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CO₂ Capture from Biomass Gasification Producer Gas Using a Novel Calcium and Iron-based Sorbent through Carbonation-Calcination Looping

Forogh Dashtestani¹, Mohammad Nusheh², Vilailuck Siriwongrungson³, Janjira

Hongrapipat⁴, Vlatko Materic², Shusheng Pang^{1,}*

ABSTRACT: In this study, a novel sorbent material based on CaO and Fe₂O₃ was investigated for its performance in CO₂ capture from simulated biomass gasification producer gas. Experiments were conducted in a fixed bed reactor and each run of the experiments included three major stages of sorbent material reduction, CO₂ capture (carbonation) and CO₂ release (calcination). The operation temperature in the CO₂ capture stage was controlled at 590°C, 620°C, 650°C and 680°C, respectively, while the temperature for the CO₂ release was maintained at 850°C. The duration of the CO₂ capture stage was 3 h and the CO₂ release stage was 2 h. Effect of cycles of carbonation-

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3 calcination looping of the sorbent material was also investigated at the carbonation
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7 temperature of 650°C. The experimental results show that effective CO₂ capture by the
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10 sorbent material occurred in the initial 20 minutes during the carbonation. In the
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14 calcination stage, the rate of CO₂ release reached the peak in 30 to 40 minutes from the
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17 start of the calcination. The carbonation temperature has a significant effect on CO₂
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20 capture and the optimum carbonation temperature was found to be 620°C at which CO₂
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23 capture efficiency was 94% for the first cycle and 90.4% as average for the first three
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27 cycles. It was also found that the CO₂ capture efficiency was reduced with cycling.
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31 Mechanisms of the CO₂ capture and effect of cycling were also examined.
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36 **KEYWORDS:** Biomass gasification, Producer gas, CO₂ capture, CaO-FeO sorbent,
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40 Carbonation-calcination looping
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47 1. INTRODUCTION

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51 With concerns on climate change due to the increasing of greenhouse gas (GHG)
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54 emissions, CO₂ capture and reuse have attracted extensive interests in the world. One
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3 possible approach to mitigate this issue is to capture CO₂ from CO₂-containing gas
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7 streams, such as flue gas from a combustion unit and producer gas from biomass
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10 gasification, and to reuse it such as injecting CO₂ into the environment of greenhouse
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13 nurseries to enhance plant growth and yield. Commercial greenhouses currently use flue
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16 gas either directly or indirectly from combustion of fossil fuels.^{1, 2} However, recently
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19 alternative renewable energy resources such as biomass have been sought to replace
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22 fossil fuels for this purpose either through combustion or gasification.³ Biomass
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25 gasification is a promising technology due to advantages of high energy efficiency and
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28 flexibility for applications of the producer gas produced from the gasification.¹ Gasification
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31 is a thermochemical process in which the solid fuels undergo a series of reactions in the
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34 presence of a gasification agent which can be air, pure oxygen, steam or a mixture of
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37 them. The producer gas consists primarily of hydrogen (H₂), carbon monoxide (CO),
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40 carbon dioxide (CO₂) and methane (CH₄) when oxygen or steam is used as the
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43 gasification agent.²
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52 There are a range of CO₂ capture processes and technologies.⁴ Calcium looping using
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55 CaO-based sorbent has been reported as an efficient technology for the CO₂ capture
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7 Post combustion capture of CO₂ with amine-based solvents is a mature technology,¹⁵
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10 ¹⁶ however, this is a very energy intensive process.^{3,17} In addition, the used solvents may
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14 induce environmental concerns as pollutants, such as sulphur-based species present in
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17 the flue gas from coal combustion, would be absorbed by the solvents.¹⁸ Previous studies
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21 have been reported on comparison between different CO₂ capture processes based on
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24 exergy analysis ^{18, 19} and the results show that the calcium-looping process has the lowest
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27 energy penalty ¹⁸ compared to solvent scrubbing ²⁰ and oxyfuel combustion.²¹ In the
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31 oxyfuel combustion, pure O₂ separated from air is used in combustion of coal or
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34 biomass.²² Research has also been conducted on integration schemes including biomass
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38 gasification with carbon capture and storage (CCS), ^{4, 23, 24} biomass integrated coal
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42 gasification combined cycle (BIGCC) with CCS, ²⁵ or co-gasification with CCS ²⁶.
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45 Abanades and Murillo ²⁷ later illustrated the concept of cyclic Ca/Cu looping in a fixed bed
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48 reactor. The use of combined calcium looping with chemical looping cycle (CaL–CLC)
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52 reduced energy penalty from 11% in amine scrubbing to 4%.²⁸ The cost of CaL–CLC was
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56 minimised by using natural limestone as the calcium looping agent. It is important to note
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3 that the use of CaO based material in the reactor not only increases efficiency but also
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7 favours the production of H₂ by removing the carbon dioxide. This enhanced water-gas
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10 shift (WGS) reaction and provided heat for the endothermic steam methane reforming
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13 (SMR) reaction.²⁹⁻³² Han et al.³³ also reported that the endothermic SMR reaction could
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15
16 be thermally balanced with exothermic carbonation and WGS reactions. Johnsen et al.³⁴
17
18 conducted experiments using dolomite as CO₂ sorbent in a bubbling fluidized bed (BFB)
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20
21 reactor with cycling of SMR-carbonation (at 600°C) and calcination (at 850°C). In this
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25 study, hydrogen concentration of 98 vol.% was achieved.
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31 The CaO based material has advantages of low costs and high reactivity at the start of
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34 the application.³⁵ Previous studies^{32, 36} have shown that the CaO based sorbents had high
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37 CO₂ capture efficiency initially, however, the sorbents were deactivated after 20 or 30
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40 cycles due to the reduction of microporosity in the sorbents.^{37, 38} It was also found that at
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43 the end of carbonation process, a layer of CaCO₃ of about 50 nm thick was formed on
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46 the pore surfaces that reduced accessibility of the reactant gases and this phenomenon
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49 became more significant with cycling.³⁹ Most natural CaO-containing sorbents, such as
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52 limestone and dolomite, may be used for the CO₂ capture, however, these materials
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3 undergo declining of reactivity with an increase in the cycling of carbonation-calcination
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7 looping.^{8, 40} Barker⁴¹ conducted experiments to investigate the effect of the number of
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10 carbonation-calcination cycles on the sorbent material's reactivity for CO₂, and the results
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13 showed that the CO₂ capture efficiency of the CaO based sorbent decreased rapidly with
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16 the cycles of the carbonation-calcination looping.^{33, 42, 43} On the other hand, in the
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19 producer gas from biomass gasification, contaminant gaseous species such as nitrogen-
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22 and sulphur-based compounds as well as other impurities may adversely affect the CO₂
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25 capture reactivity of solid sorbents such as CaO.^{44, 45} These studies also illustrate that the
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28 CaO based sorbent has problem of attrition in fluidised bed reactors with cycling of the
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31 carbonation-calcium looping. Sintering of the natural CaO based material is also
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34 potentially a problem at high temperatures. Therefore, the challenges of the CaO based
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37 sorbents for CO₂ capture is to maintain the capture efficiency with cycling⁴⁶ and to
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40 improve mechanical strength.⁴⁷ Synthetic sorbent material can be made using natural
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43 materials to reduce the costs.⁴⁸ Research has been conducted to integrate a second
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46 metal oxide into the natural sorbent material to improve carbonation/calcination reactivity
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49 with cycling and to enhance the reaction rate.⁴⁹ Addition of inert but thermally stable
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3 materials is an efficient technique to mitigate CaO sintering.⁵⁰⁻⁵³ The inert material can also
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7 increase the porosity and pore surface area of the sorbent particles.⁵⁴ The reported inert
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10 materials, termed as stabilisers, include Al_2O_3 ^{55, 56}, ZrO_2 ⁵⁷⁻⁵⁹, CeO_2 ⁶⁰, MgO ⁶⁰⁻⁶³, Y_2O_3
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14^{64, 65}, MnO_2 ⁶⁶, La_2O_3 ⁶¹, TiO_2 ⁶⁷, CuO ⁶⁸ and Nd_2O_3 ⁶⁹ which have high thermal stability.
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17 Radfarnia et al.⁷⁰ also used different metal oxide with CaO sorbent to improve the sorbent
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21 stability during cyclic CO_2 capture. In the past studies, several CaO-based sorbents have
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24 been studied⁷¹⁻⁷⁶ and selected studies with promising results are briefly reviewed as
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28 follows.

