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Short Communication

Sensitivity of chemical-looping combustion to particle reaction kinetics

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HIGHLIGHTS

- In a reactor-regenerator system, if particles have mean residence times in each reactor greater than the time taken for them to react completely, it is insensitive to kinetics.
- There is scope for approximating detailed particle kinetics using simple models.
- For chemical-looping combustion, a shrinking core model under product layer diffusion control is a suitable approximation for the behaviour of oxygen carrier particles.

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ABSTRACT

A simple simulation for chemical-looping combustion (CLC) is discussed: two, coupled fluidised reactors with steady circulation of particles of oxygen carrier between them. In particular, the sensitivity of CLC to different particle kinetics is investigated. The results show that the system is relatively insensitive to different kinetics when the mean residence time of particles in each reactor is greater than the time taken for them to react completely.

1. Introduction

Chemical-looping combustion (CLC) offers the possibility of burning fossil fuels whilst separating the CO_2 produced. The process involves the redox cycling of an oxygen carrier, typically a transition metal oxide, *e.g.* the combustion of methane:

$$4MeO + CH_4 \rightarrow 4Me + 2H_2O + CO_2 \quad (1)$$

$$4Me + 2O_2 \rightarrow 4MeO \quad (2)$$

$$CH_4 + 2O_2 \rightarrow 2H_2O + CO_2 \quad (3)$$

The oxygen carriers are contacted with the fuel in their oxidised form so that the lattice oxygen in the solid reacts *via* reaction (1). The gaseous product, after removal of water, is a stream of pure CO_2 suitable for sequestration. The reduced carrier is re-oxidised with air (reaction (2)). Complete conversion from MeO to Me and back to MeO will not necessarily be obtained in a real system. Overall, the hydrocarbon has been burnt in air (reaction (3)), so the total enthalpy change is the same as for conventional combustion (Lyngfelt et al., 2001).

An option for CLC is to use two interconnected fluidised reactors, as shown in Fig. 1. Here, the two sub-reactions are separated spatially, with reduction of the oxygen carrier in the fuel reactor and oxidation in the air reactor. Most pilot-scale CLC systems use variants of this basic configuration (Adanez et al., 2012).

There has been significant research on measuring the redox kinetics of carriers at the laboratory scale (Adanez et al., 2012), but almost nothing published on the important question of how knowing the kinetics of an individual particle would affect the design of the system in Fig. 1. Indeed, in some cases, *e.g.* experiments to determine the rate of oxidation at high temperature, it is almost impossible, experimentally, to determine the intrinsic kinetics because they are so fast that experiments are confounded by

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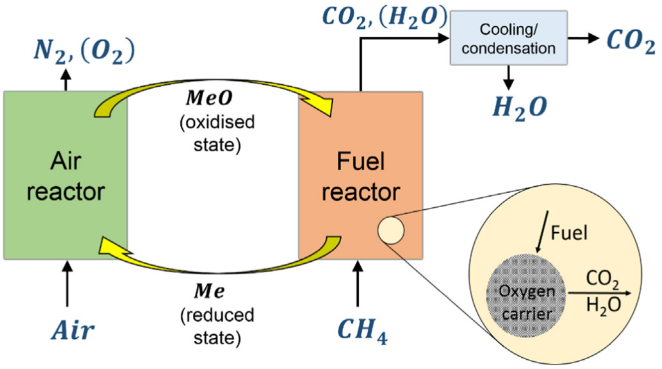

Fig. 1. Schematic of CLC concept.

various mass and heat transfer effects. Here, we investigate the sensitivity of reactor behaviour to the kinetics of individual particles.

2. Model development

2.1. Cycling behaviour

The simple situation in Fig. 1 was considered: two, coupled fluidised bed reactors, well-mixed with respect to solids, with steady circulation between them. In terms of gas-solid contact, it is assumed that the time for a particle to sample the whole bed is much less than the residence time of a particle in the bed. As a result a particle will sample the complete gas profile of the bed many times. An average gas concentration can therefore be used. No reaction or mixing was assumed to occur in the connecting lines and all particles were assumed to have identical physical and chemical properties, other than state of conversion. Since the reactors are well-mixed with respect to solids, and assuming no elutriation, the residence time distribution (RTD) function for the particles for both reactors is:

$$E(t) = \frac{1}{\bar{t}} e^{-\frac{t}{\bar{t}}} \tag{4}$$

where $\bar{t}$ is the mean residence time of particles in the reactor and t is the time a particle spends in the reactor.

