

Chemical Looping with Copper Oxide as Carrier and Coal as Fuel

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Résumé — Boucle chimique pour la combustion du charbon avec un transporteur d'oxygène à base d'oxyde de cuivre — Une analyse préliminaire a été conduite pour estimer les performances d'un procédé en boucle chimique découplé (CLOU, chemical looping uncoupling) pour la combustion du charbon avec un transporteur d'oxygène à base d'oxyde de cuivre. Les avantages de ce système sont démontrés en établissant le bilan énergétique, l'inventaire et le débit de circulation du matériau transportant l'oxygène, les taux de conversion du carbone et la pression partielle en oxygène dans le réacteur de combustion. Pour faire cette analyse, des données expérimentales de cyclage CuO/Cu₂O ont été utilisées afin de déterminer les cinétiques de décomposition et d'oxydation du matériau. Elles ont été obtenues avec un oxyde non supporté. La cinétique de décomposition est très rapide à 950°C dans les conditions du réacteur de combustion. Il est montré que la cinétique d'oxydation est maximale au voisinage de 800°C, la vitesse décroissant ensuite pour des températures plus élevées, à cause de résistances diffusionnelles liées à la formation d'une couche de CuO entourant le Cu₂O. L'analyse montre que le CLOU permet une combustion rapide du carbone, les temps de combustion du carbone étant plus lents que les temps de décomposition du transporteur d'oxygène. Pour confirmer le potentiel du procédé, des données cinétiques additionnelles sont nécessaires sur des oxydes supportés à haute température (>850°C), dans les conditions du réacteur de combustion permettant la libération d'oxygène par l'oxyde de cuivre.

Abstract — Chemical Looping with Copper Oxide as Carrier and Coal as Fuel — A preliminary analysis has been conducted of the performance of a Chemical Looping system with Oxygen Uncoupling (CLOU) with copper oxide as the oxygen carrier and coal approximated by carbon as the fuel. The advantages of oxygen uncoupling are demonstrated by providing the energy balances, the circulation rate of oxygen carrier, the oxygen carrier mass loadings, the carbon burnout and oxygen partial pressure in the fuel reactor. Experimental data on the cycling of cuprous oxide to cupric oxide and kinetics for the oxidation and decomposition reactions of the oxides were obtained for use in the analysis. For this preliminary study unsupported oxides were utilized. The decomposition temperatures were rapid at the high temperature of 950°C selected for the fuel reactor. The oxidation kinetics peaked at about 800°C with the decrease in rate at higher temperatures, a decrease which is attributed in the literature to the temperature dependence of the diffusional resistance of the CuO layer surrounding the Cu₂O; the diffusion occurs through grain boundaries in the CuO layers and the rate of diffusion decreases as a consequence of growth of CuO grains with increasing temperature. The analysis shows the advantages of CLOU in providing rapid combustion of the carbon with carbon burnout times lower than the decomposition times of the oxygen carrier. For the full potential of CLOU to be established additional data are needed on the kinetics of supported oxides at the high temperatures (>850°C) at which oxygen is released by the CuO in the fuel reactor.

NOTATION

Symbols

A	Surface area (cm ²)
d	Diameter of particle (cm)
D	Diffusion coefficient (cm ² /s)
$k_{r,C}$	Reaction rate constant for carbon oxidation (g/cm ² (atm) ^{0.5} s)
k_{r,Cu_2O}	Reaction rate constant for CuO reduction (s ⁻¹)
$k_{r,CuO}$	Reaction rate constant for pseudo Cu ₂ O oxidation (s ⁻¹)
k_m	Mass transfer coefficient (cm/s)
m	Mass (g)
N	Moles (mol)
mw	Molecular weight (-)
ρ_{O_2}	Partial pressure of oxygen (atm)
Q	Heating value (MJ/kg)
r	Rate of chemical reaction (mol/s)
R	Universal gas constant (cm ³ atm mol ⁻¹ K ⁻¹)
T	Temperature (K)
V	Volume (cm ³)
X	Mole ratio (defined in Eq. 1) (-)
[]	Concentration (mol/cm ³)

Greek Symbols

α	Fractional mass conversion (defined in Eq. 5) (-)
λ	Parameter (defined in Eq. 15) (-)
τ	Residence time (s)
σ	Number of particles (-)
Δ	Difference (-)
ξ	Conversion (-)

Superscripts

$\dot{\Xi}$	Rate of circulation (s ⁻¹)
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Subscripts

AR	Air Reactor
b	Bulk phase
C	Carbon
Cu	Copper
CuO	Cupric oxide
Cu_2O	Cuprous oxide
e	Equilibrium
f	Final
FR	Fuel Reactor
i	Initial
O_2	Oxygen
p	Particle
R	Reactor
s	Surface
S	Solids
t	Thermal

INTRODUCTION

Chemical Looping Combustion (CLC) shows potential for greatly reducing the energy penalty for carbon capture from coal fired power plants. Very significant progress has been made in the application of CLC to gaseous fuels with pilot units with capacities up to 140 kW_t having been successfully operated using a variety of oxygen-carriers [1]. The application of CLC to solid fuels, by contrast, has been limited.

The first reference to the application of CLC to solids with the use of CuO as an oxygen carrier was by Lewis, Gilliland and Sweeney in 1951 [2] for the application to CO₂ production without the use of an absorption step. Both hematite ores and supported CuO were utilized as oxygen-carriers. In this reference and a related patent [3] the importance of the O₂ release by CuO in accelerating the rate of oxidation of solid fuels was recognized. Independently, Mattisson *et al.* [4] discovered the importance of chemical carriers in Chemical Looping Combustion (CLC) that dissociate to produce oxygen; they designated CLC in which the char gasification occurs by reactions with oxygen as Chemical Looping with Oxygen Uncoupling (CLOU).

In this paper, we shall focus on the application of CLOU involving CuO as the oxidant and C as the reactant to accelerate the slow step of gasifying the char in conventional CLC. For this case, the relevant reactions in the fuel reactor are the endothermic dissociation $4CuO = 2Cu_2O + O_2$ and the exothermic oxidation $C + O_2 = CO_2$ to provide an overall exothermic reaction $4CuO + C = 2Cu_2O + CO_2$ [4]. The reduced CuO from the fuel reactor is transported to the air reactor where it is reoxidized and then recycled to the fuel reactor. The current study provides an assessment of this process with emphasis on quantifying the role of oxygen uncoupling in accelerating gasification of carbonaceous fuels, here simply represented by carbon.

The results of [2] will be used to illustrate the augmentation of the C gasification reaction by the oxygen liberated by CuO. In Reference 2, the reactions of the CO₂ gasification kinetics in a batch fluidized-bed reactor in which the dried product gases (mainly CO₂) were recycled where either (1) 40-200 mesh (75-420 μm) hematitic ore was reduced with a coke (97.8% C on ash-free basis), or (2) CuO supported on 20-200 mesh (75-850 μm) silica gel was used as the oxygen carrier. The reactor was maintained at constant temperature and pressure. The oxygen carrier was introduced to the reactor which was purged with CO₂ prior to introduction of the coke. For the case of the CuO oxygen carrier, the composition of the recirculating gases, recirculated at a rate sufficient to maintain a superficial velocity of 23.6 cm/s, was measured prior to the introduction of coke to obtain the equilibrium partial pressure of O₂. A run was initiated by charging and fluidizing a batch of oxygen carrier. After the temperature and pressure had stabilized a known amount of 100-140 mesh (104-152 μm) metallurgical coke was introduced.

