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The mechanism of agglomeration of the refractory materials in a fluidized-bed reactor

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Abstract

Olivine is one of the refractory materials well-suited for fluidized-bed reactor technology. However, this material agglomerates at high temperatures due to the presence of sticky molten ash. The aim of this work is to investigate the mechanism of olivine agglomeration in fluidized-bed reactors and to determine the risk factors for agglomeration.

A laboratory fluidized-bed reactor was designed to study the agglomeration effect between the ash and the refractory bed material. A systematic experiment was performed to determine the agglomeration ratio as a function of different parameters (operating time, bed materials, ash content, temperature, gas flow and additives). The mechanism of adhesion between the molten ash and the bed material is described, and the optimization of parameters to prevent this agglomeration is determined.

Keywords: Refractory; Olivine; Ash; Fluidized bed; Agglomeration

1. Introduction

Agglomeration is a current research topic in fluidized bed technologies. This phenomenon is due to the presence of sticky molten ash and refractory bed materials in the reactor. It has been extensively studied in recent years in the gasification and combustion field [1,2] to find solutions to limit and avoid this phenomenon [3–6] and has also been investigated to determine a detection method [1,7–10].

In situ measurements by detection of pressure and temperature fluctuations allow us to monitor agglomeration [2,10]. For instance, Bartels et al. [11] describe the agglomeration mechanisms involving a complex interaction of phenomena, comprising aspects of hydrodynamics, chemical transformations and interaction between refractory particles. Moreover, Brus et al. [10] and Öhman et al. [1] have demonstrated two routes for agglomeration referred to as "melt-induced" agglomeration and "coating-induced" agglomeration.

The two aspects of physical interactions and chemical interactions can be considered. Physical interaction involves Van der Waals and electrostatic forces due to the stickiness of liquid-coated bed particles, whereas chemical interactions involve covalent bonds as a consequence of the high-temperature interaction between the liquid phase and the bed particles.

The presence of a liquid phase is due to the transformation of biomass ash at high temperature and the formation of alkali-silicates having a lower melting point than the process temperature (800 °C). Fuel indices, based on the elemental composition of the biomass ash, are used to predict the tendency toward liquid phase formation and agglomeration in fluidized beds [12]. The alkali index ($I = [\mathrm{Si}+\mathrm{Na}+\mathrm{K}]/[\mathrm{Ca}+\mathrm{Mg}+\mathrm{P}]$) used by Visser et al. defines the tendency of a material to stick by the ratio of alkali metals and silicon to the alkaline earth metals and phosphorous. The latter can increase the melting temperature of silicates [12]. Fast-growing biomass such as energy crops have a high alkali content and are considered as risky fuels.

Usually, agglomeration during industrial fluidized-bed gasification or combustion is monitored via on-line detection of pressure and temperature fluctuations [2,10,11]. Nevertheless,

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information about the agglomeration of bed particles remains insufficient. Studies performed at a laboratory scale use a high quantity of biomass compared with the amount of bed material. This process generates syngas, tars and char making it difficult to study the agglomeration mechanism of the refractory bed particles [7,10,13–15].

The purpose of this work is to describe and examine the interaction mechanisms between the refractory materials and molten ashes with an alternative approach at the laboratory scale.

Three different bed materials, silica sand, olivine and calcined olivine in contact with miscanthus ash were evaluated. Silica sand is the most common bed material in fluidized-bed processes; most agglomeration-related studies were conducted with this bed material [11,12,16,17].

Olivine is an annealing bed material, as it has a catalytic effect in tar decomposition due to its iron content. The catalytic effect can be enhanced via calcination of the particles above 900 °C which increases the Fe concentration at the surface of the particle. In the literature, olivine is studied mostly as catalyst, but its role in agglomeration is less understood [18,19].

2. Materials and methods

2.1. Refractory materials and additives

The main refractory bed material was a standard olivine mined at the Åheim Plant in Norway and provided by the Sibelco Company, France. Olivine is an orthosilicate corresponding to the complete solid solution between forsterite (Mg_2SiO_4) and fayalite (Fe_2SiO_4). This material was formulated as $(Mg_{0.92}Fe_{0.08})_2SiO_4$ [20].