Monte Carlo (MC) simulation was used to determine the mean conversion and rate of reaction of particles as they leave the reactors. The simulation was begun with a fully-oxidised particle fed to the fuel reactor. The particle leaves having spent time in the reactor chosen by inverse transform sampling (ITS) from the RTD function:

$$t = -\bar{t} \ln(U) \tag{5}$$

where U is a random number between 0 and 1. Once the particle has spent this time in the fuel reactor, it was fed to the air reactor. Similarly, the time spent in the air reactor was determined by ITS. When the particle exited the air reactor, the first cycle was complete. The process was repeated for 1000 cycles. The methodology is similar to that used by Kimura et al. (1979). Tracking the local state of conversion of particles is important, since particles can build up complex local distributions of reactant and product as they are cycled between the two reactors. Chuang et al. showed experimentally that sharp transitions between reactant and product can be present after both oxidation and reduction reactions (Chuang et al., 2010, 2009). In the present work, the simulation was performed for shrinking core models (SCMs) (chemical reaction, product layer diffusion and external gas film control), uniform reaction, and for a detailed model of a single particle, described in Section 2.2.

2.2. Detailed model of a single particle

Here, the expressions for intrinsic kinetics were coupled with the Stefan-Maxwell equations. Allowance was made for external mass transfer by applying the Stefan-Maxwell equations to the transport of gases over a defined film thickness of particulate phase (Saucedo et al., 2014). The thickness of the diffusion boundary layer was calculated as described by Hayhurst (2000) and Dai et al. (2016). To account for temperature gradients, an appropriate form of the energy equation was used (see Supplementary Information). The particle was assumed to be spherical with a homogeneous structure of monosized pores, which were unaffected in size by the reaction.

3. Results

The detailed particle model was used to model the reduction (reaction (6)) and oxidation (reaction (7)) of a single particle of oxygen carrier containing CuO and Al_2O_3 (82.5 wt% CuO) at 850 °C, with properties given in Table 1. The reducing environment was, on a molar basis, 5% CO in 2.5% CO_2 and 92.5% N_2, while the oxidation was with 5% O_2 in N_2. For oxidation in air at 850 °C, the equilibrium lies towards CuO rather than Cu_2O (Gayán et al., 2012).

$$CuO + CO \rightarrow Cu + CO_2 \tag{6}$$

$$2Cu + O_2 \rightarrow 2CuO \tag{7}$$

The predicted behaviour of a particle over two redox cycles is shown in Fig. 2, for the case of the particle having insufficient time to react completely. Even after two cycles, the particle has a complicated distribution of reactant and product, confirming that the modelling approach, described in Section 2.1 is essential.

Using the detailed and simple models, a single particle of oxygen carrier was cycled 1000 times between the reactors for different values of θ, given by:

$$\theta = \frac{t_{tot}}{\bar{t}} \tag{8}$$

where t_{tot} is the time taken for a fresh particle to react completely in a reactor, and $\bar{t}$ is its mean residence time in that reactor: t_{tot} is not necessarily the same for different kinetics. The smaller θ is, the longer the particle spends in the reactors. Since every particle carries the complete statistics of the process, which remain constant throughout the simulation, the ergodic hypothesis can be invoked. This says that cycling a particle 1000 times is equivalent

Table 1
Properties of the oxygen carrier particle for the detailed particle model (Chuang et al., 2009).