During a run the rates of hematite or CuO reduction and coke gasification were followed by carbon and oxygen material balances on samples withdrawn from the bed at short time intervals. The gas composition was also monitored for CO₂ and the sum of O₂ and CO (predominantly O₂ in the early stages and CO in the late stages).

From runs at 900°C, 950°C, 1000°C, and 1050°C, the rate of the C + CO₂ reaction rate was determined and correlated. These results can be used to determine the augmentation of the carbon gasification rate for the case of the CuO carrier when the C + CO₂ and C + O₂ reactions occur in parallel. For the CuO run (CC-6 in [2]) at a temperature of 955 ± 5°C and pressure of 1.095 atmosphere, the initial charge contained 1141 milli-gram moles of CuO and 1039 milli-gram atoms of C. The initial oxygen concentration fell to 0.133% in 240 seconds during which over 40% of the CuO had decomposed. The oxygen concentration remained around this value for more than 2000 additional seconds with an approximate constant rate of reaction of 8.3 × 10⁻⁵ s⁻¹ (i.e. 8.3 × 10⁻⁵ atoms C gasified per second per atom carbon in bed) until the O/C ratio reached 0.5 (corresponding to Cu₂O). The 0.13% O₂ increased the rate of carbon gasification over that expected from that of the CO₂ (over 99% of the gas concentration) by a factor of 2.56. The O₂ concentration and the ratio of the gasification by O₂ divided by that due to CO₂ is summarized in Figure 1, showing a maximum increase in rate for the CuO oxygen carrier over that observed for the hematite by a factor of about 60. The oxygen partial pressure at the start of the run (O/Cu = 1) was initially at the equilibrium value of 4.5% and decreases as the O/Cu decreases as the run progresses. Analysis of the results for runs made with a CuO oxygen carrier at 845°C and 890°C showed maximum increases in rate

over those for the C + CO₂ reactions at equal temperatures of 24 and 32, respectively. The advantage of CLOU is these high increases in carbon gasification rate. It is noteworthy that a 50 fold increase in reaction rate when burning a Mexican petroleum coke with CuO oxygen carrier at temperatures (950°C to 985°C) where CLOU prevailed relative to the rate for CLC with an iron-based carrier was reported [4], an increase comparable to that reported in [2].

The major advantage of CLOU is the large reduction in the time needed to convert solid carbon in the fuel reactor, a property especially important for low reactivity fuels. In studies of CLC and CLOU in a batch reactor [4-8] it was determined that, for a low reactivity solid, such as petroleum coke, the times for reaction of the coke with CO₂ was impractically long (50 minutes to reach 95% conversion at 950°C for the injection of 0.2 g of coke in 20 g of fluidized carrier composed of 60% Fe₂O₃ and 40% MgAl₂O₄, compared to 8 minutes when steam was added to produce an atmosphere of 50% H₂O [6]). These times can be compared with a time of 30 s required to react 0.1 g of petroleum coke completely in 15 g of fluidized CuO/ZrO₂ at 955°C [5]. The reduced reaction times for carbon achievable with CLOU will result in reductions in the size for the fuel reactor and the total amount of oxygen carrier.

A second advantage of CLOU relative to CLC is that the reactions in both the fuel and air reactors are exothermic. The circulation rate of the oxygen carrier can therefore be determined solely on the basis of providing the oxygen to the fuel in the air reactor, in distinction to CLC reactors where the circulation rate is determined by the need to transfer energy from the air reactor to supply the endothermic reactions in the fuel reactor.

A third advantage is that the fuel reactor is overall oxidizing so that sulfur compounds released by high sulfur fuels will be in the form primarily of SO₂. This has the advantage of eliminating problems with sulphide formation by the oxygen carrier. The formation of CuSO₄ is also not favored thermodynamically with unrealistically high concentrations of SO_x, in excess of 30 000 ppm, required to form the sulfate at 600°C and the concentration needed increase rapidly as temperature is increased [7].

A comprehensive study of the reaction of copper-based oxygen-carriers with syngas and methane fuels has been conducted with definitive studies on the: preparation and characterization of oxygen-carriers [9-13] with different substrates (Al₂O₃, SiO₂, TiO₂ and yttrium stabilized zirconia); chemical kinetics of the oxidation and reduction of the oxygen-carriers at both atmospheric and elevated pressures [9, 13-14]; development of design criteria [13, 15], including detailed maps for the circulation of the oxygen carrier and the weight of oxygen carrier as functions of different oxygen carrier conversions in the fuel and air reactors, and oxygen carrier reactivity; the successful operation of a 500 W_t [16]

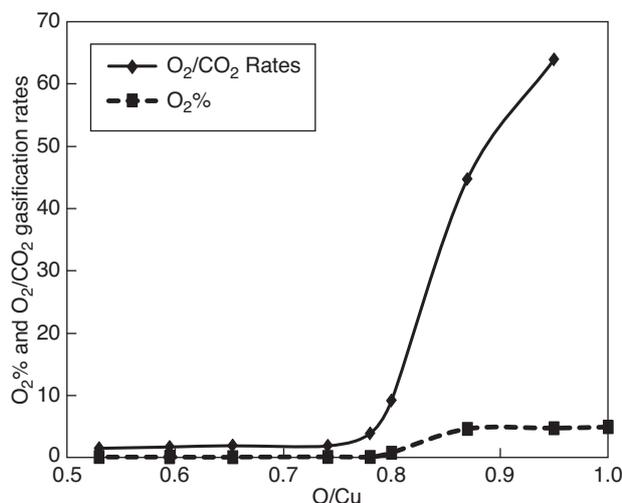


Figure 1

Enhancement in gasification rates by using copper oxide as an oxygen carrier based on results of Lewis *et al.* [2].

and 10 kW_t [17, 18] CLC system of two interconnected fluidized beds; development of a detailed mechanistic model [19] of the CLC system and validation with data from the 10 kW_t unit; the reclamation of copper from spent oxygen carrier [20]. These studies have shown that copper oxide based carriers have great potential because of their high reactivity and resolved questions that had been raised on attrition, agglomeration, and sulfur contamination. Furthermore, preliminary analysis showed the economic viability of the copper oxide based oxygen-carriers [15].

The study of the use of copper oxide carriers for the combustion of solid fuels has by comparison received little attention. Reference has been already made of the early studies of oxygen uncoupling [2, 3] which were largely forgotten until the independent discovery of CLOU [4]. ZrO₂ supported CuO was utilized [4] as the oxygen carrier and the system was operated at temperatures high enough to produce a significant partial pressure of oxygen to react with solid carbon (equilibrium O₂ partial pressure for CuO/Cu₂O > 0.005 atm for $T > 850^{\circ}\text{C}$). Small batches of fuel were added to a laboratory electrically heated fluidized bed reactor with the gas concentration cycled from oxidizing to inert. The times for conversion of a Mexican petroleum coke ranged from about 127 s at a set temperature of 885°C (bed temperatures were slightly higher due to the exothermic reactions) to about 14 s at a set temperature of 985°C [4]. The times to reoxidize the Cu₂O were also fast although not quantified in the publication. These studies were extended to the combustion of a lignite (Lausitz, Germany) which reacted in times of 30 to 45 s in the temperature range of 850 to 985°C [7]. Other CLC applications of copper carriers with solid fuels involve:

- the study of the reaction of two bituminous coals (Taldinskaya, Russia and US Illinois No. 5, USA) and a lignite (Hambach, Germany) in a batch fluidized bed reactor with cycling of gas composition and of the oxygen carrier between Cu and Cu₂O has been reported for a reactor temperature of 930°C, with high rates of reaction observed for the lignite but incomplete combustion of the bituminous coals [21], and;
- a TGA study of packed carbonaceous fuels and CuO that demonstrated very fast reactions at relatively low temperatures of 500 to 700°C apparently as a consequence of solid-solid reactions [22, 23].

