



Research article

Pressurised chemical-looping combustion of an iron-based oxygen carrier: Reduction kinetic measurements and modelling

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ABSTRACT

Chemical-looping combustion (CLC) is a novel combustion technology offering the potential to provide uninterrupted and reliable heat and power production from fossil or bio-derived fuels with integrated, intrinsic CO₂ capture and minimal energy penalty. Operation of CLC at elevated pressures provides the potential for integration with a combined cycle, which makes the use of solid fuels significantly more feasible. To date, only a few experimental studies investigating CLC processes and oxygen carrier performance under pressurised conditions have been reported in the open literature. This article reports findings from investigations into the effect of pressure, temperature and CO concentration on the intrinsic reaction kinetics of an Al₂O₃-supported Fe-based oxygen carrier. Our study employed an innovative pressurised fluidised-bed reactor, designed for operation at temperatures up to 1273 K and pressures up to 20 bara, to simulate ex-situ gasification of solid fuels at elevated pressures. An intrinsic reaction model was developed and pseudo-intrinsic rate constants were derived. Differences in the activation energies and pre-exponential factors of the Al₂O₃-supported Fe₂O₃ and a pure Fe₂O₃ oxygen carriers were observed, indicating a change in reaction mechanism when Al₂O₃ was present. Subsequently, an adapted random pore model was developed to describe the variation of reaction rate with solid conversion. The good agreement between the adapted random pore model and empirical measurements indicated that the change in mechanism was due to a significantly higher product layer diffusivity for the Al₂O₃-supported Fe₂O₃ oxygen carrier compared with the pure Fe₂O₃ material. When pressurised, the observed reaction order with respect to CO was slightly lower than 1. The model developed using atmospheric pressure measurements was successfully applied to predict reaction kinetics at elevated pressures up to 5 bara providing further validation of the model.

1. Introduction

The development and wide scale deployment of low-carbon power generation technologies over the next decade will be crucial in the effort to avoid dangerous climate change and limit global heating to < 1.5–2.0 °C above pre-industrial levels [1]. Chemical-looping combustion (CLC) offers the potential for efficient, low-carbon, heat and power production where CO₂ separation is achieved intrinsically at minimal energy penalty and cost [2]. CLC employs a metal oxide oxygen carrier (OC) to transfer oxygen from the combustion air to the fuel for fuel oxidation which takes place in a separate reactor and/or process step. Extended pilot scale trials at multiple international facilities have demonstrated the feasibility of ambient pressure CLC with gaseous fuels [3–8]. However, the process must be pressurised allowing for integration with a combined cycle if it is to prove competitive with current best available technology (i.e. natural gas combined cycle (NGCC) with MEA-based CO₂ capture) and even then, the process

efficiency is likely to be lower-limited by maximum inlet and operating temperatures, larger relative pressure drops through CLC systems and parasitic energy requirements for loop-seal fluidisation [9]. Further technological challenges associated with high temperature particulate control and the development of more efficient ruggedized turbines capable of long term operation must also be overcome if pressurised chemical-looping combustion (PCLC) based on pressurised fluidised bed (PFB) technology is to be commercially viable [10–12].

Recently, CLC with solid fuels such as coal or biomass has received increasing attention reflecting its significant potential when compared to conventional pulverised coal combustion (PCC) technology with and without retrofittable CO₂ capture technology [13–15]. Solid-solid reactions between char and metal oxides are either non-existent or take place at an extremely slow rate [16,17]. As such, solid fuels must be gasified to produce a syngas before effectively reacting with the oxygen carrier [16–20]. Solid fuel gasification can be achieved either in a separate gasifier upstream of a conventional gaseous-fuel CLC unit or in-

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situ where the fuel is introduced directly to the fuel reactor as in a coal-direct chemical-looping combustion (CDCLC) process. A modified fuel reactor is required for CDCLC to facilitate the addition and conversion of solid fuel and prevent crossover of char particles to the air reactor with the circulating OC solid flow [13,14,21,22].

CDCLC offers the benefits of process intensification, lower capital expenditure and improved char gasification rates compared to syngas CLC with ex-situ solid fuel gasification [14,23]. The results of an energy and exergy analysis carried out by Mukherjee et al. [15,24] indicate that a pressurised CDCLC process could outperform both an integrated gasification combined cycle (IGCC) process without CO₂ capture and an IGCC-CLC process with a net electrical efficiency of 44.2% compared with 39.7% and 37.1% respectively. Both CLC technologies were favourable in terms of electrical efficiency and CO₂ capture rate to IGCC with pre-combustion Selexol and oxyfuel combustion CO₂ capture processes.

Syngas-CLC with ex-situ gasification does however offer some benefits compared to CDCLC in that ex-situ gasification via IGCC is well developed and already being operated commercially [25]. Ex-situ gasification also allows for gas conditioning measures to be installed prior to the CLC unit for removal of problematic contaminants such as sulfur-containing gases, refractory tar compounds and ash that can lead to enhanced oxygen carrier degradation, increased process downtime and reduced fuel conversion and CO₂ capture efficiencies [26–28]. Furthermore, the design and operation of a CLC unit for gaseous fuels is simpler and better developed than a CDCLC unit.

Despite the significant potential pressurised-CLC (PCLC) of solid fuels offers, the number of published experimental studies focusing on CLC with solid fuels or solid fuel derived syngas under pressurised conditions is limited [29–31].

