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Measuring attrition resistance of oxygen carrier particles for chemical looping combustion with a customized jet cup

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ABSTRACT

A customized jet cup for measuring attrition resistance of oxygen carrier particles for chemical looping combustion has been constructed and used to evaluate 25 different material samples, all of which previously have been subject to continuous operation in chemical looping reactors at Chalmers University of Technology. The effect of continuous operation has been assessed by comparing attrition behavior of fresh particles with that of used ones. It is concluded that the correlation between the jet cup tests and operational experience is robust, and that there is always considerable difference in attrition resistance between fresh and used particles of the same batch. Composite materials with NiO or Fe_2O_3 as active phase and Al_2O_3-, $NiAl_2O_4$- or $MgAl_2O_4$-based support and materials based on the $CaMnO_{3-\delta}$ perovskite structure typically had high attrition resistance, which improved further following operation with fuel. Combined $(Fe_xMn_{1-x})_2O_3$ oxides and all materials containing smaller or larger amounts of either CuO or ZrO_2 experienced reduced attrition resistance during operation with fuel, and usually also had low attrition resistance to begin with. Fresh particles of the commonly used oxygen carrier ilmenite had reasonably high attrition resistance, while ilmenite that had been subject to chemical looping combustion of natural gas showed higher rate of attrition. No strong correlation between the commonly used crushing strength index and attrition resistance measured with jet cup could be established, but it was clear that particles with a crushing strength above 2 N were much more likely to have high attrition resistance compared to softer particles. As compared to crushing strength, the jet cup testing was better correlated to attrition in actual operation.

1. Introduction

Chemical looping combustion (CLC) is an upcoming technology for CO_2 capture currently under development. Chemical looping combustion requires solid particles with specific properties that are capable of enduring the extraordinary harsh conditions of fluidized-bed reactors. Development and selection of such particles are not trivial and considerable attention has been given to it in recent years. In order to find suitable materials we have adopted a scheme which is described in Fig. 1. One of the objectives with this paper is to highlight the benefits of point 3d in this scheme.

Generally speaking, it does not require large effort to be successful up to stage 3b in the scheme described in Fig. 1. It is possible to produce small samples of particles in any well-equipped laboratory with standard methods, and reactivity can be accurately measured in e.g. a simple fluidized bed quartz reactor. There are also numerous common but useful characterization techniques that require only very small amounts of solids (e.g. TGA, TPR, XRD, EDX, SEM, BET). Stages 4 to 7 on the other hand require more solids, larger and more complex reactor systems and a much more significant effort in terms of material, manpower, time and money. Therefore it is critical that the activities in stage 3 of the scheme are capable of producing reasonably adequate indications of whether a certain oxygen carrier material is promising or not. Else there is a risk that a lot of time and effort are spent in producing and testing large batches of materials that are not useful.

As explained above, there are many good tools available for determining reactivity and chemical properties of small particle samples. In contrast, there is a lack of tools to characterize small samples of particles with respect to attrition behavior in fluidized-bed reactors. The standard method is ASTM D5757 [1] which involves vertical air jets of very high velocity and requires comparably large particle samples (50 g) and long operation time (5 h). This method is unsuitable for our specific needs. In recent years we have examined more than 400 different oxygen carrier materials in fluidized-bed batch reactors (stage 3a in Fig. 1) using samples of 15 g. As will be shown in this article, it is a very significant advantage if materials can be tested both before and after such laboratory testing. Thus the ASTM D5757 method cannot be used since we have less than 50 g available of used samples. Also 5 h of operation time was considered too extensive for a method intended for material screening.

Crushing strength tests have been used extensively by us and others since the last 10 years [2,3], and while useful it is not a very reliable indicator on behavior in fluidized-bed reactor. Moreover, crushing

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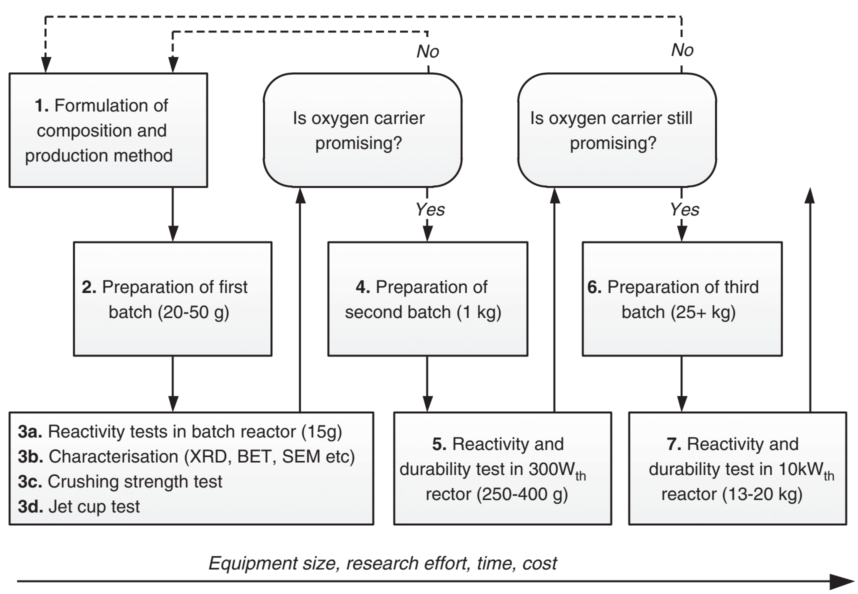