1 DESIGN CRITERIA

The objective of the present work is to develop design criteria for a Chemical Looping with Oxygen Uncoupling (CLOU) process, providing order of magnitude estimates of:

- the temperatures of the fuel and air reactors (*Sect. 4*);
- the rate of circulation of the oxygen carrier (*Sect. 2*);
- the total oxygen carrier loading (*Sect. 4*);
- the carbon loading and oxygen partial pressure in the fuel reactor (*Sect. 5*).

As an initial step, an ASPEN PLUS Simulation was developed to determine the requisite energy and material flows, incorporating the following assumptions:

- the solid fuel has been assumed to consist of pure carbon for simplicity of order of magnitude analysis. This eliminates complications associated with the combustion of the volatiles that would be released by most solid fuels. The emphasis on carbon is motivated by the fact that carbon gasification has been shown to be the limiting factor in the combustion of coals and petroleum cokes [2-8] and significant progress has been made in developing CLC for gaseous compounds representative of volatiles;
- the flow in the fuel and air reactors is approximated by simple plug flow reactors. This leaves the final design of the CLC system open. Most of the laboratory and pilot demonstrations have utilized fluidized bed designs, but other configurations involving moving beds [24], or multiple interconnected moving or fluidized beds [3, 26, 27] have been used or proposed.

The fuel and the air reactors have been modeled using the RSTOIC Reactor model in ASPEN PLUS. The reactions occurring in the fuel reactor are CuO decomposition to yield oxygen, (by $4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$), and the oxidation of char particles, ($\text{C} + \text{O}_2$). The CuO is regenerated in the air reactor by the reaction: $2\text{Cu}_2\text{O} + \text{O}_2 \rightarrow 4\text{CuO}$. The O₂ concentration in the effluent of the air reactor is set at 3% consistent with that in coal-fired utility boilers.

The results of the ASPEN simulations are presented in Figure 2. The material and energy balance has been developed assuming a flow of 100 kg/h of carbon feed, with a mole conversion of 60% of CuO in the fuel reactor and 64% of Cu₂O in the air reactor (justification for which shall be presented in *Sect. 4*). For these conversions, and the temperatures and oxygen carrier circulation rates indicated in Figure 2, the energy release is 357 kW in the fuel reactor and 574 kW in the air reactor, distinctively different from the operation of a CLC where the fuel reactor operation is normally endothermic. The reason, as mentioned previously, is that the overall reaction in the fuel reactor, $4\text{CuO} + \text{C} \rightarrow 2\text{Cu}_2\text{O} + \text{CO}_2$, is exothermic.

2 OXYGEN-CARRIER CIRCULATION RATE

The circulation rate of the oxygen carrier, together with the total mass of oxygen-carrier, is recognized to be instrumental in the economical design of a chemical looping system [5, 13, 15, 27]. For oxygen uncoupling, as mentioned above, the circulation rate is governed by the need to supply the fuel reactor with the oxygen needed to consume the fuel. The analysis that follows assumes complete fuel consumption, an assumption that will be justified in Section 5. The moles (or mass) of Cu circulating between the fuel and air reactor has been chosen as the basis for calculation here, as it is

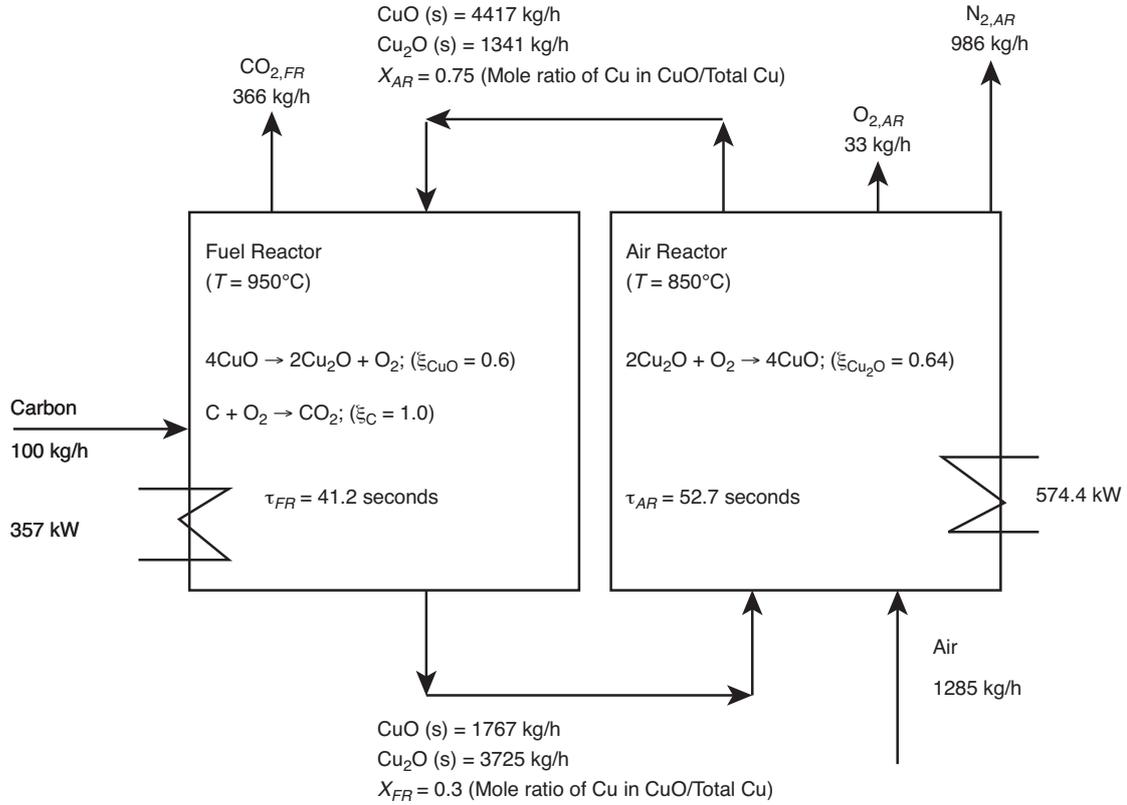


Figure 2

ASPEN simulation of material and energy balances in an idealized CLOU process with 100 kg/h carbon feed.

independent of the oxygen state of the oxygen-carrier. The calculations are based on the mole fraction of copper in the oxygen-carrier:

$$X_{\text{CuO}} = \frac{\dot{N}_{\text{CuO}}}{\dot{N}_{\text{CuO}} + 2\dot{N}_{\text{Cu}_2\text{O}}} = \frac{\dot{N}_{\text{CuO}}}{\dot{N}_{\text{Cu}}} \quad (1)$$

where, \dot{N}_{CuO} , $\dot{N}_{\text{Cu}_2\text{O}}$, and \dot{N}_{Cu} are the molar flow rates of CuO, Cu₂O, and Cu, respectively. For the fuel reactor, the difference in the oxygen in the oxygen-carrier entering and leaving the reactor is consumed in the combustion of carbon fuel. For a stoichiometric equation of $4\text{CuO} + \text{C} = 2\text{Cu}_2\text{O} + \text{CO}_2$, the following relation therefore exists between the molar rate of carbon feed \dot{N}_{C} and the difference in flow of \dot{N}_{CuO} , entering and leaving the reactor:

$$\dot{N}_{\text{C}} = \frac{\dot{N}_{\text{Cu}}(X_{\text{CuO,AR}} - X_{\text{CuO,FR}})}{4} \quad (2)$$

where AR and FR refer to Air and Fuel Reactor, respectively. Rearrangement yields:

$$\frac{\dot{N}_{\text{Cu}}}{\dot{N}_{\text{C}}} = \frac{4}{(X_{\text{CuO,AR}} - X_{\text{CuO,FR}})} \quad (3)$$

The difference in mole ratio X_{CuO} at the exit of the Air and Fuel Reactors is defined as $\Delta X_S = (X_{\text{CuO,AR}} - X_{\text{CuO,FR}})$.

