 10- and 100-kW unit, respectively, was reached with black pellets.

To compare the tested material with the state-of-the-art oxygen carrier ilmenite, some tests were conducted with a bituminous coal that had been used in the same pilot with ilmenite. The results indicate a higher conversion performance for the tested manganese material.

1. Introduction

CO_2 emissions are the single most important contributors to global warming. While renewable energy technologies, such as wind and solar technology, have become more wide-spread over the past few years, studies have shown that the use of renewables alone will not suffice to maintain global warming below 2 °C [1].

Emission reduction scenarios simulated by the International Energy Agency (IEA) indicate that the most cost-effective way to reach this target also includes the deployment of Carbon Capture and Storage (CCS) [2]. In CCS, CO_2 is captured from large stationary emitters, such as power plants and industrial facilities, and stored in underground aquifers or depleted oil and gas fields.

Assuming full carbon capture during fossil fuel combustion, CCS could be employed to afford a carbon neutral process. Such results might delay the transition towards renewables, an argument which has been used against the use of CCS technology. However, CCS could also be used to capture CO_2 from biomass combustion and similar processes, which would result in net negative emissions. This concept is known as BECCS or Bio Energy CCS. Thus, since other concepts for carbon dioxide removal from the atmosphere are still in the concept phase, very expensive, or offer limited volumes, BECCS might well be the only possible solution able to deliver the vast negative emissions demanded by the IPCC in their 1.5 and 2 °C scenarios by the year 2100 [1,3–5].

The basic principles of separating CO_2 from a gas mixture have been known and utilized for a long time in other contexts such as the food and chemical industries. However, separating gas from a mixture inevitably comes with an energy penalty, lowering the plant efficiency if CO_2 is to be captured from an exhaust gas stream and ultimately involving considerable cost.

Chemical Looping Combustion (CLC) was already patented in the 1950s [6]. However, more recently, it has been discussed as a

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https://doi.org/10.1016/j.fuel.2018.05.071
Received 13 February 2018; Received in revised form 10 May 2018; Accepted 13 May 2018

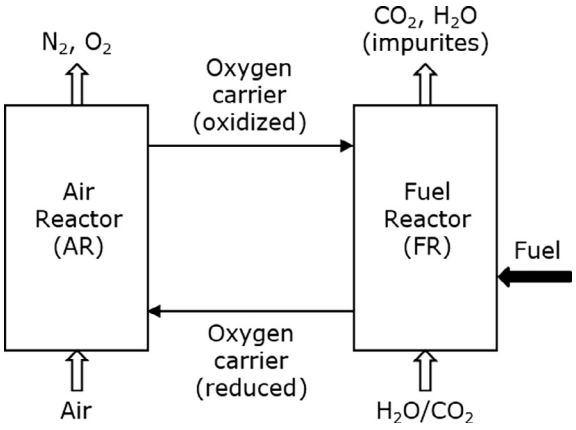

Fig. 1. Schematic of the solid fuel chemical looping combustion (CLC) process.

possibility to obtain a pure stream of CO_2 while avoiding the efficiency loss inherent to active gas separation [7,8]. In this process, solid metal oxide particles are used to transport oxygen between two separate reaction chambers. Thus, the particles are oxidized in the air reactor before being transported to the fuel reactor where they are reduced by solid, gaseous, or liquid fuel. Recycling the particles to the air reactor for re-oxidation then closes the loop in which fuel and air are never mixed. Ideally, the exhaust stream only consists of water, which can be easily condensed, and CO_2. Moreover, a subsequent compression step is needed before transport and injection to the storage site.

When gaseous fuels are employed, they can also serve as fluidization agents in the fuel reactor. On the other hand, the conversion of solid fuels requires an additional gasification step as solid-solid contact between oxygen carrier and fuel would not be sufficient for satisfactory reaction rates. In practice, both steam and CO_2 can be used for fluidization and gasification (Fig. 1).

The conversion of solid fuels is a challenge in CLC because char gasification is a comparably slow process. However, active bed materials that can be used as oxygen carriers have been shown to also increase the rate of gasification [9].

Due to advantages with respect to gas-solids contact and heat and mass transfer, interconnected fluidized beds are often chosen as a design solution for the process, even though other approaches have been realized [10,11].

