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The effect of different particle residence time distributions on the chemical looping combustion process

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HIGHLIGHTS

- Model for a reactor-regenerator system has been developed.
- Residence time distribution of solids is important in chemical looping combustion.
- Reducing the extent of solid mixing increases the extent of conversion and rates.
- Residence time distribution of solids should be accounted for in simulations.

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ABSTRACT

A model for chemical looping combustion has been developed to allow the effect of different residence time distributions of oxygen carrier particles in the air and fuel reactors to be investigated. The model envisages two, coupled fluidised bed reactors with steady circulation of particles between them. The results show that the process is sensitive to the residence time distributions, particularly when the mean residence time of particles in the reactors is similar to the time required for them to react completely. Under certain operating conditions, decreasing the variance of the residence time distribution, leads to a greater mean conversion of the particles by the time they leave the reactors and higher mean rates of reaction in the beds. In this way the required inventory and circulation rate of solids could be reduced, which would lower the capital and operating costs of a CLC process. Since the residence time distribution of solids is important, it should be taken into account when modelling or designing a chemical looping combustion process, *e.g.* by using a tanks-in-series model. This work indicates that if the number of tanks, $N \leq 5$, knowing N to the nearest integer is generally sufficient, unless a high degree of accuracy is needed. As N increases, the sensitivity of the coupled system decreases, so for $N > 5$, knowing the value to the nearest 5 or 10 tanks is sufficient. This is valid whether N is the same or different in the two reactors. Chemical looping combustion is one example of a reactor-regenerator system, so the results are also relevant for other processes of this type, such as fluidised catalytic cracking.

1. Introduction

Chemical looping combustion (CLC) is a technique which allows fossil fuels to be burnt with inherent capture of the carbon dioxide emissions. It is based on the redox cycling of an oxygen carrier, which is typically an oxide of a transition metal. The carrier supplies oxygen from its crystal lattice in the fuel reactor and is reduced in the process. It is then transferred to the air reactor where the oxide is regenerated by reaction with air. CLC is thus a type of reactor-regenerator system, often exemplified by fluidised catalytic cracking [1]. Generally CLC is designed in a configuration consisting of two interconnected fluidised bed reactors [2,3], as shown in Fig. 1. Reduction of the oxygen carrier takes place in the fuel reactor, while regeneration is conducted in the air reactor.

A significant amount of research has been conducted on CLC, ranging from the scale of the oxygen carrier materials [2,4] up to the industrial scale, such as modelling the integration of CLC reactors with a power cycle for generating electricity [5]. At the scale of the interconnected fluidised bed reactors, a number of different pilot scale units have been built and operated with a variety of different oxygen carrier

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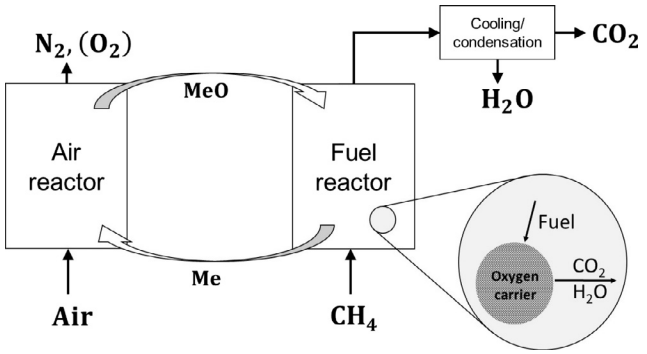

Fig. 1. The CLC process. Me is an appropriate transition metal.

materials and fuels up to 3 MWth [6–9]. Modelling of such reactors has also been conducted, ranging from empirical [10] or semi-empirical [11] to CFD [12–15]. Virtually all modelling has been applied to particular reactor designs, oxygen carrier materials and fuels, which has enabled certain aspects of these configurations to be evaluated. For example Cuadrat et al. [16] optimised different conditions such as the carbon separations system, the fuel reactor temperature and the solids inventory for an iG-CLC system for solid fuels with ilmenite as oxygen carrier. Zhang et al. [17] modelled an interconnected double loop circulating fluidised bed and analysed the influence of different operating conditions such as the temperature of the fuel reactor and the fuel power on its performance. Ohlemüller et al. [18] developed a process model for CLC with coal in a 100kWth system. They used it to study the effect of factors such as pressure drop, temperature and solid circulation on the performance of the pilot unit. A general CLC process and its sensitivity to different factors has rarely been considered. This would be valuable for reverse engineering an optimal process and also for developing computationally-efficient and accurate simulations by accounting for each factor at the right level of detail.