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31 Tian et al.⁷⁷ investigated the effect of addition of Fe_2O_3 to CaO in the carbonation-
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34 calcination looping which was applied in steel manufacturing process. They found that,
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38 with addition of Fe_2O_3 , the sorbent structural stability was improved and, in the same time,
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42 the heat demand for the endothermic calcination process was reduced. These findings
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45 were further verified by separate studies^{78, 79} which showed that the use of metal oxide
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49 resulted in fast reaction kinetics, high CO_2 capture efficiency, and sustained performance
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52 of the sorbent over a large number of cycles.⁷⁸ Zamboni et al.⁸⁰ found that the reactivity
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56 reduction of CaO in Fe–Ca synthetic absorbent was slower than other combined materials
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3 with cycling. Han et al.⁸¹ also developed iron-calcium based material with stable reactivity
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7 and performance with cycling. With screening of metal-based sorbents, Feng et al.⁸²
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10 found that Fe₂O₃ was the most promising one.⁸³
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14 With the addition of metal oxide to CaO based sorbent, an exothermic reaction between
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17 the reduced metal and oxygen occurs (such as $\text{Fe} + \text{O}_2 \rightarrow 2\text{Fe}_2\text{O}_3$) which provides heat
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20 for the endothermic calcination reaction. In addition, when Fe₂O₃ is used as additional
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23 metal oxide to the sorbent,⁸⁴⁻⁸⁷ sintering and attrition properties also need to be
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27 considered for practical applications,⁸⁸⁻⁹² thus support material can be included if
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31 needed.⁹³
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35 Nevertheless, there are still unknowns in optimisation of the sorbent material
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38 formulation and fundamental understanding of the performance of the sorbent material.
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42 Therefore, further investigation is needed on the effect of formulation and performance of
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45 different sorbent materials on the CO₂ capture through carbonation-calcination looping.⁹⁴⁻
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49 ¹⁰¹ In some of the previous studies, carbonation temperature of 650°C was used,^{79, 96, 98,}
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52 ¹⁰²⁻¹⁰⁶ considering the favoured equilibrium gas composition and the kinetics of
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55 carbonation reaction for CO₂ capture. It is known that the operation conditions both for
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3 carbonation and for calcination affect the sorbent material performance for CO₂ capture.^{96,}

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7 ¹⁰⁰ Other studies have shown that the carbonation may be favoured at temperatures lower
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10 than 650°C. Lab-scale studies by Charitos et al.¹⁰⁷ have shown an optimum temperature
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13 in the range of 630-650 °C for CO₂ capture using the CaO based sorbent. A separate
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16 study by Sánchez-Biezma et al. found that the carbonation temperature of 700 °C resulted
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19 in a reduced CO₂ capture efficiency than that at 650°C.¹⁰⁸ Interestingly, a study by Plötz
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22 et al. found that carbonation temperatures lower than 620°C were kinetically unfavourable
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27 for the CO₂ capture process.¹⁰⁹

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31 From the above discussion, important factors that affect the CaO based materials
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34 performance on CO₂ capture include sorbent material formulation, carbonation and
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37 calcination temperatures, elapsed time of carbonation process, cycling of the
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40 carbonation-calcination looping and the composition of the CO₂-containing gas stream.
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45 The modification of the CaO sorbent by addition of metal oxides is a critical approach to
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48 enhance the sorbent performance and to maintain lasting high reactivity.
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52 The aim of this work is to investigate the performance of a newly developed sorbent
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55 material based on CaO and Fe₂O₃ in the simulated biomass gasification producer gas,
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3 and to examine the effects of carbonation temperature as well as the carbonation-
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7 calcination cycling. Mechanisms of the CO₂ capture process by the synthetic sorbent is
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10 also investigated.
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16 2. MATERIAL AND EXPERIMENTS

17 2.1. Sorbent material

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20 CaO based sorbent material with enhancement of Fe₂O₃ was developed and provided
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23 by Hot Lime Labs (HLLs) in New Zealand. The CaO and Fe₂O₃ are natural minerals, and
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26 were sourced locally in New Zealand. The composition of the sorbent material was 70
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29 wt% CaO, 20 wt% iron ore (Fe₂O₃) and 10 wt% inorganic binder. The raw materials at
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32 pre-set composition were physically mixed and pelletised to required pellet size of about
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37 5 mm. BET surface area, sorption cumulative pore volume and average pore diameter of the as
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40 arrived fresh sorbent material were measured which values are, respectively, 1.24 m²/g, 0.020
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43 cm³/g, and 60.1 nm. The sorbent material was first treated at 650°C to remove adhesives and other
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46 volatiles before the experiments. After the treatment, the values of BET surface area, sorption
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49 cumulative pore volume and average pore diameter of the sorbent material were measured again
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52 which values are, respectively, 1.52 m²/g, 0.0054 cm³/g, and 15.5 nm. Bulk density of the fresh
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55 sorbent material was provided by HLLs as 1000 kg/m³. We have noted that the BET surface area
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3 and the sorption cumulative pore volume were low for the sorbent material. However, these values
4 were for large pores between individual components in the composite pellets but not for micro-
5 pores of each component. For characterisation of the sorbent materials, XRD and SEM analyses
6 were also performed.
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15 **2.2. Experimental system and procedures**

