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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 15bar, 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].

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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 X'Pert³ 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 15bar 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 (X'Pert³ 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].

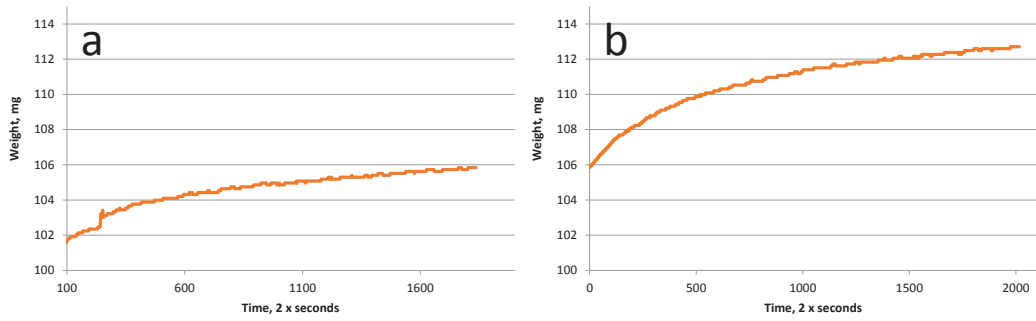


Figure 1. TGA profile of CO₂ sorption at (a) 380°C and (b) 500 °C.

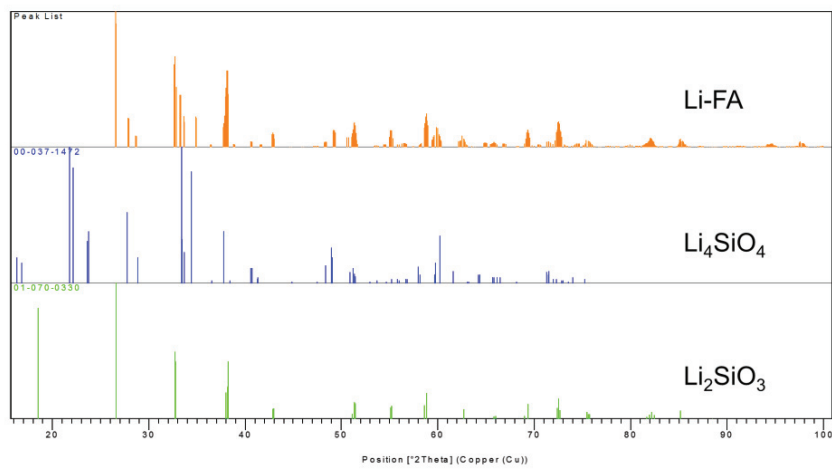


Figure 2. XRD of the material after CO₂ sorption/desorption.

The calculated amount of Li₂SiO₃ that can be related to presence of Li₂CO₃ ($\text{Li}_4\text{SiO}_4 + \text{CO}_2 \leftrightarrow \text{Li}_2\text{SiO}_3 + \text{Li}_2\text{CO}_3$) in the used Li-FA (17%) confirms that some Li₂CO₃ 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 CO₂ desorption.

	Li ₄ SiO ₄	Li ₂ SiO ₃	Li ₂ SiO ₃ from carbonation
LI-FA after experiment	67.6	32.4	17

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

- [1] Asadullah M, Ito SI, Kunimori K, Yamada M, Tomishige K. Biomass Gasification to Hydrogen and Syngas at Low Temperature: Novel Catalytic System Using Fluidized-Bed Reactor. *J. Catal.* 2002;208:255-259.
- [2] Rosen M, Scott D. Comparative Efficiency Assessment for a range of hydrogen production processes. *Int. J. Hydrogen Energy* 1998;23:653-659.
- [3] Kenarsari SD, Zheng Y. CO₂ capture using calcium oxide under biomass gasification conditions. *J. CO₂ Util.* 2015;9:1-7.
- [4] Florin NH, Harris AT. Enhanced hydrogen production from biomass with in situ carbon dioxide capture using calcium oxide sorbents. *Chem. Eng. Sci.* 2008;63:287-316.
- [5] Li ZS, Cai NS, Huang YY. Effect of Preparation Temperature on Cyclic CO₂ Capture and Multiple Carbonation–Calcination Cycles for a New Ca-Based CO₂ Sorbent. *Ind. Eng. Chem. Res.* 2006;45:1911-1917.
- [6] Duan Y, Pfeiffer H, Li B, Romero-Ibarra IC, Sorescu DC, Luebke DR, Halley JW. CO₂ capture properties of lithium silicates with different ratios of Li₂O/SiO₂: an ab initio thermodynamic and experimental approach. *Phys. Chem. Chem. Phys.* 2013;15:13538.
- [7] Kato M, Yoshikawa S, Nakagawa K. Carbon dioxide absorption by lithium orthosilicate in a wide range of temperature and carbon dioxide concentrations. *J. Mater. Sci. Lett.* 2002; 21:485-487.
- [8] Olivares-Marín M, Drage TC, Maroto-Valer MM. Novel lithium-based sorbents from fly ashes for CO₂ capture at high temperatures, *International Journal of Greenhouse Gas Control* 2010;4:623-629.