Equation (4) can be used to determine the proportionality between the energy in the fuel introduced to the fuel reactor in megawatts of thermal energy and the mass flow rate of Cu circulating in the system, \dot{m}_{Cu} :

$$\dot{m}_{\text{Cu}} = \frac{4(mw_{\text{Cu}})}{\Delta X_S(mw_{\text{C}})Q_C} \quad (4)$$

This relation is shown in Figure 3 in which the mass of copper circulated in the system per MW_t of carbon introduced in the fuel reactor is plotted *versus* the difference in mole ratio ΔX_S for different values of $X_{\text{CuO,FR}}$ (Fig. 3). It should be noted that the circulation mass in Figure 3 needs to be corrected for both oxidation of the Cu (increases of a factor of 1.13 to 1.25 depending on the oxidation state of the Cu) and on the percent of copper loading on the oxygen-carrier when calculating the total mass of oxygen carrier. Supported oxygen-carriers with CuO loadings of up to 80% have been prepared with binders (substrates) of Al₂O₃, Sepiolite, SiO₂, TiO₂, and ZrO₂ [9]. However, studies of agglomeration of Al₂O₃-supported oxygen-carriers suggested

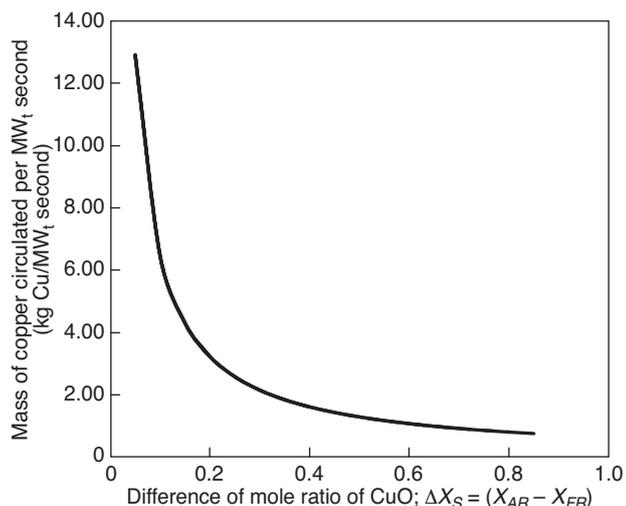


Figure 3

Variation in mass (kg) of copper circulated per MW_t s with variation in difference of CuO mole ratio.

that the CuO loadings should not exceed 20% in order to prevent agglomeration. Operation of a 10 kW_t chemical looping combustor with a CuO initial concentration of 14% with an Al_2O_3 substrate stabilized at a loading of about 10% CuO after 100 h of operation. In order to compare oxygen-carrier rates on a common basis the rates will be converted to the rates of CuO circulated on a support free basis.

The rates of circulation for CLOU are compared with selected values in the literature assuming that the value of ΔX_S is about 0.45 (see Fig. 2), to be justified later. Given the results of Figure 3, a circulation of approximately 1.8 $kg/(s)(MW_t)$ is required on a support-free basis. The total rate of material circulated is equal to this value divided by the weight percent of CuO for oxygen carriers consisting of supported CuO. In order to compare the present result with results reported in the literature the data in the literature need to be converted to a support-free basis by multiplying the reported rates by the weight percent of active material on the supported oxygen carrier. On a support-free basis, the circulation rate of 1.8 $kg/(s)(MW_t)$ are comparable to values reported in the literature of 2 $kg\ CuO/(s)(MW_t)$ (at $\Delta X_S = 0.4$) for the combustion of petroleum coke using CLOU [5] and 1 $kg\ CuO/(s)(MW_t)$ for a fuel gas [15].

3 KINETICS OF OXIDATION AND REDUCTION OF OXYGEN CARRIER

The masses of oxygen-carrier in the fuel and air reactors can be estimated from the products of the oxygen-carrier circulation rate and the time to reduce the CuO for the fuel reactor

and the time to oxidize the resultant Cu_2O in the air reactor. This section describes the determination of the chemical kinetics of oxidation and reduction of the oxygen carrier that are needed for such an analysis. For the present order-of-magnitude analysis, the kinetics were determined for unsupported copper oxide; later studies are planned with supported catalysts.

The kinetics were determined using two TGAs, a TA Q500 and a TA Q600. Quartz sample pans were used. The gas flows for the TA Q500 was 40 mL/min to the balance arm and 60 mL/min to the sample. Samples of CuO powder from Johnson Matthey Chemicals in the size range of 1-10 μm were used for most of the runs. The BET surface area of the initial sample was in the range of 0.22 to 0.27 m^2/g , which corresponds to a mean diameter of about 4 μm . Runs were conducted by introducing samples of about 20 mg into the TGA at ambient temperature and pressure. The TGA was heated to the reaction temperature in nitrogen and then the gas through the reactor was cycled between nitrogen and air, with a rapid switching of the gases. After an initial transient of 6 cycles a steady cycling was observed.

In order to provide time to purge the gases from the TGA between cycles and to achieve complete oxidation, the cycle times were 30 minutes for air and 40 minutes for nitrogen. The results of 33 cycles are shown in Figure 4 for runs conducted isothermally at 850°C. The difference between the asymptotic weights during oxidation and reduction is in good agreement with the mass difference between Cu_2O and CuO: $(2\ CuO - Cu_2O)/(2\ CuO) = 0.1006$. The explanation for the high conversion of the unsupported CuO and Cu_2O during cycling is that the particles swell and develop porosity during reaction, as determined from electron micrographs of the samples before and after sampling and from an increase in BET surface area from an original value of 0.2 m^2/g to 0.8 m^2/g after 20 cycles [28]. The particles sintered at the higher temperatures but continued to show high reactivity and ability to cycle. The sintering is expected from the low Tammann temperatures (equal to half the absolute temperature of melting) for CuO and Cu_2O of 526°C and 481°C, respectively. Although the mobility of the oxides at low temperatures is responsible for sintering and excludes the use of the unsupported oxides, the mobility is beneficial in providing good coverage for supported oxides.