Property	Value
Diameter	300 μm
Skeletal density	4500 kg/m^3
Porosity	0.75
Tortuosity	$\sqrt{3}$
BET surface area	4.5×10^7 m^2/m^3
Mean pore radius	37 nm
Intrinsic first order rate constant (reduction)	$6.5 \times 10^7 \exp(-52\ \text{kJ/mol}/RT)\ \text{s}^{-1}$
Intrinsic first order rate constant (oxidation)	$8.2 \times 10^6 \exp(-44\ \text{kJ/mol}/RT)\ \text{s}^{-1}$
Diffusion boundary layer thickness (reduction)	1196 μm
Diffusion boundary layer thickness (oxidation)	1263 μm

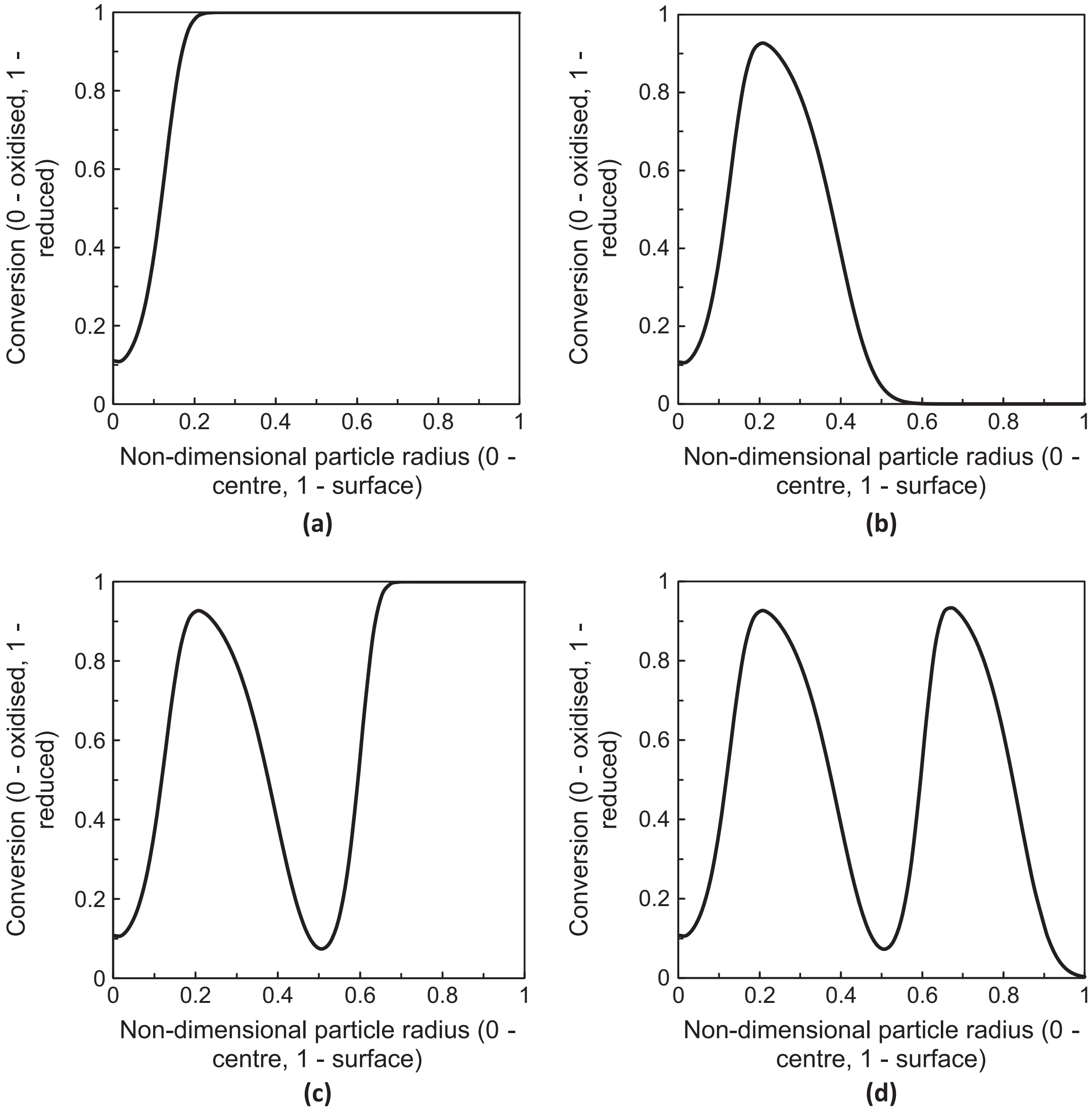

Fig. 2. Evolution of particle conversion with cycling. The particle is initially fully oxidised, it exits the fuel reactor after 20 s (a), then spends 6 s in the air reactor (b), followed by 8 s in the fuel reactor (c) and finally 1 s in the air reactor (d). The times have been chosen to illustrate the importance of conversion history.