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18 A fixed bed quartz reactor system was used in the experiments which flow diagram is
19 shown in Figure 1. This quartz reactor, with an inner diameter of 40 mm and length of
20 815 mm, is housed inside a three-zone heating furnace, in which temperatures of each
21 zone are controlled separately. The temperature profile within the reactor was examined
22 before experiments, and stable temperature was found between 300 and 500 mm from
23 the bottom of the reactor where the bed of sorbent material was located. The sorbent
24 material section of the reactor is detachable, which enables easy removal and loading of
25 the sorbent material.
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46 The reactor temperatures were monitored using Type-K thermocouples at three
47 locations in the reactor: at the bed bottom (gas inlet) below the distributor, at mid-height
48 of the bed, and at the reactor top (gas outlet) in the freeboard. The thermocouples were
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3 also connected to a data logger for data recording. Each run of the experiment consisted
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7 of four essential stages including hydrogen reduction, carbonation (or charge), purge and
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10 calcination (or discharge) plus heat-up and cooling-down as given in Table 1. In the table,
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14 test gases in each stage are also included.
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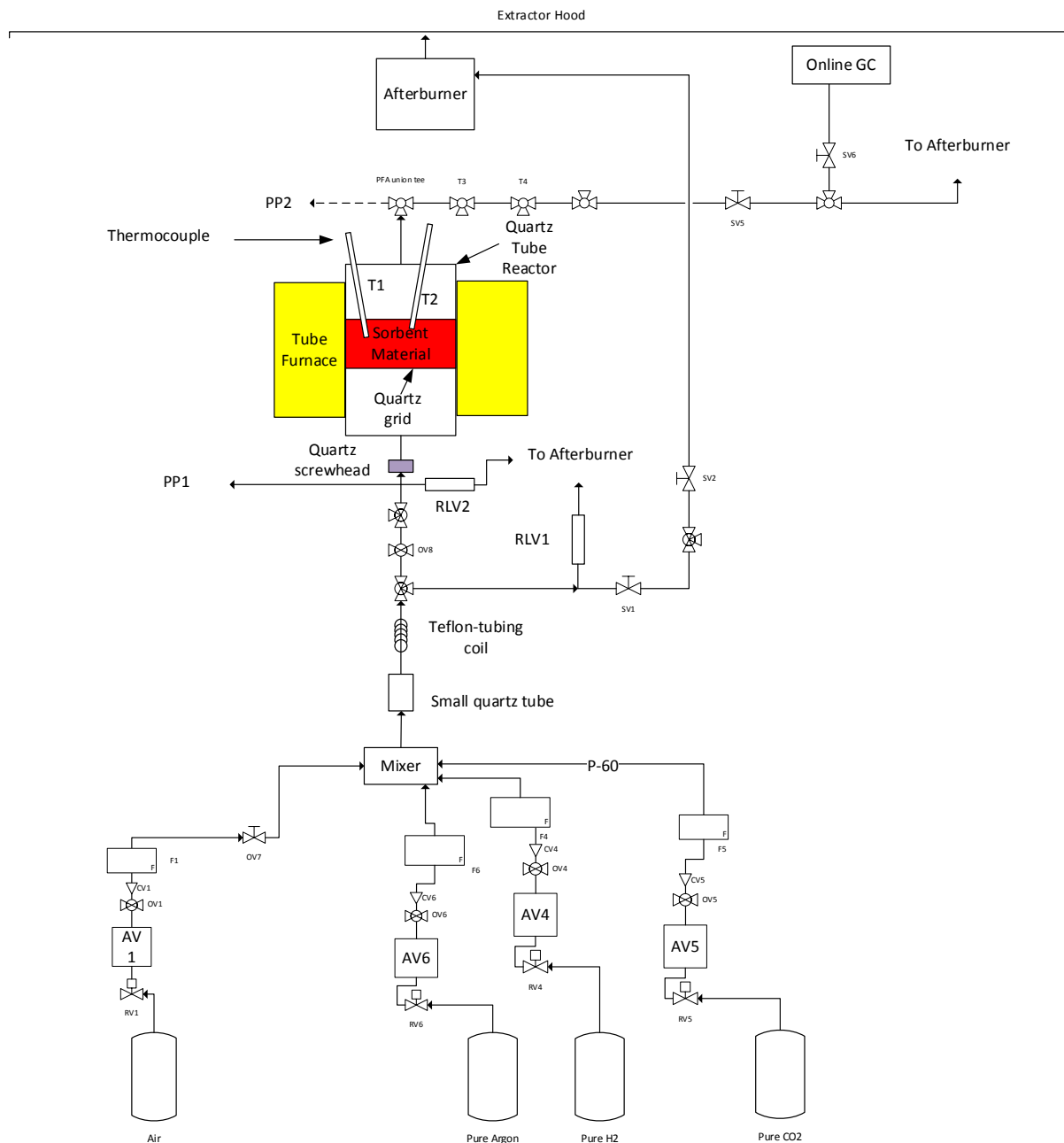


Figure 1. Flow diagram of the reactor system used in this study.

Table 1. Operation Conditions for an Experimental Run

Stage	Temperature, °C	Test gas*	Duration or criteria for finishing
Initial calcination of the as arrived sorbent material	850	Air	Until no CO ₂ was detectable at outlet
Purge	850	Argon (Ar)	Until no air was detectable at outlet
Hydrogen reduction	850	50 vol.% Ar and 50 vol.% H ₂	40 - 65 minutes
Cooling down to target carbonation temperature		50 vol.% Ar and 50 vol.% H ₂	~ 30 minutes
Carbonation (charge)	590, 620, 650 or 680	25 vol.% CO ₂ , 30 vol.% H ₂ and 45 vol.% Ar	180 minutes
Purge	As above	Argon (Ar)	Until no H ₂ was detected at outlet
Calcination (discharge)	850	Air	120 minutes

Note: * Overall gas flow rate in each stage was controlled at 1 standard litre per minute (SLPM).

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4 In each run, the 200 g pretreated sorbent material was placed into the quartz reactor
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7 bed. Wool was placed on the top of the bed to keep the material in place during the
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10 experiment. Once the initial calcination stage was completed with pure air, the sorbent
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13 particles were then exposed to 50% H₂ and 50% Ar for hydrogen reduction. Then, gas
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16 mixture (25 vol. % CO₂, 30 vol. % H₂ and 45 vol. % Ar) as simulated biomass gasification
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19 producer gas was introduced into the reactor for starting the stage of carbonation. Once
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22 this was finished, the reactor was switched to purge with Ar gas to avoid air and simulated
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25 gas mixed, and then to calcination (discharging) by switching the Ar gas to air as carrier
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28 gas. When the calcination stage was completed, the reactor was cooled down again to
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31 room temperature.
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38 The gas flowrate in all of the stages was set at 1 standard litre per minute (SLPM) and
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41 controlled by flowmeters of the inlet gases based on preset gas composition. The
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44 concentrations of CO₂, CO, H₂ and O₂ from the reactor were analysed using a micro-GC
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47 (Agilent 3000). The Ar gas was regarded as inert and its outlet concentration was
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50 determined from mass balance. The outlet gas composition was determined based on
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53 the gas analysis results and the inlet flowrate of the inert gas (Ar).
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4 This study has also examined the effects of cycling of carbonation-calcination looping
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7 on the material performance for its CO₂ capture, by repeating the experiment over 8
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10 cycles at the carbonation temperature of 650°C. The characterizations of the sorbent
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13 materials were performed before and after the carbonation-calcination looping to provide
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16 information about the evolution of the iron species and Fe-Ca interactions during catalytic
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19 tests. BET and BJH methods were based on nitrogen adsorption-desorption
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22 measurements using a Gemini VI instrument. BET was used to determine the specific
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25 surface area of materials while BJH was used to determine the values of pore volume
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28 and pore size. To better understand the chemical changes of the materials upon CO₂
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31 adsorption and desorption, X-ray diffraction analysis was performed using X-ray
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34 diffractometer (XRD, Bruker D8, and Co K α radiation). Furthermore, SEM (Scanning
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37 Electron Microscopy) images were taken for the sorbent materials by using a JEOL 7000F
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40 FE-SEM analyser (JEOL Ltd, Japan) with a probe current of 10 mA and under an
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43 acceleration voltage of 5kV.
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3. RESULTS AND DISCUSSION

3.1. Performance of the materials on CO₂ capture and release

One cycle of each experimental run can be classified into four stages including initial calcination, H₂ reduction, carbonation and calcination. Figure 2 shows typical results of gas composition of the outlet gas from the reactor for a complete carbonation and calcination cycle at carbonation temperature of 650°C. In the figure, the concentrations of gaseous species of O₂, CO, CO₂ and H₂ as well as operation temperatures are illustrated. O₂ in the outlet gas was from air, and CO₂ and H₂ were from the feeding gas while CO was produced from reverse water-gas shift reaction, as described by Equation (3) below, as well as oxidation of Fe by CO₂.



