Refereed Proceedings

The 13th International Conference on Fluidization - New Paradigm in Fluidization Engineering

Engineering Conferences International *Year* 2010

A PERSPECTIVE ON DEVELOPMENT OF NOVEL FLUIDIZED BED PROCESSES FOR A MORE SUSTAINABLE GLOBAL FUTURE

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Abstract:

Faced with the need for transformative changes to solve global problems, fluidization could play a major role in contributing in areas like carbon capture, use of renewable resources, and recovery of valuable materials from waste streams. Some current examples are discussed where the fluidization community can help to find solutions

1. INTRODUCTION

Human beings and the world in which we live face a number of serious challenges, such as climate change, exhaustion of resources, poverty, and communicable diseases. Although new policies and non-technological measures are often more important, there are areas where improved technological processes could contribute to global solutions. Emissions of greenhouse gases responsible for climate change and over-use of limited resources are examples of problems where engineers and scientists can have a positive impact. Although incremental improvements will always be worthwhile, new processes must be sought which are truly innovative and transformative, capable of making substantial contributions to reducing the human impact on the environment to provide a more sustainable future.

Fluidized bed reactors have unique properties which have been chiefly exploited in traditional industries, especially those related to upgrading and utilizing fossil fuels (especially oil and coal), as well as in metallurgical processes and in the manufacturing, chemical and pharmaceutical industries. The same features that have made fluidized beds attractive in these cases can be exploited in designing new processes, although always with new issues to be addressed. This paper outlines several of the many areas where fluidized beds could be a key element in significant break-throughs if major challenges associated with the technologies can be overcome.

2. FLUIDIZATION ATTRIBUTES, LIMITATIONS AND CONSTRAINTS

Fluidized bed reactors have attributes and deficiencies which must be considered when deciding on which type of reactor is best suited to each given application. Those that are commonly cited are listed in Table 1, relative to competing reactors, in particular fixed or moving bed reactors, conveyed reactors and rotary kilns, all of which are applied in some industrial processes. While the listed items are important, and likely to be major factors in the choice of the type of reactor, it must be remembered that the reactor, though the “heart” of any process, relies also on a host of auxiliary system components – compressors, materials of construction, feeders, valves, heat exchangers, separation devices, instrumentation, control systems – any of which can cause the overall process to fail. As we will see, these issues may be major factors in determining whether or not given processes are viable.

Fluidized beds are subject to constraints when they are designed, some of which are easily overlooked. Some of these are identified in Table 2. New processes which seek to incorporate fluidized bed reactors need to be designed within the constraints, or to find ways of overcoming them. At the same time, though not commonly considered explicitly, there are other features of fluidized beds, listed in Table 3, which may be exploited in certain circumstances. Some of these are, or could conceivably be, relevant to particular processes, as noted in the right column.

3. COMBATTING CLIMATE CHANGE

Most of the anthropogenic greenhouse gases (GHGs) being dispersed into the atmosphere originate from fossil fuels. In the longer run, humans must greatly curtail their appetite for fossil fuels. In the shorter term, some switching from coal and oil to natural gas will help, but the rapid growth in energy demand in many countries is likely to continue to increase overall GHG emissions for at least the next decade. Several technical solutions involving fluidization could play a significant role:

3.1 Carbon Capture and Storage (CCS)

There is some capacity for sequestering CO_2 underground in saline aquifers or in enhanced oil recovery sites. The capture (i.e. concentrating CO_2 to nearly a nearly pure stream) typically represents 50-80% of the cost of CCS (1). Several capture technologies are under active investigation, with fluidized beds playing a key role:

3.1.1 Oxy-firing: Combustion or gasification of coal or other solid fuels (e.g. petroleum coke) with pure oxygen results in a flue gas that, after condensing steam, is predominantly CO_2. The temperature uniformity, fuel flexibility, and the possibility of co-firing with biomass favour the application of circulating fluidized beds for this purpose (2). Various large-scale commercial options are under investigation.

3.1.2 Chemical looping of oxygen carriers: A second option under active development is to circulate oxygen carriers with multiple valence states (e.g. Ni/NiO, FeO/Fe_2O_3 or $CaS/CaSO_4$) between two connected units, with the release of oxygen to a gaseous fuel on one side, and regaining the higher oxidation state (i.e. being regenerated) on the other (3, 4). Since this avoids the nitrogen which makes up ~79% of the air used in conventional combustion, the process results in a product gas which, after condensing water, is almost pure CO_2. Fluidized beds are potentially ideal for such operations as they are able to circulate solid particles between vessels, as they do, for example, in catalytic cracking, fluid coking and CFB combustion with external heat exchangers. Much of the work involves testing of alternative oxygen carriers. Both combustion and hydrogen generation of syngas can be conducted in this manner. Leading work in this area is being done with fluidized beds, with very promising results (e.g. 5, 6). Challenges include slippage of gas with the recirculating solids and limited carrying capacity of the oxides (mass of oxygen per mass of solid carrier).