to cycling 1000 particles once. This MC method therefore provides a useful insight into the behaviour of particles during cycling. All the results shown are for identical θ in both reactors.

The relationship between the conversion of the particle, when it leaves a reactor, and the mean residence time in the reactors is shown for different simple models in Fig. 3. Since the reactors are well-mixed with respect to solids, the mean conversion when leaving the reactor is equivalent to the mean conversion within the reactor. The analytical solution (Kimura et al., 1979) for a SCM under chemical reaction control is also shown. Fig. 3 shows that for mean conversion, the agreement between the simple models is good for $\theta < 1$, except for a SCM under external gas film control, where agreement is good for $\theta < 0.1$.

In Fig. 4, the result for the detailed particle model is compared to that for a SCM under product layer diffusion control. Overall there is excellent agreement, with only slight deviations at high θ.

Fig. 5 shows how the mean rate of reaction of a particle for different simple models varies with mean particle residence time. The analytical solution for a SCM under chemical reaction control is also shown. As for conversion, the mean rate when leaving the reactor is equivalent to the mean rate in the reactor. The rate has been normalised with respect to the analytical value for a SCM under chemical reaction control when θ=1, thus the results for reduction and oxidation are the same. Agreement between the

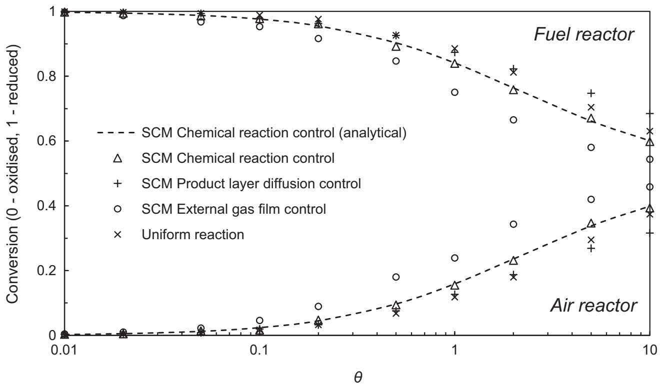

Fig. 3. Mean particle conversion for simple models.

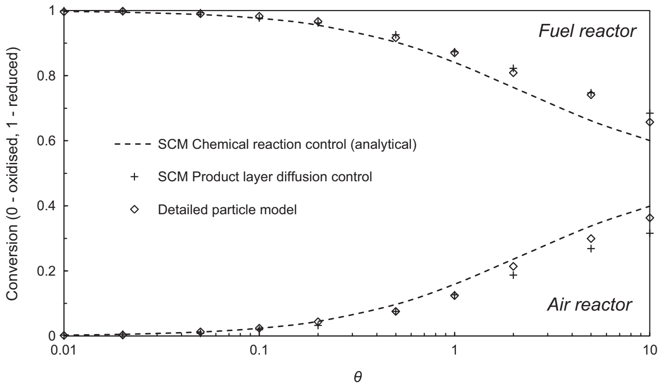

Fig. 4. Mean particle conversion for the detailed particle model to a SCM under product layer diffusion control.

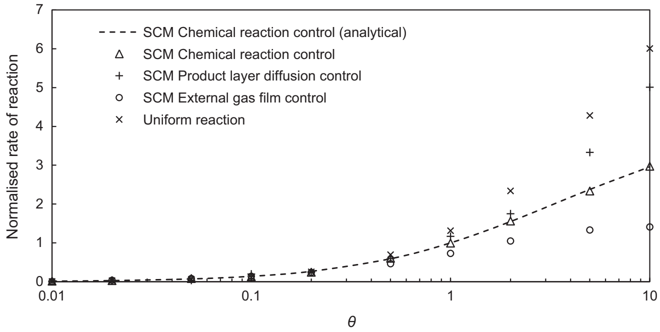

Fig. 5. Mean particle reaction rate for simple models.