García-Labiano et al. [32] were amongst the first to investigate the effect of pressure on the performance of CLC oxygen carrier materials using a pressurised thermogravimetric analyser (TGA). Increasing the pressure was found to have a negative effect on the apparent reduction kinetics of commonly used oxygen carriers (Fe-, Ni-, Cu-based) with CO or H₂. However, the ‘low’ activation energies reported for the reduction of different oxygen carrier materials are unusual when compared with other similar studies at atmospheric pressure and may be linked to inter-particle or intra-particle mass transfer limitations of TGA reactor setups [33–35].

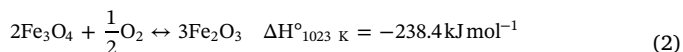
A few studies have been carried out investigating pressurised CDCLC. Xiao et al. [29] were the first to demonstrate pressurised CDCLC in a 50 kW_{th} pilot plant at Southeast University in China. They tested the PCLC performance of an iron ore oxygen carrier with bituminous coal at 1223–1243 K and total pressures of 1–5 bara over a 19-hour period of which 13.5 h were at stable operation. The purity of CO₂ exiting the fuel reactor (FR), carbon conversion and CO₂ capture efficiency all improved with increasing pressure to maximum values of 84.7, 95.5 and 97.2% respectively at 5 bara.

More recently Chen et al. [36] reported findings from their investigations into steam gasification with iron based CLC oxygen carriers at pressures up to 6 bara. They found that the rate of gasification improved with increasing steam partial pressure and oxygen carrier reactivity. The combustion efficiency was independent of pressure (1–6 bara) when using OC materials with high WGS catalytic activity but decreased when WGS catalytic activity was low.

A pilot-scale 250 kW_{th} syngas PCLC facility (also capable of CDCLC) is currently being commissioned at the US National Carbon Capture Centre (NCCC) [8]. Investigations into PCLC with natural gas and/or syngas in packed bed reactors have also been reported in the open literature [31,37].

This article presents findings from investigations into the intrinsic kinetics and reaction mechanisms of an alumina-supported iron oxide (Fe₂O₃/Al₂O₃) oxygen carrier with carbon monoxide, the major component of a coal-derived syngas. Iron oxides attract significant research attention as an oxygen carrier for CLC of solid fuels, due to their low

cost and minimal toxicity compared with most other oxygen carrier materials [13]. In this work, the reduction of Fe₂O₃ was limited (to the best of our ability) to Fe₃O₄. Further reduction to Fe^{0.97}O and Fe⁰ was prevented (through careful selection of the p_{CO_2}/p_{CO} ratio) due to thermodynamic limitations and poor reactivity associated with these reactions that will lead to decreased fuel conversions and CO₂ purity [38]. The CLC reduction and oxidation reactions studied in this work are presented in Eqs. (1) and (2), respectively:



This study employed a 3 kW_e lab-scale, pressurised fluidised-bed reactor, capable of operating at temperatures up to 1273 K and pressure up to 20 bara, to simulate CLC with syngas under pressurised conditions. The OC reduction kinetics over multiple simulated CLC cycles were assessed at high temperatures and pressures up to 5 bara. A significant increase in the reduction rate was observed with increasing pressure. Finally, a model was developed to describe the reaction kinetics of the material at elevated pressures.

2. Experimental

2.1. Materials

The 60 wt% Fe₂O₃ OC supported with 40 wt% Al₂O₃ (henceforth referred to as 60Fe₂O₃/40Al₂O₃) was prepared via a simple mechanical mixing method from Fe₂O₃ (5 μm, Sigma-Aldrich > 99.9 wt%) and Al(OH)₃ (Sigma-Aldrich, reagent grade) precursor powders. Deionised water was used as the binder. The Fe₂O₃ and Al(OH)₃ powders were first homogenised in a high shear mini-mixer (Caleva Process Solutions Limited). Deionised water was added in a dropwise manner to form a paste. The resulting paste was extruded through sieves (mesh size dependant on target particle size) yielding extrudates of controlled diameter. Spherical particles were produced from the extrudates using a spinning plate spheronizer (Caleva Process Solutions Limited). The particles were then calcined at 1173 K for 4 h in a horizontal tube furnace (Lenton) before sieving to narrow particle size fractions. During the calcination process, the Al(OH)₃ precursor decomposed into Al₂O₃, releasing water vapour to create a highly porous structure. The particles were strengthened by chemical and physical sintering processes that took place during the high-temperature calcination step.

2.2. Experimental apparatus and procedures

A laboratory-scale, fluidised- (spouted) bed reactor was upgraded for pressurised operation and used to study the intrinsic reduction kinetics of a 60Fe₂O₃/40Al₂O₃ oxygen carrier with CO in the presence of CO₂ at temperatures (723–973 K) and pressures up to 5 bara over 5 reduction and oxidation cycles. A detailed description of the reactor setup and procedure for atmospheric operation has been published elsewhere [33]. Here we will provide details of modifications made to the gas handling setup for pressurised operation as well as a brief description of the experimental protocols. The previously cited paper also serves to provide a comprehensive justification and validation for using this type of reactor to study high temperature gas-solid reaction kinetics at atmospheric pressure. A schematic diagram of the spouted, fluidised bed reactor is shown in Fig. 1.

Following assembly and successful leak testing, the reactor was heated to the experimental temperature setpoint. A flow of N₂ was established and silica sand (40 g, 450–700 μm, purity > 98%, ρ_{sand} = 2600 kg/m³, David Ball Co. plc) was added as an inert bed medium through the top of the reactor to create the fluidised bed. Once the bed temperature had stabilised at the setpoint, a single-point calibration of the gas analysers was carried out using a certified calibration

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