3.1.3 Chemical looping of CO_2 sorbents: Another option to capture CO_2 (3, 4) is to use a reversible reaction involving a "dry sorbent", such as $CaCO_3 \rightleftharpoons CaO + CO_2$, in a looping cycle, where the forward calcination reaction produces a nearly pure stream of CO_2 on one side of the loop, and the reverse carbonation reaction absorbs CO_2 as it is produced on the other side. The cyclic exchange of fresh and spent sorbent is depicted in Figure 1. While this type of looping can be combined with combustion, it is more suitable in combination with gasification or steam reforming for several reasons:

- Carbonation is exothermic, whereas reforming and steam gasification are endothermic, so that the carbonation can provide heat where it is needed, with the heat required for the overall process added on the calcination side of the loop.
- Steam reforming, water-gas-shift and most other gasification reactions are largely equilibrium controlled. Extracting CO_2, a major product of these reactions, helps to shift forward the chemical equilibria (by Le Châtelier's principle), so that capture of CO_2 actually assists gasification and reforming, a unique and major advantage.
- Calcium is likely to be mildly catalytic to gasification and tar cracking.

As in oxygen-carrier looping, fluidized beds allow circulation of solids between the two vessels (7). However, there are a number of serious issues that need to be resolved:

- Limestone and dolomite are inexpensive, but subject to serious loss of activity upon repeated cycling (8, 9) and to severe attrition (10). Techniques for pelletizing the sorbent and alternative sorbents are under investigation and development (11).
- Any sulphur present in the fuel irreversibly accelerates the decline in activity (12).
- If sorbent looping is practised in conjunction with steam reforming or catalytic gasification, there is a need to separate, or avoid mixing, the sorbent and catalyst.
- Due to the limited calcium utilization of most sorbents, raising and lower the

temperature to effect calcination and carbonation, respectively, results in having to continuously heat and cool large quantities of inert solids through "temperature swings" of ~150-200ºC. Raising and lowering the pressure cyclically to pass back and forth between calcination and carbonation conditions may well be advantageous (13), possibly using the hydrostatic pressure variations within a tall fluidized bed reactor to provide the pressure swing.

3.1.4 Direct capture of CO_2 from ambient air: Another option, perhaps a "last resort", is to capture CO_2 directly from the atmosphere. While this may seem far-fetched given the low CO_2 concentration (in mass transfer terms), ~380 ppm, there are several advantages (14): (i) the capture could be on any conceivable scale; (ii) the capture could be located at the optimum point for storage, rather than having to transport CO_2, captured at a power station, gasification facility or refinery to a distant site. As a result, this option is receiving serious attention in some quarters. In at least one of the technologies being explored (15), a fluidized bed is an integral part of the process.

3.2 Biomass Processing

Biomass can also play a significant role in many countries by displacing fossil fuels. Because of its relatively short (growth and decay) life cycle relative to the geological times needed to generate fossil fuels, the International Panel on Climate Change (IPCC) considers biomass to be neutral in terms of CO_2 emissions. Hence switching from fossil fuels to biomass reduces net greenhouse gas emissions. The primary sources of the biomass are agricultural, forestry and municipal wastes, though "energy crops" have also generated interest, as well as controversy. Operations can be biological or thermochemical, the latter based primarily on combustion, gasification and pyrolysis, all of which benefit from considerable previous experience with coal. However, relative to coal, biomass almost always has a higher volatile content, less ash, more moisture and lower density. Extreme particle shapes (fibres, wafers, etc.), coupled with pliability, compressibility and very wide particle size distributions, render biomass feedstocks heterogeneous, and difficult to handle or to feed in a reliable and continuous manner (16). Feeding is especially challenging when the reactor operates at high pressures, requiring sophisticated lock hoppers and plug feeders.

While the use of biomass in itself reduces GHG emissions, the various techniques for capturing CO_2, discussed in section 3.1 can again be used, providing an opportunity for "negative CO_2 emissions". For example, CO_2 capture could be realized while producing hydrogen (17), or by blending biomass with coal (18).

3.3 Solar-Grade Silicon

Of the various forms of renewable energy, only solar energy has the potential to satisfy a very major fraction of the world's energy demand, for example by locating photovoltaic collectors in desserts and transmitting power electrically, coupled with measures to cover night-time periods, e.g. by pumping water into reservoirs where this is feasible. Silicon, one of the world's most abundant elements, is of key importance for solar energy capture, and demand for silicon associated with solar energy is increasing rapidly. In the past, most industrial silicon has been produced for semi-conductors, with extremely high purity. The specifications for solar-grade silicon are much less stringent, though still demanding, opening up the possibility of less expensive processes capable of meeting the lower purity requirements. High-temperature fluidized bed reactors are playing a major role in several such processes, commercialized worldwide (19, 20).