N₂ in the air and Ar in the feeding gas are not shown in the figure as these are regarded as inert through the reactor.

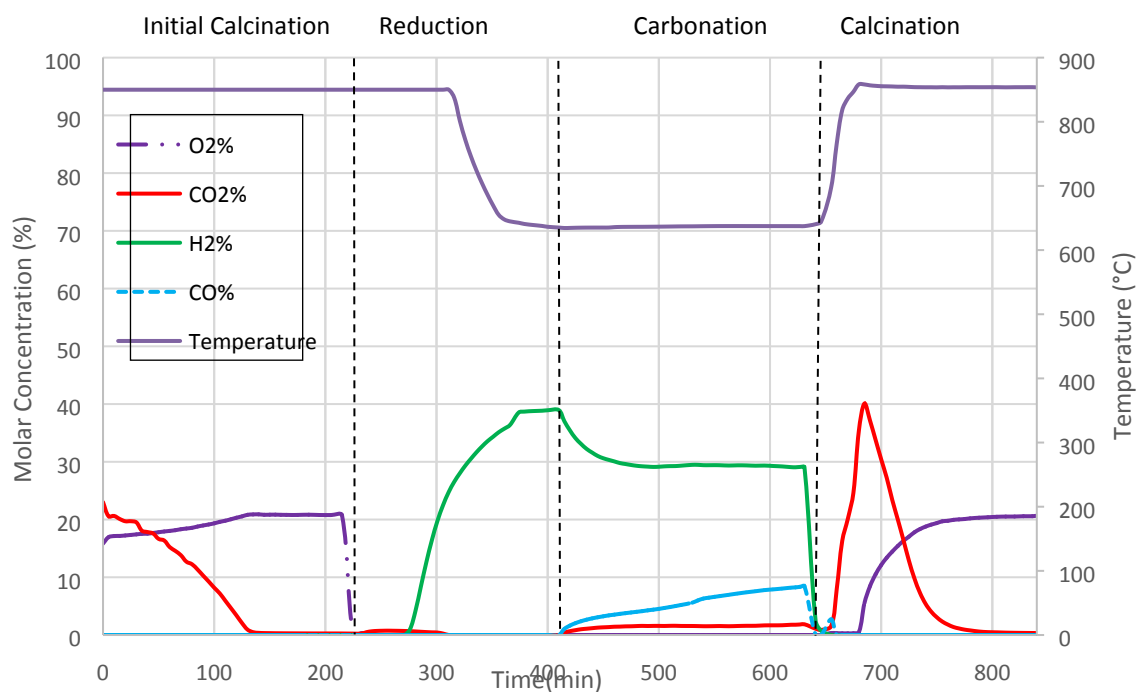


Figure 2. Composition of outlet gas streams from the reactor in all stages of the experiment in the first cycle of carbonation-calcination looping and carbonation temperature of 650°C.

As mentioned above, in the experiments, the heat-pretreated material was initially heated at the rate of 10°C/min to 850°C which was then maintained for over 4 hours until no CO₂ was detected in the outlet gas. In this process, the carbonate in the fresh material was completely calcined and all CO₂ was released.

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4 Following this, the Fe_2O_3 in the sorbent material was reduced at $850\text{ }^\circ\text{C}$ by introducing
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7 50% H_2 and 50% Ar. This reduction process was through multiple steps ($\text{Fe}_2\text{O}_3 \rightarrow \text{Fe}_3\text{O}_4 \rightarrow$
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10 $\text{FeO} \rightarrow \text{Fe}$) and the overall reaction is endothermic as described by Equation (4) below.



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17 . In the hydrogen reduction process, when all of the lattice oxygen on the surfaces of
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20 the sorbent particles and the pores was consumed to oxidise the H_2 , further reduction
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23 process became diffusion-controlled and the rate was slow with low H_2 consumption.
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27 Therefore, the outlet H_2 concentration was stable. This changing point was identified as
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30 the first H_2 reduction breakthrough point which was used for termination of the reduction
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33 stage. It is noted that the observed H_2 breakthrough also reflects the gradient of
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36 conversion along the bed height. After the reduction, the activity of the sorbent material
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39 was also enhanced for the CO_2 capture in the carbonation stage through Equation (1).
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45 This has been reported by previous studies that the CO_2 molecules acquired the clean
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48 metal surfaces for activation of the $\text{C}=\text{O}$ bond to proceed the carbonation reaction.¹¹⁰⁻¹¹²
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52 The next key stage of the experiment was the charging at carbonation temperature of
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55 $650\text{ }^\circ\text{C}$. In this stage, the feeding gas was composed of 25% CO_2 , 30% H_2 and 45% Ar
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3 which was used to simulate the producer gas from biomass gasification. CO₂ was
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7 captured from the simulated producer gas and the sorbent material was “charged”. CO
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10 was not included in the simulated producer gas as our previous studies have shown that
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14 CO was generated through the CO₂ capture process using similar sorbent materials.
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16

17 In the carbonation process, a turning point was observed as CO₂ breakthrough point
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19
20 which is defined as the completion of fast CO₂ capture through the bed and characterised
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22
23
24 by the start of rapid increase in outlet CO₂ concentration. This indicated a rapid reduction
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26
27
28 of CO₂ capture efficiency by the sorbent material. The breakthrough time was dependent
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31 on the operation temperature, gas flowrate and bed height. The second breakthrough
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35 point may be observed when the CO₂ capture rate was further reduced. In the present
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39 study, the results demonstrated that CO₂ capture was most effective in the initial 20
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42 minutes of carbonation which covered the first breakthrough point.
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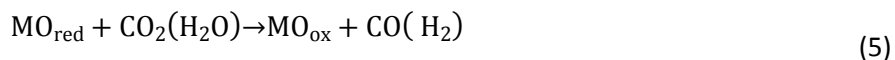
45 The fast carbonation started once the feeding gas was injected. As observed in Figure
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49 2, the CO₂ concentration in the outlet gas was very low at the start, showing that initially
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53 the sorbent material had high capacity to absorb CO₂ almost completely from the
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56
57 simulated producer gas stream through carbonation reaction and CO₂ reduction by Fe or
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3 FeO. In the reduction reaction, CO₂ reacted with iron metal to produce CO and iron oxide.
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6
7 Fe-containing material would also promote the reverse water-gas shift reaction.¹¹³⁻¹¹⁵ In
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9
10 the carbonation-calcination looping process, ¹¹⁶ CO₂ is converted to CO in a two-step,
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14 cyclic redox scheme: A redox material (commonly referred as the oxygen carrier
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17 materials) is firstly reduced by reducing gas (H₂) to release its lattice oxygen, and then
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21 the reduced metal oxide is reoxidised by being exposed to CO₂ to regain its lost oxygen,
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23
24 ¹¹⁷ thereby producing carbon monoxide. The results from the present study are similar to
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26
27
28 those reported by Hare et al. ¹¹⁶ who investigated the performance of dolomite and
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30
31 limestone for CO₂ capture. When the CO₂ capture rate became slow, the outlet CO₂
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35 concentration increased gradually with elapsed time. In the meantime, CO was detected
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38
39 in the outlet gas stream, confirming that the reverse water-gas reaction occurred.
40
41
42 However, if CO was included in the feed gas, reverse water-gas shift reaction would be
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46 slowed down or may be changed to forward direction depending on its initial concentration
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48
49 in the feed gas.
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52 As the carbonation proceeded, the CO₂ concentration in the outlet gas further
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56 increased, and this indicated reduced reactivity of the sorbent material due to the
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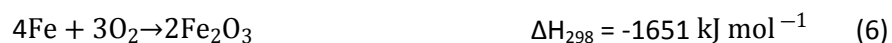
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3 decreasing availability of reactant components (CaO and Fe) in the sorbent material and
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7 the resistance for CO₂ diffusion into the material for carbonation reaction.^{118, 119} The latter
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10 mechanism will be further analysed later in this paper.