The results of a single cycle at temperatures of 850°C and 950°C are presented in Figures 5 and 6. The fast rise and decline in the mass traces in Figures 5 and 6 occur at the times of changes in gas concentration. In Figure 5, the decline in the mass corresponds to the decomposition of CuO in a N_2 environment at 850°C. When the N_2 is switched to air, the increase in mass corresponds to the oxidation of the Cu_2O . Reaction goes to completion for both decomposition and oxidation. The slope for the oxidation is steeper than that for decomposition indicating a faster rate of oxidation of Cu_2O than decomposition of CuO. Conversely, at 950°C

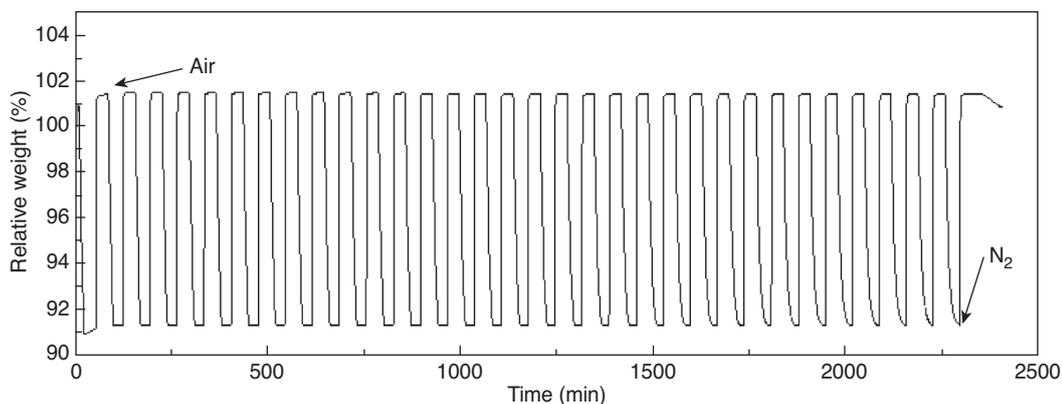


Figure 4

Results of Chemical Looping with Oxygen Uncoupling experiments (between CuO and Cu₂O) conducted at 850°C for 33 cycles with a cycle time of 30 minutes for air and 40 minutes for N₂.

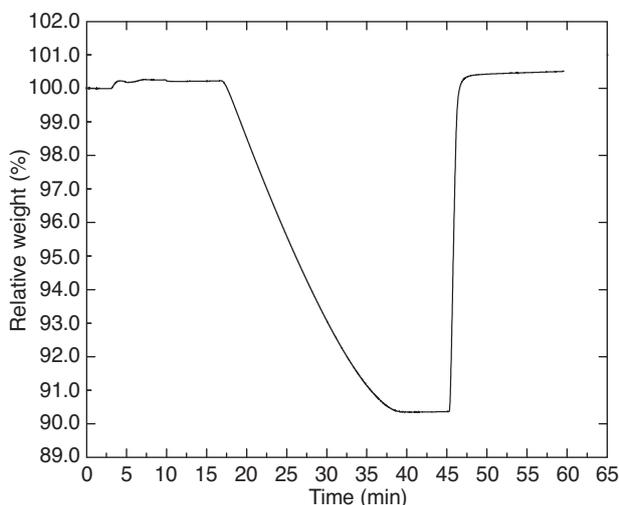


Figure 5

Chemical Looping with Oxygen Uncoupling results with copper oxide at 850°C for a single cycle.

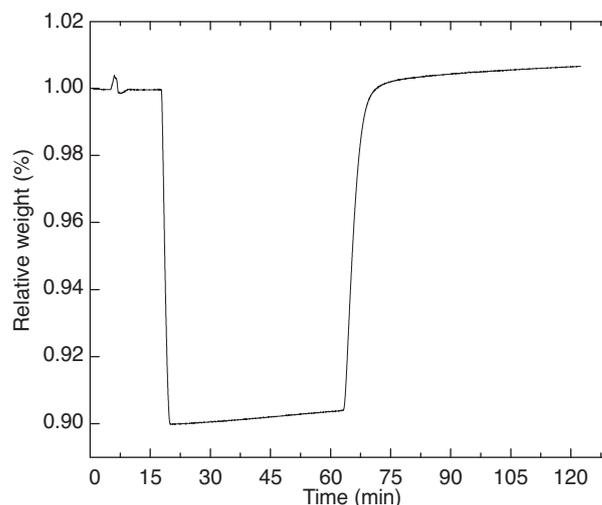


Figure 6

Chemical Looping with Oxygen Uncoupling results with copper oxide at 950°C for a single cycle.

(Fig. 6) the decomposition of CuO is faster than the oxidation of the Cu₂O. The individual cycles were studied to obtain reaction kinetics. The fractional mass conversion, α , is defined as:

$$\alpha = \frac{m - m_i}{m_f - m_i} \quad (5)$$

where m is the transient mass, m_i the initial mass at the start of a run, and m_f the final mass at the end of a run. The data for the decomposition of CuO at 850, 900, and 950°C are shown in Figure 7 together with an empirical first order fit developed for purposes of modelling. The adequacy of the first order fit decreases with increasing temperature, as has

been observed by other investigators [9, 28]. The corresponding curves for oxidation of Cu₂O in air are shown in Figure 8. The oxidation curves show a decrease in reaction rate at high temperature.

The kinetic rate constants are plotted *versus* temperature in Figure 9. The decomposition of CuO can be described by an Arrhenius expression with an activation energy of 327 kJ/mol. Above 800°C, oxidation of Cu₂O shows a progressive decrease in rate with increasing temperature. This unusual behaviour has been observed previously for the oxidation of copper [29] and cuprous oxide [30]. These references underline the complexity of the mechanism of

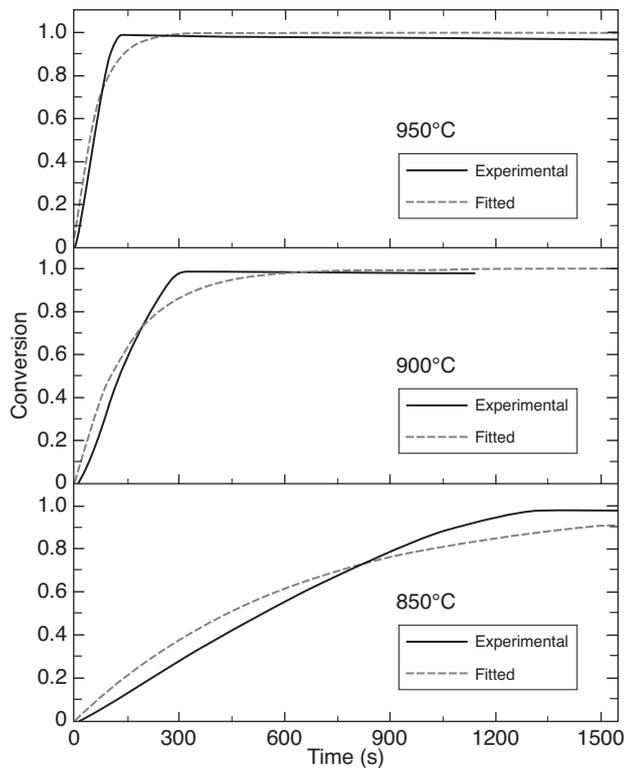


Figure 7

Reduction of cupric oxide vs time at temperatures of 850, 900 and 950°C. Solid lines represent experimental data; dashed lines first order fits to the data.

