

Redox Reactions of Copper-Oxide Particles with Light Alkanes and Alkenes for Chemical Looping Combustion

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1 Background

There is an increasing need for the control of global emissions, particularly the emission of CO_2 . Since the pre-industrial era, mean atmospheric CO_2 concentration has increased from 280 ppm to over 405 ppm in 2018 [1]. This increasing trend is expected to continue, as it is predicted that energy from fossil fuels will satisfy over 80% of global energy demand in the first part of the 21st century [2]. While it may be possible to reduce emissions through technologies that increase energy efficiency or through the adoption of renewable energies, Carbon Capture and Sequestration (CCS) has been a topic of recent interest for the reduction of global emissions. CCS technologies are meant to produce concentrated flows of CO_2 in the exhaust produced from combustion devices. This is such that the CO_2 can be captured and stored as opposed to being released into the atmosphere. This differs from what occurs in current air-fed commercial powerplants, which, due to the inclusion of nitrogen in the air, result in a considerable amount of nitrogen in the exhaust gases. This nitrogen must be removed before the CO_2 can be stored.

Conventional methods of ensuring that there is no nitrogen in the exhaust gas involve separating the CO_2 from the other exhaust products post-combustion, or by using Oxy-fuel combustion systems so that no nitrogen is present in the exhaust [3]. Both methods involve a significant increase in operational cost and complexity. Chemical looping Combustion (CLC) systems have been named as a potential alternative for producing a CO_2 rich

exhaust with reasonable costs [4]. The basic idea behind CLC systems is that the reaction of the fuel with the oxygen is achieved through use of two coupled reactors and metal intermediate, referred to as an oxygen carrier. As seen in Figure 1, there is first an oxidation reactor, where air is used to add oxygen to the reduced metal oxide $\text{Me}_x\text{O}_{y-1}$. This process releases heat and results in a hot exhaust of N_2 and O_2 . The metal oxide Me_xO_y is then transported to a reduction reactor, where it is reduced by a fuel. This reaction may or may not be exothermic, depending on the fuel and oxygen carrier combination. The reduced metal oxide is then transported back to the oxidation reactor, and the cycle continues. During the process, the air and fuel never mix. This results in the reduction reactor producing an exhaust of concentrated CO_2 and H_2O , assuming complete combustion. The H_2O can be easily removed by cooling the gas and condensing out the water, resulting in the desired concentrated exhaust of CO_2 .

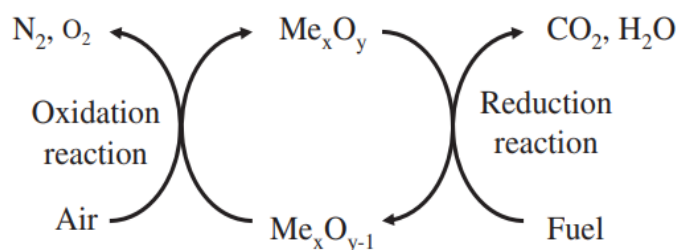


Figure 1: General Scheme of Chemical Looping Combustion systems for gaseous fuels [5]

One of difficulties in advancing this reactor scheme from the small scale to large scale is the sustainability and lifetime of the metal oxygen carriers.

For the system to be effective, the oxygen carrier must readily accept oxygen in the oxidation reactor and release oxygen in the reduction reactor. To make the transport of the metal oxides from one reactor to another manageable, the metal oxide is in the form of small particles which can be entrained in a flow of gas. However, attempts at larger CLC systems have noted the degradation of these metal oxide particles over time, finding reduced efficiency as the particles agglomerate or deform. In order for CLC technology to further develop the study into oxygen carrier particles, how these particles react with fuels, and how they change with time while looping through oxidation and reduction cycles need be performed.

Much of the past research in the literature has been performed using combinations of oxygen carriers with light fuels such as CO, H₂, and CH₄ [5]. Various models have been proposed for the mechanisms by which the gaseous fuel reacts with the solid particle, including the Shrinking Core Model, the Changing Grain Size Model, and the Nucleation Model [5]. These models have had relatively good success matching experimental trends for light hydrocarbons. Bio-fuels and heavier hydrocarbons produced from oil and refinery industry have been a proposed as potential fuels in CLC systems [6]. However, current kinetic data for anything other than the lightest of hydrocarbons is sparse.

2 Objectives

There exists a gap in knowledge relating to the behavior of heavier hydrocarbons reacting with solid oxygen carrier particles. How well existing models that describe the behavior of lighter fuels with solid oxygen carrier particles can describe the behavior with heavier fuels is unknown. In particular, most models involve the diffusion of the fuel into the oxygen carrier through a reacted outer-shell. How well heavier fuels can diffuse into the particle, and how the size and shape of the particle affect that diffusion, is something to be explored. In addition, much of the modeling involving lighter fuels has been done assuming one-step chemistry,

which will be inadequate for larger fuels. The aim of this work is to produce experimental results of various hydrocarbons with oxygen carriers of assorted sizes, and compare with their corresponding modeling results. The initial oxygen carrier to be studied was chosen to be copper oxide (CuO). This a popular choice of oxygen carrier in the literature, resulting from its low cost and exothermic reduction reactions both with carbon and CH₄. The experimental study will be performed into a flow reactor that has been converted into a fixed bed. Known amounts of CuO particles will be placed in the fixed bed while diluted amounts of fuel will be flown through the fixed bed, at temperatures ranging from 600 C to 800 C. Stable species in the exhaust will be measured with a micro gas chromatography system. Once the model and experiments have been used to replicate past literature results of CuO with CH₄ as a control, larger hydrocarbons will be run. The effect of how fuel size affects the diffusion of the fuel into the particles will be explored by varying the size of the particles in the fixed bed.

3 Research Progress and Next Steps

Initial attempts to reduce and oxidize CuO particles in a fixed-bed resulted in severe agglomeration of the particles after only a few cycles. This is believed to have been a joint result of the low melting point of copper (~1100 C) and the cohesive nature of the 10-micron particles used in the fixed bed. Work has been done to combat this issue of agglomeration by redesigning our fixed-bed such that the particles are dispersed in quartz wool. This is to reduce/remove the amount of contact between particles and thus avert agglomeration. A multi-step shrinking-core model is being produced for the CuO particles based on a literature model done with NiO. The next steps involve the completion of the shrinking core model and verification by performing the experiment with known conditions from literature. It is only after the model has been developed with the assumption used in the model justified, and that the light hydrocarbon control case from literature has been run, that the new conditions with larger hydrocarbons be tested.

4 References:

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