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14 The concept of using metal-oxide materials, which can spontaneously be reduced at
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17 high temperatures and then are reoxidised by interaction with CO₂ to produce CO (or
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19
20 alternative with H₂O to form H₂), has been investigated in literature.¹²⁰⁻¹²² This process
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22
23
24 can be described as a general case by the following reaction:



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28
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30 In the experiment, the final stage was calcination or discharging in which air was used
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33 as the carrier gas. Although not presenting in the feeding gas, significant CO₂ was
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35
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37 detected in the outlet gas stream, indicating that the CO₂ was released from the sorbent
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40 material. The CO₂ concentration represents the reactivity of the sorbent material through
41
42
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44 CaCO₃ decomposition by calcination reaction and the iron oxidation reaction. As the
45
46
47 calcination reaction is endothermic, heat is needed to maintain the target temperature of
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50
51 850°C, which was provided by the furnace and from the iron oxidation reaction as given
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53
54 in Equation (6).^{123, 124}

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3 In the stage of calcination, reoxidation of the reduced metal also occurred in the reactor
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7 which supplied additional heat to the endothermic calcination reaction.
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13 From Figure 2, it is found that the CO₂ concentration in the outlet gas stream during the
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16
17 calcination stage was at the peak once the temperature reached 850°C. Afterwards, the
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20
21 CO₂ outlet concentration decreased with time and was eventually non-detectable,
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23
24 indicating that all CO₂ was released from the material and calcination was completed. It
25
26
27
28 was also found that the outlet O₂ concentration was reduced during the calcination stage,
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30
31 indicating that O₂ was consumed for the Fe reoxidation as shown in Equation (6).
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35 Similar trends of gas composition changes were also observed for other carbonation
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37
38 temperatures in the experiments, thus these results are not presented here.
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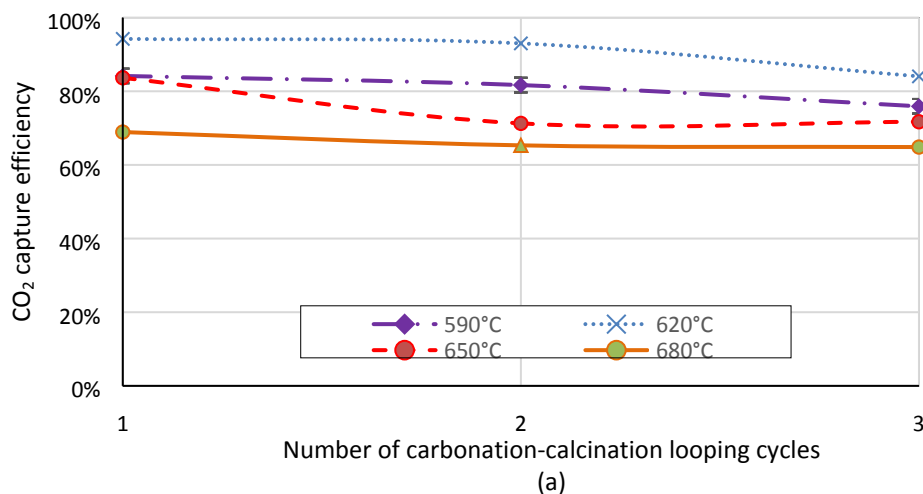
41
42 For analysis of the CO₂ capture efficiency (η), the following equation was used based
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44
45 on the molar ratio in the carbonation stage in which the gas volumes over a given period
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47
48
49 of time were used at standard conditions:
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$$\eta = 1 - \frac{n_{\text{CO}_2, \text{out}} + n_{\text{CO}, \text{out}}}{n_{\text{CO}_2, \text{in}}} = 1 - \frac{V_{\text{CO}_2, \text{out}} + V_{\text{CO}, \text{out}}}{V_{\text{CO}_2, \text{in}}} \quad (7)$$

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3
4 Where $V_{CO_2, in}$ is the total CO_2 volume entering the system in the feeding gas mixture
5
6
7 over a given period of time (L), and $V_{CO_2, out} + V_{CO, out}$ are the total volume of outlet CO_2
8
9
10 and CO in the same period of time (L). The above equation is based on assumption that
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12
13 part of the inlet CO_2 was adsorbed by the sorbent material, and part of the inlet CO_2 was
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15
16 transformed to CO through reverse water-gas shift reaction and CO_2 reduction (Equations
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18
19 3 and 5). The remaining CO_2 injected into the reactor flew out of the reactor in the outlet
20
21
22 gas stream. The total inlet CO_2 volume was determined from the controlled gas flow rate
23
24
25 and the CO_2 concentration in the inlet gas stream while the outlet CO and CO_2 volumes
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27
28 were calculated based on the measured gas composition and the total volumetric flowrate
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30
31 of the outlet gas. It is noted that the total volume of the outlet gas was reduced due to the
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34 CO_2 adsorption and water vapour condensation. The total gas volume was determined
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37 by assuming the Ar gas to be inert thus the total moles of Ar remained unchanged through
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3.2. Effect of carbonation temperature on CO_2 capture and conversion of the sorbent material

To investigate the effect of carbonation temperature on CO₂ capture efficiency of the sorbent material, experiments at carbonation temperature of 590°C, 620°C, 650°C and 680 °C were conducted through three cycles for each temperature run. Figure 3 shows the calculated CO₂ capture efficiencies in each experimental run during the initial 20 min in the carbonation stage. It is worthwhile to note that the overall CO₂ capture efficiencies for the whole carbonation stage were lower as the most effective CO₂ capture occurred in the initial short period of the carbonation.



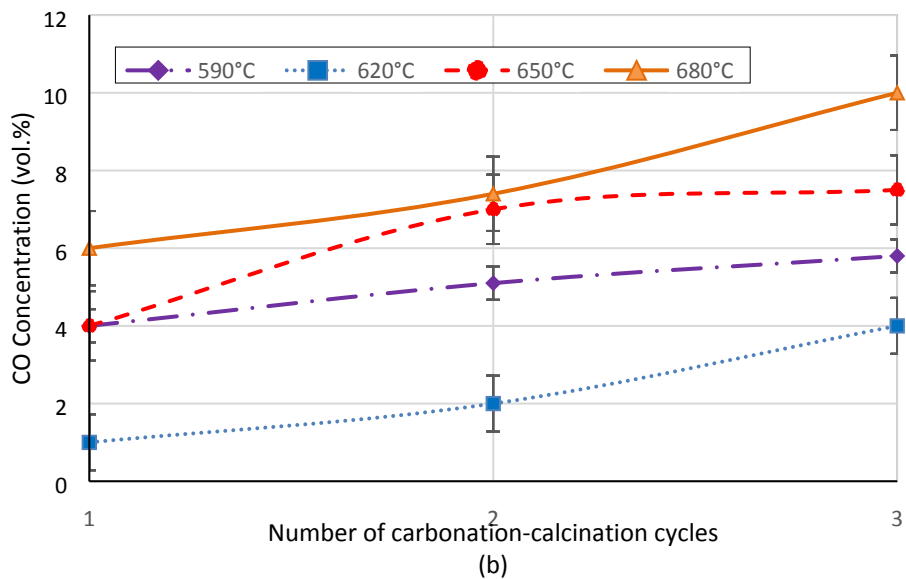


Figure 3. The effect of carbonation temperature and carbonation-calcination looping cycles on: (a) the CO₂ capture efficiency and (b) the outlet CO concentrations from the reactor with the sorbent material.