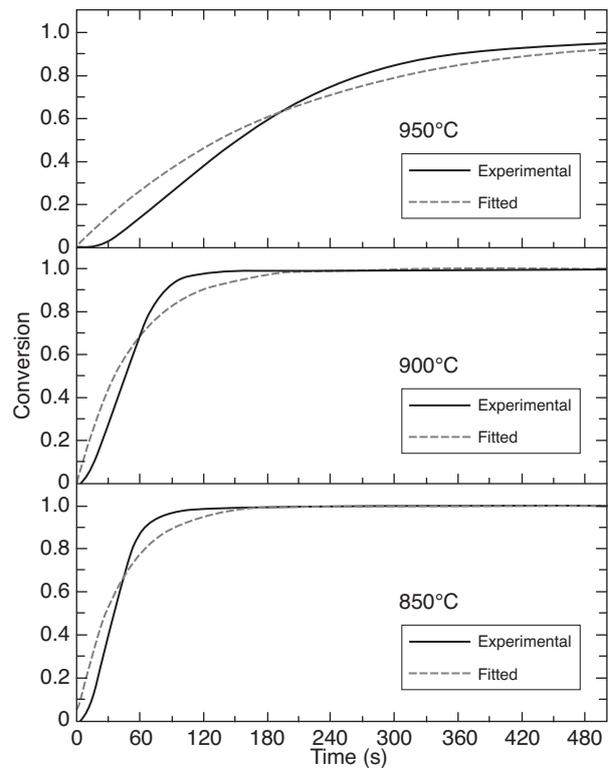


Figure 8

Oxidation of cuprous oxide vs time at temperatures of 850, 900 and 950°C. Solid lines represent experimental data; dashed lines first order fits to the data.

oxidation of copper and cuprous oxide. Relevant to the current study is the observation that the oxidation rate is controlled by the diffusion through the CuO layer engulfing the Cu₂O. Since bulk diffusion through the CuO is slow, the rate is controlled by the diffusion through grain boundaries in the CuO. As temperature increases, the grains grow rapidly, reducing the rate of increase in oxidation [29] and even leading to a decrease in rate [30]. A further complication is provided by the changes in surface areas resulting from the changes in porosity governed in part by the difference in molar volumes of CuO and Cu₂O. Clearly the order of the reaction will be complicated by the complex mechanism involving kinetics, multiple diffusional steps, and changing surface area. The first order representation of the data was purely for ease of analysis and no mechanistic implication is implied nor is the first order fit the best representation of the data (an Avrami-Erofeev expression gives a better fit of the data).

The rates found in this study for the decomposition of CuO and oxidation of Cu₂O have been compared with data in the literature. The results compare well with those obtained in the study of Chadda *et al.* [28] for the decomposition rate

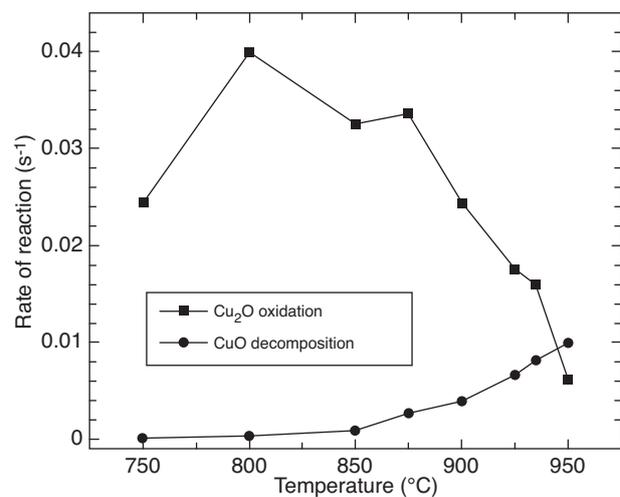


Figure 9

Plot of rate constants vs temperature for the oxidation of Cu₂O and the decomposition of CuO.

of CuO over a temperature range of 760 to 910°C, for oxides produced from copper of similar size to those in the current study [28]. The activation energy for their first order fit of the data of 322 kJ/mol is very close to the value of 327 kJ/mol obtained in this study. However, the current rates are somewhat faster with a preexponential of 1.488×10^{14} compared to their value of 1.595×10^{13} . Their oxidation data were obtained at temperatures under 550°C and are strictly not comparable. The data of Garcia-Labiano *et al.* [13] of oxidation of an oxygen carrier of 10%CuO on an Al_2O_3 substrate at temperatures of 500 to 800°C in air are also relevant. The oxidation time at their maximum temperature of 800°C is 8 s, a factor of about 20 smaller than the oxidation time in the present study at the same temperature. This large difference is probably a consequence of the very thin coating of the CuO, which was estimated to be 0.4 nm [13]. This thin coating, planar in nature results in a reaction rate ($d\alpha/dt$), that is independent of time or conversion [13].

4 MASS LOADING OF THE OXYGEN CARRIER

The masses of the oxygen-carrier in the fuel and air reactors are calculated here for an assumed plug flow of the solid. This assumption simplifies the analysis and provides a lower limit for the loading. It is approximated in practice by the use of multiple reactors, one of the options proposed in [3] or that has been adopted in a pilot reactor [25]. The reaction order with respect to the reactant was assumed to be first order, an approximation to the data as shown in Figures 7 and 8. Temperatures that minimize the oxygen carrier were also selected. A temperature of 950°C was selected to approximate the highest temperatures used in laboratory reactors with solid fuels without bed agglomeration and attrition [2-8, 11]. A temperature of 850°C was used in the air reactor, a temperature a little higher than the peak rate of oxidation found at around 800°C in the present study (Fig. 9).

The residence time of a plug-flow reactor for the cupric oxide decomposition from an inlet concentration of $X_{\text{CuO,AR}}$ to an exit concentration of $X_{\text{CuO,FR}}$ is given by:

$$\tau_{FR} = \frac{1}{k_{r,\text{CuO}}} \ln \left[\frac{1}{\left\{ 1 - \left(\frac{\Delta X_S}{X_{\text{CuO,AR}}} \right) \right\}} \right] \quad (6)$$

where $k_{r,\text{CuO}}$ is a first order decomposition rate constant (s^{-1}) given in Figure 9.

The residence time of a plug-flow reactor for oxidation from an inlet concentration of $(1 - X_{\text{CuO,FR}})$ to an exit concentration of $(1 - X_{\text{CuO,AR}})$ is given by:

$$\tau_{AR} = \frac{1}{k_{r,\text{Cu}_2\text{O}}} \ln \left[\frac{1}{\left\{ 1 - \left(\frac{\Delta X_S}{(1 - X_{\text{CuO,FR}})} \right) \right\}} \right] \quad (7)$$

where $k_{r,\text{Cu}_2\text{O}}$ is pseudo first order oxidation rate constant (s^{-1}) reported for oxidation in air in Figure 9. The pseudo first order rate constant was adjusted from a rate for 21% oxygen to one at the log mean concentration of an inlet oxygen concentration of 21% and exit concentration of 3%; in making the adjustment, a square root dependence on oxygen partial pressure was assumed consistent with preliminary TGA oxidation results with different oxygen concentrations.

The mass of Cu metal required per MW_t of carbonaceous fuel burnt in a CLOU system, can be obtained from Equation (8):

$$m_{\text{Cu}} = \dot{m}_{\text{Cu}} (\tau_{FR} + \tau_{AR}) \Big|_{\Delta X_S, X_{\text{CuO,FR}}} \quad (8)$$

where the residence times are determined by Equations (6) and (7) as a function of $X_{\text{CuO,AR}}$ and $X_{\text{CuO,FR}}$, or, alternatively $X_{\text{CuO,FR}}$ and ΔX_S . The resulting mass of the copper in the oxygen carrier per MW_t input of fuel is provided in Figure 10, mapping similar to those developed previously [13, 15].