Apart from optimization of plant design and operating conditions, current research focuses on discovering applicable oxygen carriers. While many transition metal oxides are theoretically suitable, some materials such as cobalt and nickel can in practice be ruled out due to health and safety issues. Iron, copper, and manganese are therefore considered as suitable alternatives. Thermodynamic analyses [12,13] have identified oxides of these metals as feasible candidates with respect to reactivity.

To date, ~10,000 h of operation have been achieved in 34 pilots reaching from 200 W to 10 MW of thermal input [14]. For solid fuels, the corresponding number is > 3000 h. Ilmenite, an iron-titanium oxide, is the most frequently used material because it is comparably cheap, durable, environmentally benign, and commercially available [15–21]. Although these advantages have made ilmenite the state-of-the-art material in solid fuel CLC [22], it does not afford full gas conversion. Copper-based materials have been used with different biomass fuels [23–25], exhibiting high reactivity but limited lifetimes [26,27]. Notably, when used with ash-containing solid fuels, the high price of copper could also represent a problem.

Due to these issues, natural manganese materials have started to attract interest as they present a reasonable compromise between gas conversion properties, particle durability, and cost. The total operation duration reported with solid fuels and natural manganese materials is slightly more than 200 h. Higher gas conversions over those produced with ilmenite have previously been reached with mixtures of ilmenite and manganese ore [28], pure manganese ores [29–31], and a manganese ore impregnated with a copper solution [32]. Some of the tested materials were burdened with low lifetime; however, sintered materials were predicted to exhibit higher durability [33]. In this study, a potentially durable sintered manganese ore was tested in chemical looping pilots of two sizes to investigate its performance and lifetime.

2. Experimental

The units used in this study are based on interconnected fluidized bed technology with design thermal power inputs of 10 and 100 kW, respectively. In both cases, the different parts of the reactor are separated by loop seals to avoid gas mixing. As neither the 10-kW nor the 100-kW unit can sustain autothermal operation, the pilots were enclosed in electrical furnaces. For both units, a fraction of the air reactor and fuel reactor exhaust gases was dried, filtered, and analyzed [infrared-(CO, CO_2, and CH_4), thermal conductivity (H_2), or paramagnetic (O_2) analyzers]. The used calibration gases are ambient air, nitrogen and a gas mix containing 6% CO, 6% CH_4, 4% H_2 and CO_2 with maximum analysis errors of 1% (relative). The infrared instruments' measurement error lies within ± 1%.

2.1. 10-kW pilot

Fig. 2 depicts the layout of the 10-kW pilot. This unit employs a bubbling bed fuel reactor, while the air reactor features higher gas

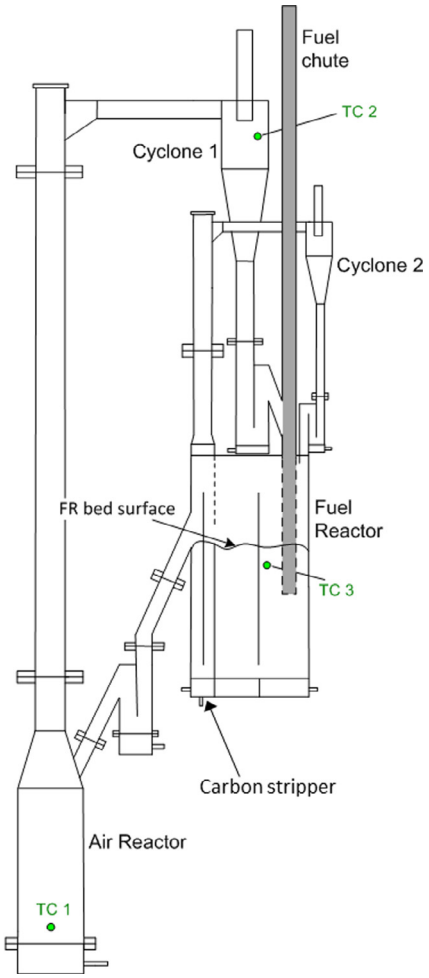

Fig. 2. Layout of the 10-kW pilot. TC 1–3 mark the positions of the thermocouples. FR: fuel reactor.