The experimental results in Figure 3(a) show that the CO₂ capture efficiency was reduced with the cycling of carbonation-calcination looping. The carbonation temperature also has significant impact. The maximum CO₂ capture was achieved at the carbonation temperature of 620°C with efficiencies of 94.2%, 93.0%, and 84.0%, which corresponded to 0.31, 0.28 and 0.29 CO₂ uptake by the sorbent material (g CO₂/g sorbent), during the three cycles in the initial 20 minutes of carbonation in each cycle.

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4 Similar pattern of results was also obtained for other carbonation temperatures. At
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7 carbonation temperature of 590°C, the corresponding CO₂ capture efficiencies were
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10 84.2%, 81.7% and 75.9% (0.28, 0.26, 0.17 g CO₂/g sorbent), respectively, in the three
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12
13 cycles. The CO₂ capture efficiencies for carbonation temperature of 650°C were slightly
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15
16 reduced to 83.7%, 71.3% and 71.7%, in the first, second and third cycle, corresponding
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18
19 to 0.23, 0.15, 0.15 g CO₂ uptake/g sorbent. At carbonation temperature of 680°C, the CO₂
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21
22 capture efficiencies in the three cycles were significantly reduced to 68.9%, 65.3% and
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25 64.9% and exhibited a CO₂ uptake of 0.14, 0.10, 0.10 g CO₂/g sorbent, respectively.
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32 In order to investigate the effect of carbonation temperature and carbonation-calcination
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34 looping on CO₂ conversion to CO, CO concentrations in the outlet gas stream from the
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37 reactor during the initial 20 minutes of carbonation stage were calculated and the results
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40 are shown in Figure 3 (b). From the results, we found that at 680°C the outlet CO
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43 concentration was the highest among all of the carbonation temperatures investigated,
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46 varying from 6 % in the first cycle to 10% in the third cycle. This trend is in the opposite
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49 direction with the CO₂ capture efficiency, confirming that the CO conversion had adverse
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52 impact on the CO₂ capture. As expected, the outlet CO concentration was the lowest at
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3 the carbonation temperature of 620°C, varying from 1 % in the first cycle to 4% in the third
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7 cycle, at which the highest CO₂ capture efficiency was achieved.
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10 The above results are in agreement with previous studies wherein the low temperature
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12 favours the exothermic carbonation reaction to produce CaCO₃ from CaO and CO₂ based
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14 on the equilibrium gas compositions.¹⁰⁷ However, it is noted that the reaction kinetics also
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18 decreases with decreasing the temperature.
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24 The experimental results in Figure 3 also illustrate that the CO₂ capture efficiency of the
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26
27 sorbent material decreased with cycling at all carbonation temperatures which have been
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29
30 reported in the literatures.^{125, 126} Abanades and Alvarez¹²⁷ investigated the effect of the
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33 cycling of carbonation-calcination looping and found that with each cycle, there was a
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35
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37 certain loss in small pores due to the filling of formed CaCO₃ and in the same time there
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40 was a certain increase in large pores. This phenomenon decreased the pore surface area
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44 and thus the sorbent reactivity.
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49 From the results of this study, it is found that during the carbonation stage, majority of
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52 the inlet CO₂ was captured by the sorbent material through carbonation. A fraction of CO₂
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55 was converted to CO through reverse water-shift reaction. These findings are consistent
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3 with the report by Han and Harrison³³ who conducted experimental and theoretical
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7 investigation, and found that the optimum temperature for the shift and carbonation
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9
10 reactions represents a compromise between equilibrium gas composition and kinetics
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14 factors.

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17 Symonds et al.¹²⁸ confirmed that 620°C is the optimum carbonation temperature for
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20 the tested sorbent material for CO₂ capture. Higher temperature has an adverse effect on
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23 both the water-gas shift and carbonation reactions but temperatures lower than 620 °C
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25
26 were kinetically unfavourable for the process.^{107, 109} Further micro structure analysis was
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28
29 conducted on the tested sorbent material and the results will be presented in the
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31
32 subsequent section. It was found that the surface area of the sorbent material tested at
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35 high carbonation temperatures was significantly lower than that tested at lower
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38 temperatures. Therefore, the sorbent material was more stable at lower temperatures and
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41 thus could retain effective CO₂ adsorption capacity.
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49 In these experiments, it was also observed that the CO₂ capture efficiency of the sorbent
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52 material tended to decrease with the number of cycles, as shown in Figures 3. This can
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55 be attributed to a number of factors including the reduction of pore surface area as
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3 mentioned above,¹²⁷ the regeneration of a thin layer of calcium carbonate at the CaO
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7 surface forming a plug. ¹²⁹ These mechanisms have also been investigated through BET,
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10 XRD and SEM analyses and these will be presented in the following section. Results from
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14 further investigation with larger number of cycles will be discussed in Section 3.4.
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19 **3.3. Sorbent material analysis**

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23 After completion of each run of experiments with three cycles, the tested sorbent
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26 material was analysed for pore volume (porosity) and surface area, and the results for all
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28
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30 of the four runs are shown in Table 2 for different temperatures. From the table, it is found
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33 that the surface area of the sorbent was the highest with the value of 1.75 m²/g at the
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35
36 carbonation temperature of 620°C and this was decreased with increase in the
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38
39 carbonation temperature, to 1.51 and 0.65 m²/g, respectively, at carbonation
40
41
42 temperatures of 650°C and 680°C. Similar trend was also observed for the pore volume
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45 with values of 0.0072, 0.0052 and 0.0015 cm³/g for the carbonation temperatures of 620,
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48 650 and 680°C. These trends are in line with the CO₂ capture efficiencies, confirming that
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51 the sorbent surface area and pore volume enhanced the carbonation reactions. However,
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3 it is interesting to note that the sorbent surface area and pore volume at carbonation
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7 temperature of 590°C were significantly lower than those at 620°C. It is also observed
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10 that the surface area and pore volume for carbonation temperature of 620°C were higher
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13 than those of the pretreated sorbent material. Further research will be conducted to
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17 investigate the causes of these phenomena.
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21 At carbonation temperature of 620°C, CaO was effectively converted to CaCO₃ through
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24 carbonation reaction with average CO₂ capture efficiency of 90.4% for the three cycles.
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28 However, at carbonation temperature of 680°C, the conversion reactions of the sorbent
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31 material were much less effective with the average CO₂ capture efficiency being reduced
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34 to 66.4%. This suggests that the surface area and pore volume are positively correlated
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37 to the conversion activity and, consequently, to the CO₂ capture efficiency.
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41 The results of the BET analysis results show that CO₂ adsorption by the sorbent
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44 material was affected by pore structures and gas diffusion because the surface layer of
45
46
47 the pore structure controlled the rate of reaction.¹³⁰ Furthermore, Borgwardt¹³¹ proposed
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49 that CaO porosity was further reduced by the presence of CO₂ and H₂O in the pores. The
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52 results from the present study suggest that CO₂ capture capacity decreased in the
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3 subsequent cycles and this is likely to be due to the closure of some small pores of CaO-
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7 based material during carbonation. Further research will also be conducted to investigate
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10 this phenomenon.
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15 **Table 2.** Surface area (S.A.) and pore volume (P.V.) of the tested sorbent materials after
16 completion of three cycles of carbonation-calcination looping at different temperatures.
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Sample	surface area (m ² /g)	Pore volume (cm ³ /g)
Sorbent material at 590°C	0.69	0.0035
Sorbent material at 620°C	1.75	0.0072
Sorbent material at 650°C	1.51	0.0052
Sorbent material at 680°C	0.65	0.0015