The results in Figure 10 show a minimum carrier loading at a specific $X_{\text{CuO,FR}}$ for each value of ΔX_S , starting with a minimum of 125 kg/ MW_t at an $X_{\text{CuO,FR}}$ of 0.5 and at a ΔX_S of 0.05, shifting to lower values of $X_{\text{CuO,FR}}$ as ΔX_S increases. For the highest ΔX_S shown on the plot, 0.65, the minimum carrier loading is 150 kg/ MW_t . The shape of each curve is determined by the increase in reaction time in the fuel reactor as the value of $X_{\text{CuO,FR}}$ decreases at a given ΔX_S because of the first order rate equation (see Eq. 6). The reaction times for the air reactor by contrast increase with increasing $X_{\text{CuO,FR}}$ at a fixed ΔX_S (see Eq. 7). Selection of the optimum values of conditions depends on selecting a high value of ΔX_S to reduce the circulation rate of oxygen carrier (see Fig. 3) as

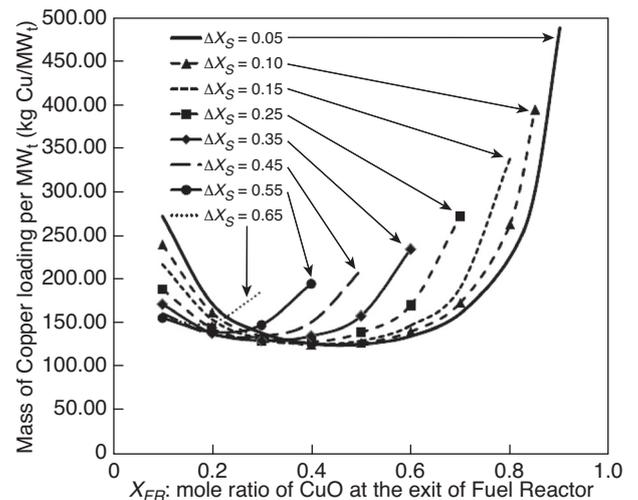


Figure 10

Mass of copper loading per MW_t vs mole ratio of CuO at the exit of fuel reactor for different values of ΔX_S .

well as minimize oxygen carrier loading. An optimization would be based on an economic analysis. ΔX_S between 0.2-0.4 has been cited for low circulation rates and low solids inventories [15]. Values of $X_{\text{CuO},FR} = 0.3$ and ΔX_S of 0.45 have been chosen as a basis to perform an order of magnitude calculation, at which copper loading in the oxygen carrier is 135 kg CuO/MW_t. Previous work has shown a minimum solids loading of approximately 13.3 kg CuO/MW_t for combustion of methane and a 10% Cu on an aluminium support [13], less than 1200 kg Fe₂O₃/MW_t for combustion of petcoke with a 60% Fe₂O₃/40% MgAlO₄ oxygen-carrier [8] and 48 to 80 kg CuO/MW_t for combustion of petroleum coke for a 40% CuO/ZrO₂ oxygen carrier operated in a CLOU mode [5]. All solid loadings are reported on a support-free basis.

5 CARBON LOADING AND OXYGEN PARTIAL PRESSURE IN THE FUEL REACTOR

Calculation of the carbon burnout needs to be addressed simultaneously with the estimation of the bulk oxygen concentration in the fuel reactor, which is determined by the oxygen release by the oxygen carrier, the oxygen consumption by the carbon, and the net transfer of oxygen to the effluent gases and in the streams to and from the fuel reactor. The major terms that will be considered in this section are the rate of production of oxygen by the oxygen carrier and the oxidation of carbon in the fuel reactor.

5.1 Rate of Net Oxygen Release by Oxygen Carrier

The kinetics of the reaction $4\text{CuO} \rightarrow 2\text{Cu}_2\text{O} + \text{O}_2$ are considered below. The rate of oxygen release from CuO can be expressed utilizing the relationship:

$$r_{\text{O}_2, \text{CuO}} = \frac{k_{r, \text{CuO}} [\text{CuO}]}{4} - \frac{k_{r, \text{Cu}_2\text{O}} [\text{Cu}_2\text{O}] \rho_{\text{O}_2}^{1/2}}{2} \quad (9)$$

When the reaction is governed by equilibrium the surface concentration of O₂ at the surface of the CuO/Cu₂O particle is $\rho_{\text{O}_2, e}$; at the opposite extreme, the reverse reaction in Equation (9) can be neglected. The analysis in the subsequent section has been conducted when the CuO/Cu₂O reaction is close to equilibrium which is relevant to the conditions in this paper.

Under the conditions of mass transfer control, the molar rate of oxygen mass transfer from CuO particles in a fuel reactor is then given by:

$$\dot{N}_{\text{O}_2, \text{CuO}} = k_{m, \text{CuO}} A_{\text{CuO}} \left(\frac{\rho_{\text{O}_2, e}}{RT} - \frac{\rho_{\text{O}_2, b}}{RT} \right) \left(\left(\frac{\sigma_{P, \text{CuO}}}{V_R} \right) V_R \right) \quad (10)$$

5.2 Rate of Carbon Oxidation

The relation between the surface oxygen partial pressure on a carbon particle and the bulk oxygen partial pressure around

the particle is obtained by equating the mass rate of oxygen transfer from bulk environment to the surface of the carbon particle and the mass consumption of oxygen at the surface of the carbon particle as shown below:

$$k_{m, C} A_C \left(\left(\frac{\rho_{\text{O}_2, b}}{RT} - \frac{\rho_{\text{O}_2, s}}{RT} \right) \right) = k_{r, C} A_C \rho_{\text{O}_2, s}^{1/2} \quad (11)$$

where $k_{r, C}$ is a reaction rate constant for carbon oxidation ($\text{g}/\text{cm}^2(\text{atm})^{0.5} \text{s}$). This equation can be solved for $\rho_{\text{O}_2, s}$.

The molar rate of oxygen mass transfer to the surface of carbon particles in a fuel reactor can be expressed as:

$$\dot{N}_{\text{O}_2, C} = k_{m, C} A_C \left(\frac{\rho_{\text{O}_2, b}}{RT} - \frac{\rho_{\text{O}_2, s}}{RT} \right) \left(\left(\frac{\sigma_{P, C}}{V_R} \right) V_R \right) \quad (12)$$

where the mass transfer coefficient is calculated assuming a Sherwood Number of 2 and obtaining the diffusivity of oxygen in carbon-dioxide using Fuller's correlation [31].

5.3 Calculation of Bulk Oxygen Concentration

The bulk oxygen concentration can be obtained by equating the molar rate of oxygen release from the CuO particles to the mass transfer to the carbon surface; that is, equating the right hand sides of Equations (10) and (12):

$$\left(\rho_{\text{O}_2, e} - \rho_{\text{O}_2, b} \right) = \left(\frac{k_{m, C} A_C}{k_{m, \text{CuO}} A_{\text{CuO}}} \right) \left[\frac{\sigma_{P, C}}{V_R} \right] \left(\rho_{\text{O}_2, b} - \rho_{\text{O}_2, s} \right) \quad (13)$$

The following assumptions have been made in developing Equation (13):

- it is assumed that the partial pressure of O₂ at the surface of the CuO particle is at equilibrium. In this study the case of mass transfer of O₂ from the CuO particle is assumed to be rate controlling as a first approximation for design. The case of O₂ decomposition from CuO being controlled by chemical reaction will be addressed in a future publication;
- the effect of chemical reaction of the carbon is included by using the empirical fit of data on carbon burnout based on its external surface area developed by Hurt and Mitchell [32].