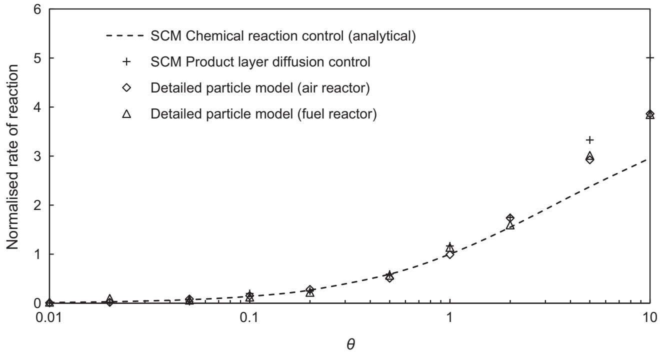

Fig. 6. Mean particle reaction rate for the detailed particle model and a SCM under product layer diffusion control.

simple models is good for $\theta<0.5$.

Finally, Fig. 6 compares the results for the detailed particle model with a SCM under product layer diffusion control; there is excellent agreement for $\theta<5$.

The results shown in this section did not depend on the initial conversion of the particle. For $0.01<\theta<10$, simulations with different initial conversions gave identical results. Initial conversion is only important for $\theta>50$.

4. Discussion

In CLC, particles will not necessarily react to completion as they are cycled between the two reactors; accordingly, their reaction history is important. Since there is a RTD for the particles, even if the mean residence time is greater than the time for complete reaction ($\theta<1$), they will nevertheless regularly spend less time in the reactor than is needed for them to react completely. Fig. 2 illustrates how; over time, a particle can build up concentric shells of reactant and product, as postulated also by Kimura et al. (1979) for cracking catalyst.

The results for simple particle reaction models (SCMs and uniform reaction) are similar provided that $\theta<1$ for conversion and $\theta<0.5$ for rate of reaction, as shown in Figs. 3 and 5. The exception is for a SCM under external gas film control, where conversion results are similar when $\theta<0.1$. CLC is likely to be operated between $0.2<\theta<1$ to achieve an optimal balance between a low circulation rate and a low inventory of oxygen carrier. The findings described in this paper are therefore important, because they show that CLC is relatively insensitive to different particle kinetics. This is expected because, as θ gets smaller, the particles react to completion more frequently. As a fraction of their residence time, they therefore spend less time in the range of conversion (0.1–0.9), where different kinetics diverge the most.

CLC is one example of a reactor-regenerator system. The observation that when $\theta<1$, CLC is insensitive to different particle kinetics, is therefore relevant for other processes, *e.g.* fluidised catalytic cracking, systems for the removal of H_2S and other gases from gasification or combustion, chemical-looping reforming and calcium-looping. There is also scope for approximating detailed particle models using simple ones. This observation is very useful when $\theta>1$, since a simple particle model decreases significantly the computational time required for an overall process model to solve. It is also beneficial for cases where the intrinsic kinetics are difficult to obtain experimentally *e.g.* oxidation at high temperatures. For the CLC process, described in this paper when $\theta<5$, there is excellent agreement between the detailed model and a SCM under product layer diffusion control. The small deviation when $\theta>5$, is because the rate of external mass transfer begins to have a limiting effect.

5. Conclusions

A simple simulation of CLC has been developed, which showed that the process was relatively insensitive to different particle kinetics, when the mean residence time of the particles was greater than the time taken for them to react completely ($\theta<1$). This is important because CLC is likely to be operated with low θ. In addition, this result is relevant for other reactor-regenerator systems. It was also shown that a SCM under product layer diffusion control was an excellent approximation for the detailed particle model when $\theta<5$, demonstrating scope for using simple models in simulations of CLC systems.

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