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40 The results of XRD analysis for fresh and tested sorbent materials are shown in Figure 4.
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43 In the figure, CaO, Fe₂O₃ and CaCO₃ were observed as main phases in all samples.
44
45
46 Ca(OH)₂ was formed by the reaction of CaO with moisture in atmosphere during XRD
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48 sample preparation. The intensity of CaCO₃ in the fresh sample was higher than the
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50 tested sample while the intensity of CaO in the tested sample was higher than the fresh
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3 material, indicating the effect of cycling on carbonation of material and deactivation of the
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6 sorbent.
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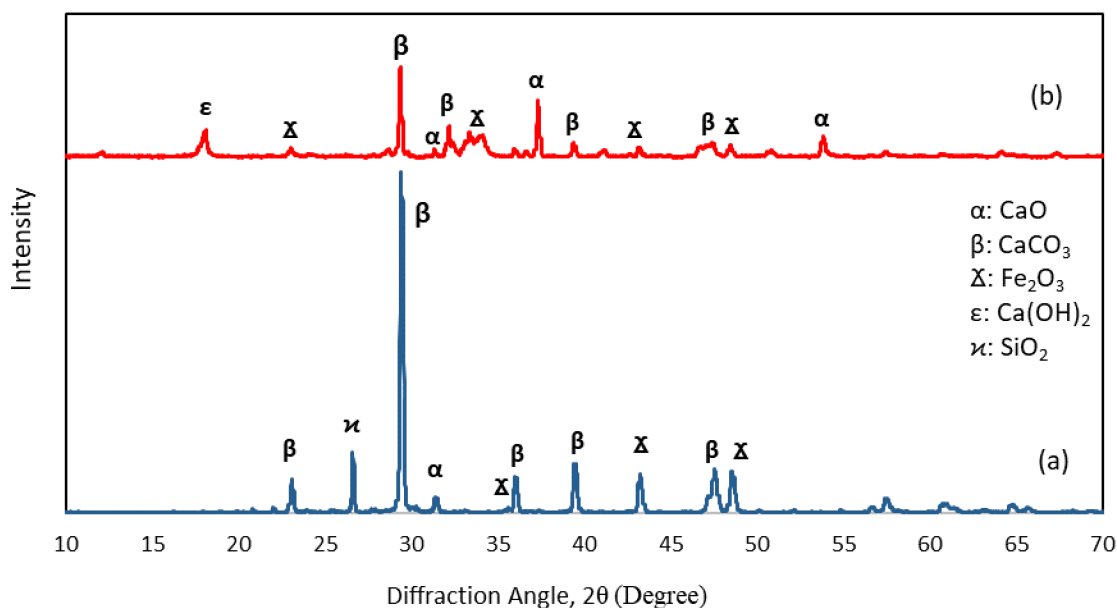
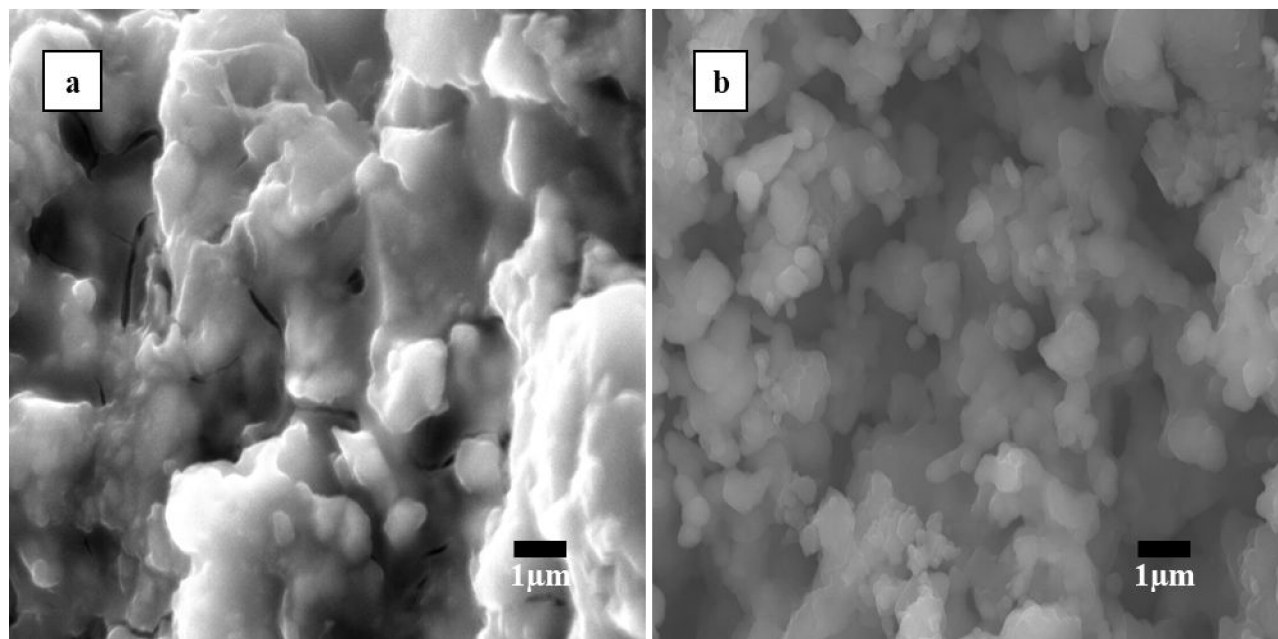


Figure 4. The XRD analysis results for: (a) fresh sorbent material, (b) tested sorbent material after three cycles of carbonation-calcination looping.

The fresh and tested materials were further analysed using SEM images to examine the pore blockage and changes in micro-structure of the sorbent material through the experiments. SEM images of the fresh and tested sorbent materials are presented in

Figure 5. It is observed from these images that the surfaces of fresh material before the

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3 first carbonation appeared to be loose, porous and rough, as shown in Figure 5(a), which
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7 are characteristics of high capacity for CO₂ uptake. On the other hand, the surfaces of
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9
10 the tested sorbent material show smooth surface as shown in Figure 5(b).



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37 Figure 5. SEM images of (a) fresh sorbent material prior to testing, and (b) tested sorbent
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40 material after three cycles of carbonation-calcination looping.