Equation (13) can be simplified to yield an expression in surface oxygen partial pressure, $\rho_{\text{O}_2, s}$ which is:

$$\rho_{\text{O}_2, s} = \frac{\left((\lambda + 1) \rho_{\text{O}_2, b} - \rho_{\text{O}_2, e} \right)}{\lambda} \quad (14)$$

where:

$$\lambda = \left(\frac{k_{m, C} A_C}{k_{m, \text{CuO}} A_{\text{CuO}}} \right) \left[\frac{\sigma_{P, C}}{V_R} \right] \left[\frac{\sigma_{P, \text{CuO}}}{V_R} \right] \quad (15)$$

By equating the surface oxygen partial pressures which are obtained from Equations (11) and (14), Equation (16) is obtained:

$$\frac{2}{\lambda} \rho_{O_{2,b}} + \left(\frac{k_{r,C}RT}{k_{m,C}(mw_C)} \right) \left[4\rho_{O_{2,b}} + \left(\frac{k_{r,C}RT}{k_{m,C}(mw_C)} \right)^2 \right]^{\frac{1}{2}} - \frac{2}{\lambda} \rho_{O_{2,e}} - \left(\frac{k_{r,C}RT}{k_{m,C}(mw_C)} \right)^2 = 0 \quad (16)$$

This equation can be solved to obtain the bulk oxygen concentration as a function of two coefficients, λ , which provides a measure of the ratio of loadings of carbon to CuO, and:

$$\left(\frac{k_{r,C}RT}{k_{m,C}(mw_C)} \right)$$

which provides a measure of the ratio of reaction rate to the mass transfer coefficient for the carbon. The equation was solved for the bulk oxygen concentration for two US coals, Pittsburgh#8 and Pocahontas [32], and an Australian brown coal [33]. A coal particle size of 115 μm and a CuO particle size of 100 μm were assumed. An equilibrium O_2 concentration of 4.5%, corresponding to a temperature of 950°C for the oxygen carrier, was also used for the calculation. The results for the bulk O_2 concentration, presented in Figure 11, shows a decrease in bulk concentration as the carbon loading relative to that of the CuO increases. This trend is consistent with the data in Figure 1 where the O_2 concentration decreased rapidly as the O/Cu ratio decreased to 0.8 (40% decomposition of the CuO) while only 10% of the carbon was consumed [2].

If the carbon particles are assumed to burn in a shrinking sphere mode, the time for complete burnout of the carbon can

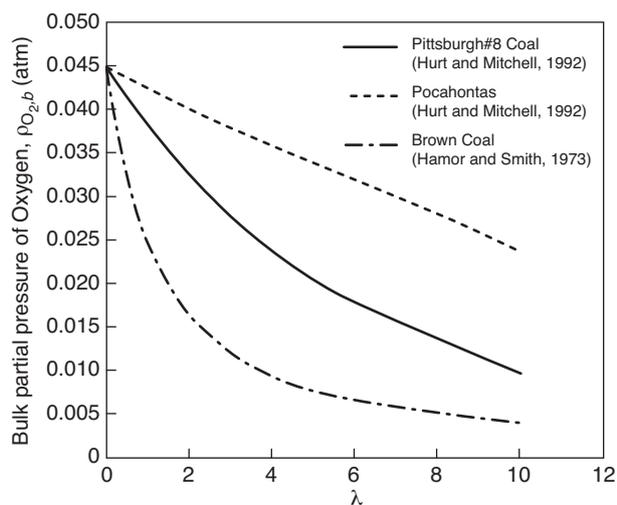


Figure 11

Bulk oxygen partial pressure vs λ (see Eq. 16) at 950°C.

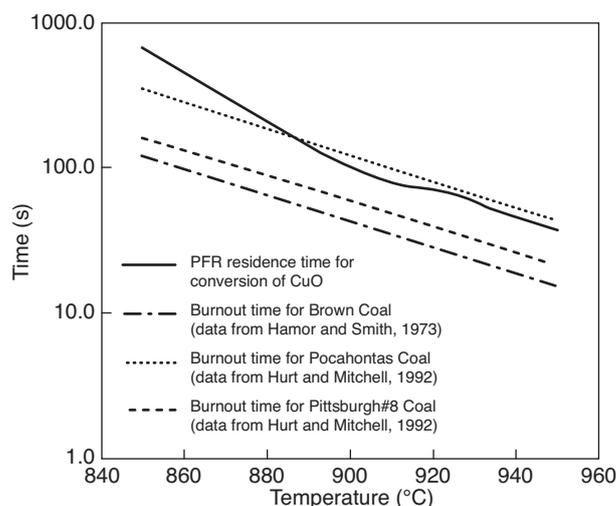


Figure 12

Calculated times vs temperature in the Fuel Reactor for CuO decomposition and the burnout of three coals: an Australian brown, a Pocahontas and a Pittsburgh#8.

be calculated, assuming the combustion time will depend on the bulk oxygen concentration. The bulk concentration for the conditions selected for the test case is close to equilibrium since the maximum value of λ for the values of coal feed and CuO circulation was found to be 0.17. The burnout times were calculated for the three coals and are compared in Figure 12 with the conversion times for the cupric oxide in the fuel reactor calculated using Equation (6). Complete conversion is found for the three coals except for the Pocahontas coal at high temperatures. For the Pocahontas coal the times for burnout are seen to exceed the cupric oxide reduction times at temperatures above 1160 K ($\sim 890^\circ\text{C}$). The difference however is small and the carbon burnout is found to be greater than 99%.

CONCLUSIONS

CLOU utilizing CuO as an oxygen carrier shows major potential for the oxidation of solid fuels. In particular, the gasification rate of carbon is no longer a major constraint in the sizing of the fuel reactor as the burnout times for carbon are comparable or smaller than the decomposition times of the CuO. A limiting expression has been developed which can be used to determine the departure from equilibrium of the bulk oxygen partial pressure in the fuel reactor as a function of fuel loading for the case in which the rate of oxygen release is mass transfer controlled, which is the case in the present analysis. The air reactor volume is greater than the fuel reactor because of the low oxidation rates of Cu_2O which is controlled by diffusion through the CuO product layer; a limitation that can be

mitigated in part by the use of supported CuO [13]. In contrast with CLC systems, the energy release between the fuel and air reactor were of the same order because of the high heat of combustion of the carbon fuel. Estimates of the optimum conditions for the conversion of the fuel reactor and air reactor were around values of $X_{\text{CuO,FR}} = 0.3$ and $X_{\text{CuO,AR}} = 0.75$. At these conditions the residence times in the air and fuel reactor were about equal. The value of the oxygen carrier mass loading at these conditions is 135 kg CuO/MW_t. This value is higher than value reported for CLC systems burning gaseous fuels, lower than the combustion of solids burned in a CLC mode and a little higher than other studies on the use of CLOU with CuO supported on ZrO₂. It should be noted that the values in this paper are for ideal reactors and do not include the resistances to the gas-solid contacting in real reactors [19].

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