4. RESOURCE RECOVERY: THE CASE OF STRUVITE FROM WASTE WATER

The world's phosphate rock resources are being rapidly exhausted, due to heavy usage of phosphorus in fertilizers. Intensive cultivation of soils to sustain increasing numbers of human beings and their livestock is accelerating the use of phosphorus. Large-scale growth of energy crops such as corn will only exacerbate the situation. Currently most of the phosphorous spread on fields as fertilizer ends up being washed by rainfall into streams and other waterways, where it causes blooms. In conventional municipal wastewater treatment, much of the phosphorus (~1.5 g/person/day) resides in biosolids, but some ends up as ammonium magnesium phosphate, $(NH_4)Mg\ PO_4{\cdot}6H_2O$, struvite, a solid product that tends to cause scale on pipes, resulting in eventual clogging. Struvite is also a cause of stones in urinary tracts, especially in cats. However, struvite can act as a fertilizer, returning both phosphorous and nitrogen to the soil. Hence phosphorus recovery as struvite is very promising.

Liquid-fluidized beds are proving to be useful in several countries for the production of uniform large crystals (21), ideal for fertilizers. For example, Ostara Nutrient Recovery of Vancouver has installed large-scale units in both Edmonton, Alberta and Portland, Oregon. Among the challenges have been how to scale up liquid fluidized beds from the laboratory to units of meters in diameter, how to control the size distribution and other properties of the crystals and process modelling (21, 22).

5. CONCLUSIONS

In the cases considered in this paper, technologies are under development which may be able to contribute in a significant manner to the alleviation of serious global problems. Incremental improvements in these area, while useful, will be insufficient to reverse the serious over-consumption of fossil fuels, increasing levels of greenhouse gases in the atmosphere, and exhaustion of scarce resources like phosphorous. Transformative changes demand imagination, willingness to pursue many avenues and hard work. As demonstrated in this paper, fluidized beds are at the heart of a number of the technologies with the greatest potential for positive impact.

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Table 1: Relevant positive features and drawbacks of gas-fluidized beds as reactors

Positive Features	**Drawbacks**
Excellent bed-to-surface heat transfer	Substantial axial dispersion of gas
Temperature uniformity	Near perfect mixing of solids
Excellent catalyst effectiveness factors	Gas bypassing
Modest pressure drops	Attrition of particles
Continuous addition and removal of particles	Entrainment of particles
Ability to handle limited quantities of liquid	Wastage of surfaces
Wide particle size distributions	Agglomeration can be a serious issue
Equipment can be very large	Complexity, uncertainties, and risk in design, scale-up and modelling
Turndown over considerable ranges	Due to several factors, more outages
	Electrostatic charge generation

Table 2: Some constraints in operating fluidized bed reactors

Constraint	**Some Consequences**
"Hydrostatic" pressure gradients	Gas compression with increasing depth
Gap width/mean particle diameter $\gtrsim$ 20 - 50	Limits number and shapes of surfaces that one can immerse in the bed
Surfaces horizontal or vertical	Limits design options
Flooding	Limits solids circulation rate and gas or liquid counterflow
Be wary of multiple passages in parallel	May adversely affect overall performance
Avoid particles of extreme shapes	Affects preparation needed for biomass
Breadth limits on particle size distribution	Affects specifications of feed materials as well as extent of attrition which is tolerable

Table 3: Other features of fluidized beds which can be exploited in reactors

Feature	Possible application
Ability to operate continuously, batchwise or in semi-batch mode.	Flexibility in choice of operating mode
Ability to vary conditions over time	Cyclic operation, adapt to changes
Good insulator when in "slumped" state,	Solar collectors; load following in power generation; recovery from interruptions
Ability to incorporate internal surfaces	Heat transfer, baffles, membranes
Different environments in different regions	Complementary processes in series; classification of product solid materials
Can promote or avoid particle segregation depending on operating conditions	Ability to selectively remove one species of particles or to handle blended materials
Self agglomeration of ultra-fine particles	Catalytic processes; nanoparticle processes
Favourable bed-to-surface mass transfer	Membrane processes
Lateral dispersion << Axial dispersion	Improved solids residence time distributions

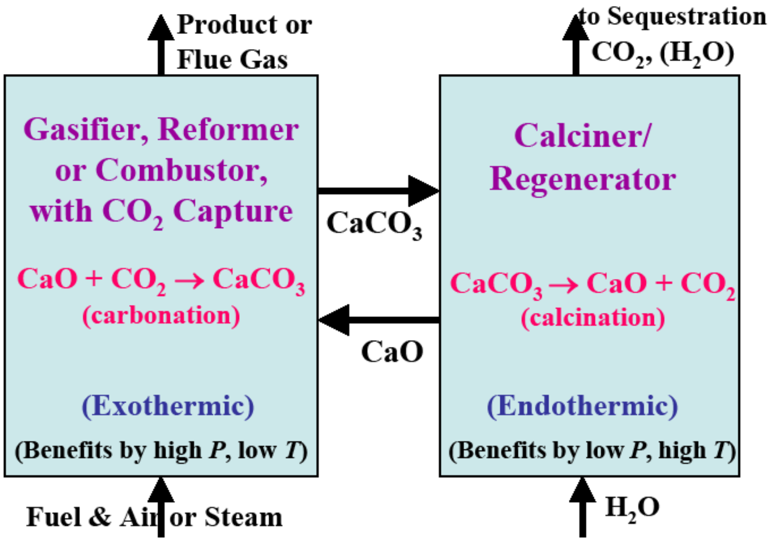

Fig. 1: Schematic of sorbent looping with limestone for CO_2 capture