82d Sorption-Enhanced Steam Methane Reforming in Fluidized Bed Reactors

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Hydrogen is often referred to an important potential energy carrier, but its advantages are unlikely to be realized unless efficient means can be found to produce it with reduced generation of CO_2. Steam reforming of natural gas is the predominant production route to hydrogen for large-scale industrial applications, but the process suffers from a number of limitations making it inefficient. For methane the reactions are:

$CH_4 + H_2O = CO + 3H_2$ (1)

$CO + H_2O = CO_2 + H_2$ (2)

$CH_4 + 2H_2O = CO_2 + 4H_2$ (3)

One way of overcoming the thermodynamic limitation of steam reforming is to remove either hydrogen or carbon dioxide as it is produced, hence shifting the thermodynamic equilibrium towards the product side. The concept for sorption-enhanced methane steam reforming (SE-SMR) is based on *in situ* removal of CO_2 by sorbent, e.g. CaO.

$CaO + CO_2 = CaCO_3$ (4)

Sorption enhancement enables lower reaction temperatures, which may reduce catalyst coking and sintering, while enabling use of less expensive reactor wall materials. In addition, heat release by the exothermic carbonation reaction supplies most of the heat required by the endothermic reforming reactions. However, energy is required to regenerate the sorbent to its oxide form by the energy-intensive calcination reaction (reverse of equation (4)). Operation of a SE-SMR process requires either that there be parallel reactors operated alternatively and out of phase in reforming and sorbent regeneration modes, or that sorbent be continuously transferred between the reformer/carbonator and regenerator/calciner. The concept of SE-SMR is well established and a lot of work over the last years has been focusing on the multi-cycle behaviour of different sorbents for CO_2 capture. However, experimental investigations have mainly been conducted in fixed bed reactors (e.g. Hufton et al. 1999, Balasubramanian et al., 1999), which will not be very suited for large-scale continuous operation. Fluidized bed reactors are commonly used in processes where catalysts must be continuously regenerated, while also facilitating heat transfer, temperature uniformity and higher catalyst effectiveness factors. Fluidized beds can be operated in different flow regimes, e.g. in bubbling or fast fluidization. Coupling of two bubbling beds would have the advantage of low rates of attrition due to low gas and particle velocities, and the relatively slow carbonation reaction rate will be facilitated in this flow regime.

The use of fluidized bed reactors for SE-SMR has been investigated. Experiments in a bubbling fluidized bed have been conducted at University of British Columbia, Vancouver. An atmospheric-pressure bubbling fluidized bed reactor (BFBR) of diameter 100 mm was operated cyclically and batchwise, alternating between reforming/carbonation conditions and higher-temperature calcination conditions to regenerate the sorbent. Equilibrium H_2-concentration of >98% on a dry basis was reached at 600°C and 1 atm, with dolomite as the CO_2-acceptor. Multiple reforming-regeneration cycles showed that the hydrogen concentration remained at 98-99 volume% after 4 cycles. Modelling of the performance of two parallel fluidized bubbling bed reactors has also been performed based on the kinetics of the combined reactions. Key parameters such as hydrogen yield, CO_2 capture efficiency and the total energy efficiency of the system are evaluated and compared with conventional steam reforming.

Hufton, J.R., Mayorga, S. and Sircar, S., (1999). Sorption–enhanced reaction process for hydrogen production, A.I.Ch.E. Journal, 45, 248-256.

Balasubramanian, B., Ortiz, A.L., Kaytakoglu, S. and Harrison, D.P., (1999). Hydrogen from methane in a single-step process, Chemical Engineering Science, 54, 3543-3552.