In this paper, a model that is general to any CLC process is used to investigate the effect of different residence time distributions (RTDs) of particles on its performance. This has received little attention in the literature on CLC or reactor-regenerator systems. It is important since the RTD is well-known to significantly influence the performance of reactors [19] and understanding these effects would allow the CLC process to be optimised, as will be demonstrated in this paper. Further, it gives insight for developing computationally-efficient and accurate simulations of the CLC process. Particularly for solid systems, RTDs are time-consuming, expensive and challenging to determine, irrespective of whether the laboratory or the industrial scale is being considered. Accordingly, experimental RTDs from a laboratory-scale circulating fluidised bed (CFB) have been used in this paper to understand how detailed an experimental determination of the RTDs of a real system must be to give useful information.

1.1. The residence time distribution function

The RTD of material in a system can be represented by the RTD function, $E(t)$, which gives the distribution of times that material spends in a system. $E(t)dt$ is the fraction of material spending a time between t and $t + dt$ in the reactor. Therefore [19]:

$$\int_0^\infty E(t)dt = 1 \tag{1}$$

The mean residence time, $\bar{t}$ is given by:

$$\bar{t} = \int_0^\infty tE(t)dt \tag{2}$$

and the variance, σ^2 by:

$$\sigma^2 = \int_0^\infty (t-\bar{t})^2 E(t)dt \tag{3}$$

In general, the solids in fluidised beds are assumed to be well-mixed [19–23]. As a result, a tanks-in-series (TIS) model is often used to represent the RTD function [24–28], where it is assumed that the system consists of N continuous stirred tank reactors (CSTRs), of equal volume, in series. Each tank is statistically independent and, in each, the solids are perfectly mixed. The RTD is given by [29]:

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

where t is the time a particle spends in the overall reactor. $N = 1$ corresponds to a well-mixed system and as $N \to \infty$, the RTD from the model approaches plug flow. The variance, σ^2, of the RTD is

$$\sigma^2 = \frac{\bar{t}^2}{N} \tag{5}$$

In this form, the TIS model is only valid for $N \in \mathbb{N}$. The model can be adapted so that N can take non-integer values *e.g.* the fractional tank model [29] or the gamma extension model [30]. In the gamma extension model, the gamma function, $\Gamma(N)$ is used as a generalised factorial function and replaces the $(N-1)!$ term in Eq. (4):

$$\Gamma(N) = \int_{x=0}^\infty e^{-x}x^{N-1}dx \tag{6}$$

where N can now be any rational number greater than zero.

2. Model development

The model developed in this work was based on two, coupled fluidised bed reactors, with steady circulation of particles between them, as depicted in Fig. 1. In terms of the gas-solid reaction, a characteristic time for a particle to react completely in the air and in the fuel reactor, $t_{tot,air}$ and $t_{tot,fuel}$ respectively was specified. These two parameters were inputs to particle models, describing the rate of reaction of oxygen carrier particles, assumed to be either shrinking core (controlled by one or more of intrinsic chemical reaction, diffusion through the product layer and external mass transfer) or uniform throughout the particle [31]. In this paper, which is general for any CLC system, a non-dimensional time, θ was used throughout, where

$$\theta = \frac{t_{tot}}{\bar{t}} \tag{7}$$

and $\bar{t}$ is the mean residence time of particles in the air or the fuel reactor. Large values of θ correspond to short residence times and small values to long residence times compared to the time taken for a particle to react completely. A non-dimensional time was used to make the model general to any CLC system, regardless of the scale. In fact it is general to any reactor-regenerator system. It also meant that it was not necessary to have precise values for $t_{tot,air}$ and $t_{tot,fuel}$.

The RTD of the particles in the reactors was modelled using a tanks-in-series (TIS) model, where N can take non-integer values (Eqs. (4) and (6)). The particles were assumed to be of equal size and it was assumed that there was no irreversible decay in performance over time. The latter is an appropriate assumption to make since the time taken for the CLC process to reach a steady state would usually be short compared to the time taken for the performance of particles to deteriorate due to repetitive redox cycling. The state of conversion of particles was tracked over time. This is important since particles can build up complex local distributions of oxidised and reduced material as they are cycled between the air and fuel reactors [32].

A Monte Carlo (MC) approach was used to determine the mean conversion of the stream of particles as they leave the air and the fuel reactors, X_{air} and X_{fuel} respectively. The mean rates of reaction of particles within the beds were also determined. When the system is well mixed ($N = 1$), the properties of the particles within the bed are the same as the properties of the particles leaving the bed. In all other cases, there is a difference, which reaches a maximum as plug flow is