The second bed material was calcined olivine. When used as a catalyst, olivine is calcined at 1400 °C in air for 4 h, which improves its mechanical properties for use in a fluidized bed [20,21].

Our previous papers have shown that natural olivine is not an inert silicate; it is transformed by thermal decomposition (dehydration and oxidation of the fayalite) at a high temperature [20,21]. The structural transformations consist of the dehydration of serpentine below 600 °C, the disappearance of the quartz phase at 1030 °C, and the formation of iron oxide phases.

It was shown that the material forms magnetite spinel and enstatite at high temperatures which spread from the inner part of the particles toward the surface [20,21].

The third bed material used in this study was silica sand, provided by the SIBELCO Company, France and composed of >99.8 wt% of quartz.

All of the bed material was sieved to obtain particle sizes ranging from 400 to 500 μm. In this way, the agglomerates above 500 μm in diameter were separated after each test.

One way to prevent agglomeration is to mix additives with the bed materials.

Additives were combined with the olivine to prevent agglomeration. Two refractory additives were used as anti-agglomerates. The first was dolomite ($Ca,Mg(CO_3)_2$), mixed at 1.2 wt% and 3 wt% with raw olivine (respectively 98.8 wt% and 97 wt%). It was mined at Neau, France and used in the form of a thin powder (<1 μm). The second was kaolin ($AlSiO_4(OH)_5$), mixed at 0.25 wt% with raw olivine (99.75 wt-%). It was mined at Quessoy, France, and was used in the form of a thin powder (<1 μm).

2.2. *Miscanthus x giganteus* ash

The current study was conducted with the ash of Miscanthus x giganteus (MXG) harvested in April 2011 at La Ferté-Chevresis, France (supplied by NovaBiom).

The miscanthus ash has an alkali Index (I) equal to 5.3 and presents a high tendency to stick and agglomerate at high temperatures. The alkali content can be decreased by washing the biomass. To study this effect, miscanthus was leached in tap water (1 L of water for 100 g miscanthus) for 24 h in a mixer. Afterwards, the sample was filtered and rinsed with tap water.

The ashes were prepared by crushing and burning dried miscanthus in a muffle furnace at 400 °C for 8 h under an atmosphere of air. The aim was to obtain an adequate amount of ashes for the study without influencing the initial inorganic phases [22]. Approximately 200 g of ash were obtained and mixed to provide a homogeneous blend ($dp<1$ μm). The composition of unwashed and washed MXG ashes as determined by ICP-MS is presented in Table 1.

The leaching of miscanthus shows a decrease in the alkali metals with a loss of 77.1 wt% of potassium and a loss of sodium. Sodium is present in trace amounts in miscanthus, therefore its role in agglomeration is minor compared to potassium. It is difficult to determine exactly the losses of Na due to the very small quantity (limit of detection). The water lixiviation shows that K and Na exist as ions which may be associated with Cl, P, CO_3^{2-} and SO_4^{2-} [23].

2.3. Bubbling fluidized bed design

A bench scale fluidized bed was designed to study the agglomeration effect between miscanthus ashes and the bed material. The reactor is made of quartz and is shown in Fig. 1. It is composed of two tubes separated by a quartz grid (pore DIA 50 μm). The reactor has a diameter of 50 mm and it is heated by an electrical tubular furnace. During the tests, the bed particles are

Table 1
Composition (wt%) of MXG ashes and washed MXG ash.

Elements (wt%)	MXG ash	Washed MXG ash
Si	26.06	39.13
K	22.27	5.12
Ca	6.17	6.41
Mg	1.91	3.21
P	1.07	N.D
Cl	2.15	N.D
Na	0.10	N.D
Traces	<0.5	<0.3

Traces: Mn, Ba, Zn, Sr, Cu, B, Ti, Fe, S not analyzed. N.D: not detected.