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45 The results of SEM analysis have further confirmed the reduction of activity of the sorbent
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48 material with cycling of carbonation-calcination looping. These results are consistent with
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51 those reported in literature. Abanades et al.^{127, 132} demonstrated that the reactivity
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54 decrease of the CaO based sorbent with cycling would be the combined consequences
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3 of the conversion associated with the filling up of the micropores existing in the calcine
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7 and that associated with the formation of a product layer in the walls of the large pores
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10 present in the calcine.^{133, 134} The limiting factor for further carbonation reaction was
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14 strongly related to the gas diffusion resistance through this product layer, as proposed by
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17 Mess et al.¹³⁵
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22 The above phenomenon has also been found in metal oxides at high temperatures which
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25 resulted in decrease of surface area and deactivation of particles.¹³⁶⁻¹³⁸ It is reported that
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28 migration of metal cations and their subsequent enrichment on the particle surface
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32 resulted in the sintering,¹³⁹ which was more significant after several redox cycles.
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36 **3.4. Effect of cycling on carbonation conversions of modified sorbent material**

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40 Further tests were conducted with eight cycles of carbonation-calcination looping at
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43 carbonation temperature of 650°C and each carbonation stage lasted for 180 min. The
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47 results of CO₂ capture efficiency over the initial 20 min of carbonation from this experiment
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51 are shown in Figure 6 in which the overall CO₂ capture efficiencies through the whole
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54 carbonation stage are also included to illustrate the decrease in CO₂ capture efficiency
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3 with time. It is found that the CO₂ capture efficiency over the initial 20 min was much
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7 higher than the overall efficiency for every cycle. This indicates that the effective CO₂
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10 capture was achieved in the initial 20 min thus prolonged carbonation is unnecessary.
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14 From Figure 6, the CO₂ capture efficiency decreased with the cycling, however, the
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17 trend was different between the overall efficiency and the efficiency over the initial 20
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20 minutes in the carbonation. For the 20 min, the efficiency dropped significantly from
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23 83.7% in the first cycle to 71.3% in the second cycle, however, the efficiency maintained
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26 at around 70% through all of the subsequent cycles. This further illustrates that the
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29 sorbent material can be used for a large number of cycles when the carbonation stage
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32 lasts 20 minutes. However, for the whole stage of carbonation, the overall CO₂ capture
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35 efficiency decreased in the second cycle from 56.2% to 49.8% and then continued
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38 decreasing from the fifth cycle at 48.9% to 16.4% in the final cycle.
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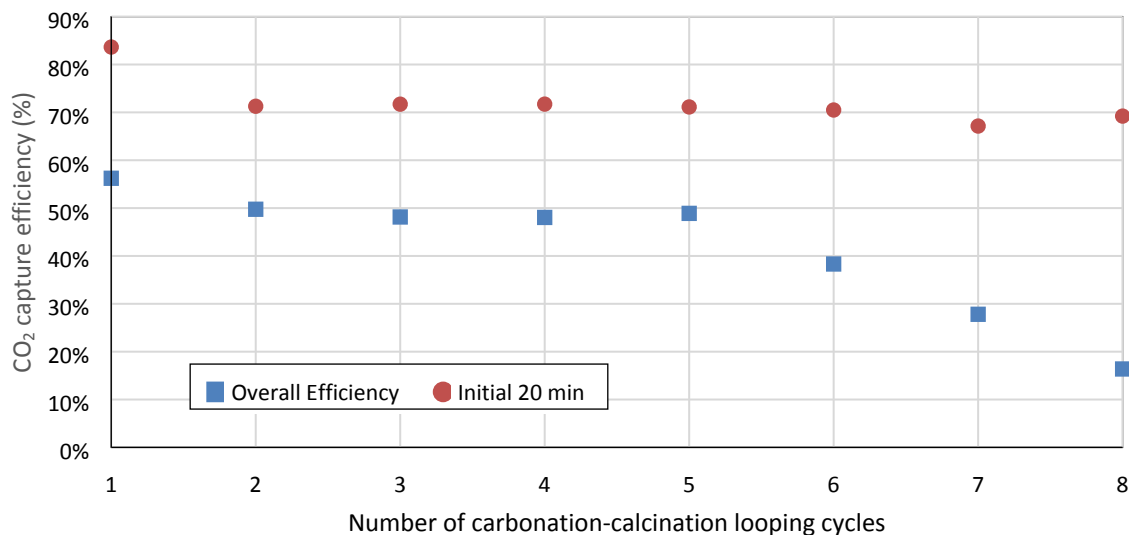


Figure 6. The effect of cycling on CO₂ capture efficiency by the CO₂ sorbent material at carbonation temperature of 650°C.

With a number of cycles of carbonation-calcination looping, part of the sorbent surface was covered by CaCO₃ and this reduced the active sites and active surface area for the target carbonation and Fe oxidation reactions. In a separate study by Grasa and Abanades,⁹⁴ degradation of limestones was also observed over multiple carbonation/calcination cycles. Grasa and Abanades⁹⁴ proposed that this degradation was due to reduction of active surface area and material porosity which is considered to be the key factor for the decrease in material's CO₂ capture efficiency with cycling.

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4 It should be pointed out that the high CO₂ capture capability of the sorbent material
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7 investigated in this study can be attributed to composite structure of the material by
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10 including Fe₂O₃ in the material which enhanced the performance of CaO.
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21 4. CONCLUSION

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24 The present study has investigated the performance of a CaO-Fe₂O₃ based sorbent
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27 material on CO₂ capture from simulated gasification producer gas through carbonation-
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30 calcination looping. Effects of carbonation temperature and the cycles of carbonation-
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33 calcination looping were examined.
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38 It is found that the optimum carbonation temperature for the sorbent material is 620°C
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41 with average CO₂ capture efficiency of 90.4% over three looping cycles. This high CO₂
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44 capture efficiency is attributed to a compromise between equilibrium gas composition and
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47 kinetics factors, and the contribution of CaO/Fe active sites. The sorbent material tends
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50 to deactivate at higher temperatures in the carbonation. Increasing carbonation
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53 temperature tends to promote conversion of CO₂ to CO due to the reverse water-gas
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3 shift reaction. High temperature for the carbonation also tends to reduce pore surface
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7 area and pore volume of the sorbent material. However, the reaction kinetics decreases
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10 at low temperatures. It is also found that the sorbent material can effectively capture CO₂
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13 in the initial 20 minutes of the carbonation stage thus prolonged carbonation is
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17 unnecessary.
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21 The sorbent material CO₂ capture capacity is reduced with the cycling of the
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24 carbonation and calcination looping. At the carbonation temperature of 650°C, the CO₂
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26
27 capture efficiency over initial 20 minutes in the carbonation dropped from 83.7% in the
28
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30 first cycle to 71.3% in the second cycle, however, the efficiency maintained at around
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34 70% through the subsequent six cycles.
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38 Addition of Fe₂O₃ in the CaO based sorbent can enhance activation of the material pore
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41 surface, which facilitates the CO₂ capture, and improve the strength of the sorbent material.
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45 This novel sorbent has excellent regenerability in cyclic CO₂ capture during calcination-
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47
48 calcination looping. Synthetic sorbent material is considered a promising aspect of cyclic
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51 stability over multiple carbonation–calcination cycles, while keeping the surface area
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54 available and active during carbonation.
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7 **AUTHOR INFORMATION**
8
9

10
11 **Corresponding Author**
12

13
14 **Shusheng Pang** - Department of Chemical and Process Engineering, University of
15
16

17
18 Canterbury, Christchurch 8140, New Zealand; Email:shusheng.pang@canterbury.ac.nz
19
20

21
22 **Author**
23

24
25
26 **Forogh Dashtestani**- Department of Chemical and Process Engineering, University of
27

28
29 Canterbury, Christchurch 8140, New Zealand
30
31

32
33
34 **Mohammad Nusheh**- Hot Lime Labs, Lower Hutt, New Zealand
35
36

37
38 **Janjira Hongrapipat**- Gussing Renewable Energy (Thailand) Co., Ltd., Bangkok 10500,
39

40
41
42 Thailand
43
44

45
46 **Vilailuck Siriwongrungson**- College of Advanced Manufacturing Innovation, King
47

48
49
50 Mongkut's Institute of Technology Ladkrabang, Bangkok 10520, Thailand
51
52

53
54 **Vlatko Materic**- Hot Lime Labs, Lower Hutt, New Zealand
55
56

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