Circulating fluidized bed reactor for sorption enhanced steam methane reforming

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Motivation and background

The motivation for this work is to carry out continuous hydrogen production from natural gas with simultaneous capture and separation of CO₂.

One possible concept: Sorption enhanced methane steam reforming, SE-SMR [1].

SE-SMR has been proposed to be an economical competitive Alternative to conventional steam methane reforming with CO₂ capture [2].


Sorption enhanced methane steam reforming

The hydrogen market

Natural gas

Steam

Steam reforming + water-gas shift + CO₂ capture

Sorbent regeneration

H₂

The hydrogen market

CO₂

Sequestration
Essential chemical equations

\[
\begin{align*}
\text{Reforming} & \\
\text{Water-gas shift} & \\
\text{Sorption} & \\
\end{align*}
\]

\[
\begin{align*}
\text{Reaction 1} \quad & \quad \text{CH}_4(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}(g) + 3\text{H}_2(g) \\
\text{Reaction 2} \quad & \quad \text{CO}(g) + \text{H}_2\text{O}(g) \rightleftharpoons \text{CO}_2(g) + \text{H}_2(g) \\
\text{Reaction 3} \quad & \quad \text{MO}(s) + \text{CO}_2(g) \rightleftharpoons \text{MCO}_3(s) \\
\text{Reaction 4} \quad & \quad \text{MO}(s) = \text{Metaloxide} \\
\text{CH}_4(g) + 2\text{H}_2\text{O}(g) + \text{MO}(s) \rightleftharpoons \text{MCO}_3(s) + 4\text{H}_2(g)
\end{align*}
\]

Reaction 1 and 2 are catalyzed by a Ni- or a noble metal (Pt, Rh,) based catalyst.
Both the catalyst and the sorbent (MO, next slide) are simultaneously present in SE-SMR.
Solid high temperature CO$_2$ sorbents, principles and examples

Metal oxide (MO) + CO$_2$ $\rightleftharpoons$ Metal carbonate (MCO$_3$)

- Li-based:
  - Li$_2$ZrO$_3$
  - Li$_4$SiO$_4$

- Ca-based:
  - CaO (lime)
  - Mg$_{0.5}$Ca$_{0.5}$O (from dolomite)
  - CaO/support (“synthetic”)

500-700°C

700-900°C
$\text{MO} = \text{CaO}$:
$K_{\text{eq}}, \ \text{CaO(s)} + \text{CO}_2(g) \rightleftharpoons \text{CaCO}_3(s)$
Thermodynamic composition of effluent with or without internal CaO sorbent. S/C=4
Reforming at 600°C: $\text{CH}_4(g) + 2\text{H}_2\text{O}(g) + \text{MO}(s) \rightleftharpoons \text{MCO}_3(s) + 4\text{H}_2(g)$

Regeneration at 900°C: $\text{MCO}_3(s) \rightleftharpoons \text{MO}(s) + \text{CO}_2(g)$

Feed gases: $\text{CH}_4 + \text{steam} + \text{N}_2$
Reactor 1 (Reformer) and loop-seal 2

Reactor 1

Loop-seal 2

Gas inlets

20 cm

5 cm

Powder outlet 4 cm above sinter
Reactor system at SINTEF

Glass tube in riser
Conditions in a SE-SMR experiment

- Catalyst: 60wt.% NiO/NiAl$_2$O$_4$
- Sorbent: Calcined dolomite (Ca$_{0.5}$Mg$_{0.5}$O)
- Total amount of powder at start up was app. 130 gram. Vol. ratio of 1:1
- The powders were pre-reduced before applied in the reactor

- $T$(reformer) = $\sim$590-600°C. Uniform bed temp., $\Delta T \leq 1$ °C
- $T$(regeneration) = $\sim$ 910-920°C. Temp. gradient ca. 5-8 °C

- 1 atm total pressure

- Reformer: 50 Nml/min CH$_4$ + 200 Nml/min steam + 450 Nml/min N$_2$
- Regenerator: $\sim$450 Nml/min N$_2$
- Loop seals: $\sim$300 Nml/min N$_2$
- Riser: $\sim$1700 Nml/min N$_2$
Regenerator effluent stream

\[ \text{CO}_2 \text{ separation efficiency} = \left( \frac{\text{amount CO}_2 \text{ from regenerator}}{\text{amount methane into reformer}} \right) \times 100 \% \]
Particle attrition

A crack has started to appear in a used particle

SEM image of a sorbent particle after 16 hours of use
Conclusions

The presented experiment had an average CO$_2$ separation efficiency around 70-75%.

Continuous SE-SMR has been demonstrated in a circulating fluidized bed reactor.

More work
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Thank you for your attention