Fig. 1. Chalmers oxygen carrier development scheme. This article concerns point 3d.

strength tests cannot easily be made on particles that have been examined in the batch reactor because of their small size. Reproducible crushing strength tests typically require particles in the size range 180–250 μm or larger, while batch experiments normally need to be performed with smaller particles in the size range 125–180 μm. Thus, no satisfactory comparison can be made of crushing strength (point 3c in Fig. 1) before and after fluidization and testing in the batch reactor (point 3a in Fig. 1).

The purpose of this paper is to assess whether measuring resistance towards mechanical attrition with a customized jet cup (point 3d in Fig. 1) could be a meaningful indicator to assist in the development of durable oxygen carrier particles for chemical looping combustion. A jet cup is a device designed to simulate the effects of grid jet attrition and cyclone attrition, typically considered to be the two main contributors to mechanical attrition in circulating fluidized-bed combustion. Jet cup testing is not a standardized method and exists in different iterations, see for example Cocco et al. [4], Zhao et al. [5] and Weeks & Dumbill [6]. Most commonly the method is used to measure attrition resistance of bed material for fluid catalytic cracking.

The device described in this paper is similar to PSRI's improved cylindrical jet cup [2], but the size of the equipment has been scaled down in order to be suitable for samples as small as 5 g. Using smaller samples may result in larger measurement error compared to using larger samples, see Cocco et al. [4]. But for our purpose using larger samples is not an option since we want to use the jet cup at stage 3 of our development scheme where we typically conduct experiments with 15 g batches. Thus by choosing a sample size of 5 g attrition resistance can be examined both for fresh and used samples.

The purpose of this work is not to develop a method capable of safe predictions. That would be unrealistic considering the complexity in the process of particle-size reduction, the very large number of completely different materials which are currently being examined as oxygen carriers for chemical looping combustion, and the absence of chemical reactions during testing at room temperature. Neither is it our intention to propose a new industrial standard for material characterization. Instead, the aim is to introduce a tool that potentially could improve the early selection process during material development in schemes similar to ours (Fig. 1).

In this study, the proposed method has been used to examine a number of oxygen carrier particles which already have been subject to continuous operation (stage 5 or stage 7 in Fig. 1). The results have been compared with operational experience in order to determine if there is a meaningful correlation between attrition resistances measured with jet cup and performance in fluidized-bed reactor under operating conditions. A comparison is also made to results from testing of crushing strength.

2. Background

2.1. Chemical looping combustion

Chemical looping combustion is an innovative method to utilize fuels in which the fuel is oxidized using two separate reactor vessels, one air reactor (AR) and one fuel reactor (FR). A solid oxygen-carrier, typically a transition metal oxide (MeO_x), performs the task of transporting oxygen to the fuel and circulates continuously between the two reactors. In the fuel reactor it is reduced by the fuel, which in turn is oxidized to CO_2 and H_2O. In the air reactor it is oxidized to its initial state with O_2 from air. The net energy released in the reactor system is the same as in ordinary combustion, and the operating temperature of each reactor is expected to be in the range of 800–1050 °C. A schematic description of chemical looping combustion can be found in Fig. 2.

Compared to conventional combustion, chemical looping combustion would provide some intriguing benefits. Most importantly, fuel is never mixed with N_2 from the combustion air. Hence condensation of the steam produced in the fuel reactor is sufficient to obtain almost pure CO_2. There is no inherent energy penalty or cost associated with

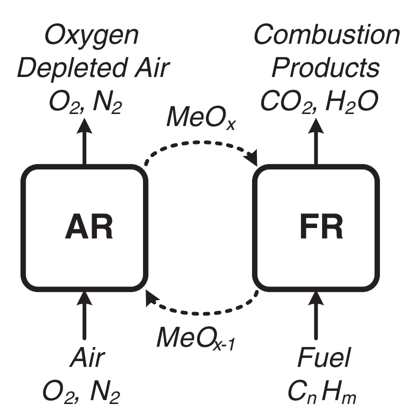

Fig. 2. Schematic description of chemical looping combustion.