Fly Ash Derived Lithium Silicate for In-situ Pre-combustion CO2 Capture
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Fly ash derived lithium silicate for in-situ pre-combustion CO₂ capture

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Abstract

Steam gasification process converts biomass into a mixture of CO, CO₂, CH₄, and H₂. In this work, a fly ash derived lithium silicate material (Li-FA) was tested for the removal of CO₂ using simulated syngas at low gasification temperature. The CO₂ uptake tests were carried out using a high-pressure thermogravimetric system at 380°C and 500°C, 15 bar and simulating a synthetic biomass derived syngas mixture. The tests confirmed that the material is able to selectively absorb CO₂ at 380°C (1.2 mmol CO₂/g sorbent) and 500°C (2.77 mmol/g) and in presence of 50% H₂O, 30% H₂, 20% CO₂ at 15 bar. However, only 75% of the adsorbed CO₂ was desorbed under the same capture temperatures and 15 bar, by switching the reactor atmosphere from CO₂ to N₂. This suggests that a pressure swing process or a higher desorption temperature are required for complete desorption.

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Keywords: CO₂ capture; Li-based sorbents; sorption-enhanced gasification; carbonation; biomass

1. Introduction

Steam gasification process converts biomass into a mixture of CO, CO₂, CH₄, and H₂. Biomass gasification at temperatures as low as 500 °C can be achieved by using appropriate catalysts [1]. During gasification, the reversible water gas shift (WGS) reaction continues until reaching equilibrium and decreases with increasing temperature [2].
An effective strategy to drive the WGS reaction forward is to take out CO₂ from the product mixture by combining H₂ production and capture of CO₂, i.e. sorption-enhanced steam gasification of biomass [3]. Through in-situ CO₂ capture, H₂ production can be achieved at lower temperatures than the traditional gasification process (550 °C instead of ~ 800 °C), which lowers energy requirement, coking and sintering of catalyst and capital expenditure [3,4]. Therefore, there is a need to conduct in-situ removal of CO₂ under gasification conditions at low temperature (~500°C), since most of the work reported using CaO sorbents is at higher temperatures [3,5].

Lithium silicate has been widely investigated as CO₂ sorbent at high temperatures in the last fifteen years [6,7]. In the recent years, there has been a rising interest in producing lithium silicates from waste materials to decrease the sorbent costs and find alternative pathways for minimising environmental problems associated to landfilled waste [8].

Under the optimal experimental conditions (600 °C and 40 mol% K₂CO₃), the maximum CO₂ sorption capacity for the sorbent derived from fly ash (FA) was 2.4 mmol/g. The Li₄SiO₄-based sorbents was able reach the plateau of maximum capture capacity in less than 15 min [8]. Despite this, this waste derived sorbent has not been tested in pre-combustion conditions yet. Therefore, the aim of this work is to evaluate the feasibility of Li-FA as pre-combustion CO₂ sorbent.

2. Methodology

In this work, a fly ash derived lithium silicate material (Li-FA) developed at Heriot-Watt University was tested for the simultaneous removal of CO₂ using simulated syngas at low gasification temperature at the University of Utah. The CO₂ uptake tests at high pressure were carried out using a high pressure thermogravimetric system at 380°C and 500°C, 15 bar and using a synthetic biomass derived syngas mixture (50%H₂O, 30%H₂, 20%CO₂ (or N₂). The thermogravimetric set-up comprised a high temperature furnace, a sample holder and a gas system able to reproduce pre-combustion conditions. The SS316 sample holder was designed for samples with particle size > 150 μm, so that the starting lithium silicate powder was screened to select particles larger than 150 μm. Weight variation, temperature and pressure profiles were electronically recorded using a dedicated software.

XRD analysis of the parent Li-FA sample and the materials after CO₂ sorption/desorption cycles were carried out using a XPert³ Powder.

3. Results and Discussion

Before the CO₂ uptake tests, the material was firstly run in presence of 50%H₂O, 30%H₂, 20%N₂ at 15 bar to desorb any water from the surface. It was observed that the weight decreased about 7%, indicating that no sorption of H₂/H₂O occurred. The capture tests confirmed that the material is able to absorb CO₂ at 380°C (1.2 mmol CO₂ / g sorbent) and 500°C (2.77 mmol/g) in presence of 50% H₂O, 30% H₂, 20% CO₂ at 15 bar. Desorption studies were carried out at 15bars switching the reactor atmosphere from CO₂ to N₂, and it was found that the desorption was not completed (75% completed) under these conditions. This indicates that pressure swing process or a higher desorption temperature are required for complete desorption.

XRD analysis (XPert³ Powder) of the parent Li-FA sample and after CO₂ sorption/desorption cycles were carried out. The main mineral phases identified in the parent sample were tetra-lithium silicate, Li₄SiO₄ (85%) and lithium catena-silicate, Li₂SiO₃ (15%). The XRD of the material after the CO₂ sorption/desorption cycle shows that the Li₄SiO₄ phase decreased to 68%, whilst the Li₂SiO₃ phase increased to 32%. Above 262°C, Li₄SiO₄ absorbs CO₂ to form Li₂SiO₃ and Li₂CO₃ [6].
The calculated amount of Li$_2$SiO$_3$ that can be related to presence of Li$_2$CO$_3$ (Li$_4$SiO$_4$ + CO$_2$ ↔ Li$_2$SiO$_3$ + Li$_2$CO$_3$) in the used Li-FA (17%) confirms that some Li$_2$CO$_3$ is present in the material due to incomplete desorption under the tested conditions, which is in agreement with the thermogravimetric results.

Table 1. Mineral phases in Li-FA after CO$_2$ desorption.

<table>
<thead>
<tr>
<th></th>
<th>Li$_4$SiO$_4$</th>
<th>Li$_2$SiO$_3$</th>
<th>Li$_2$SiO$_3$ from carbonation</th>
</tr>
</thead>
<tbody>
<tr>
<td>LI-FA after experiment</td>
<td>67.6</td>
<td>32.4</td>
<td>17</td>
</tr>
</tbody>
</table>

Figure 1. TGA profile of CO$_2$ sorption at (a) 380°C and (b) 500 °C.

Figure 2. XRD of the material after CO$_2$ sorption/desorption.
4. Conclusions

In summary, Li-FA may be an efficient CO₂ sorbent under pre-combustion conditions since it is not affected by the presence of H₂ and H₂O, but further work is required to achieve complete regeneration and establish its stability over a larger number of cycles.

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References