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# Chemical-Looping Gasification of Biomass for Hydrogen-Enriched Gas Production with In-Process Carbon Dioxide Capture

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The research presents an innovative idea of developing a continuous H<sub>2</sub> production process employing fluidized-bed technology from agricultural biomass with *in situ* CO<sub>2</sub> capture and sorbent regeneration. Novelty of the process lies in the generation of relatively pure H<sub>2</sub> from biomass with CO<sub>2</sub> as a byproduct using steam as the gasifying agent. Another unique feature of the process is internal regeneration of the sorbent, fouled in the gasifier. Thus, the technology will serve the twin purpose of regenerating the sorbent and generation of N<sub>2</sub>-free H<sub>2</sub> and CO<sub>2</sub>. This work reports theoretical energy analysis and experimental investigation of the process. The system efficiency of the chemical-looping gasification process at an ideal scenario is found to be 87.49% with biomass as fuel. A sensitivity analysis for system efficiency is also conducted by varying carbon-capture and regeneration efficiencies. The experiments conducted in a batch-type fluidized-bed steam gasifier using CaO as the sorbent shows a 71% concentration of H<sub>2</sub> and nearly 0% concentration of CO<sub>2</sub> in the product gas when sawdust was used as the feedstock. In a separate test using a circulating fluidized-bed reactor as the regenerator, a 40% regeneration of CaO is also achieved at a calcination temperature of 800 °C.

## Introduction

A “decarbonizing” energy supply is a technological solution to address global CO<sub>2</sub> emissions, and in this context, the idea of “hydrogen energy economy” has significant merit. The major challenge in moving toward a H<sub>2</sub> economy is to produce sufficient H<sub>2</sub> economically, sustainably, and environmentally friendly to meet future demand. Currently, 96% of the total H<sub>2</sub> production is sourced from fossil fuels. Thus, clean and renewable resources and sustainable pathways are necessary if H<sub>2</sub> is to become a fundamental energy resource for the future. In this context, biomass represents an immense and renewable source (carbon neutral) for the production of H<sub>2</sub>.

A variety of reaction processes are suggested by the researchers for the conversion of biomass to H<sub>2</sub>. The merits of these pathways have been cited in the literature;<sup>1,2</sup> however, the most suitable conversion pathway is reported to be thermochemical conversion via steam gasification.<sup>3</sup> The value and interest for further uses of this raw gas can still be improved if the H<sub>2</sub> content is increased and CO<sub>2</sub> is eliminated. This can be achieved by eliminating CO<sub>2</sub> *in situ* in the same bed of the gasifier. Past studies demonstrate the suitability of fluidized-bed reactors (FBRs) for biomass gasification,<sup>4,5</sup> and the superior solid–gas contacting, which occurs in a

fluidized bed,<sup>6–8</sup> is expected to enhance CO<sub>2</sub> capture if a suitable sorbent is used.

However, the very few studies that are available on the production of H<sub>2</sub> from biomass with CO<sub>2</sub> separation possess a number of limitations. Ni et al. investigated the production of H<sub>2</sub> with post-capture of CO<sub>2</sub> in a conventional gasifier.<sup>2</sup> This type of system requires additional investment on a water–gas shift reactor and in separation/cleaning. Mahishi and Goswami carried out their experiment in a batch-type fluidized-bed steam gasifier,<sup>9</sup> as well as Hanaoka et al. in an autoclave.<sup>10</sup> The major disadvantage of their processes is that a continuous H<sub>2</sub> production cannot be achieved and, after every batch experiment, the absorbent bed used in the process had to be replaced by a fresh one; therefore, there is no provision for regeneration of absorbent within the process. Guan et al. and Pfeifer et al. proposed improved processes based on a dual FBR.<sup>11,12</sup> However, in the process, air supplied during the combustion results in a production of flue gas, which contains mainly N<sub>2</sub> and CO<sub>2</sub>. Therefore, an expensive postcombustion separation system is required if one wishes to capture CO<sub>2</sub>. Supplying O<sub>2</sub> alone as the gasifying agent is energy-intensive and expensive because it has to be separated from air. Therefore, there is a dire need for developing a continuous process

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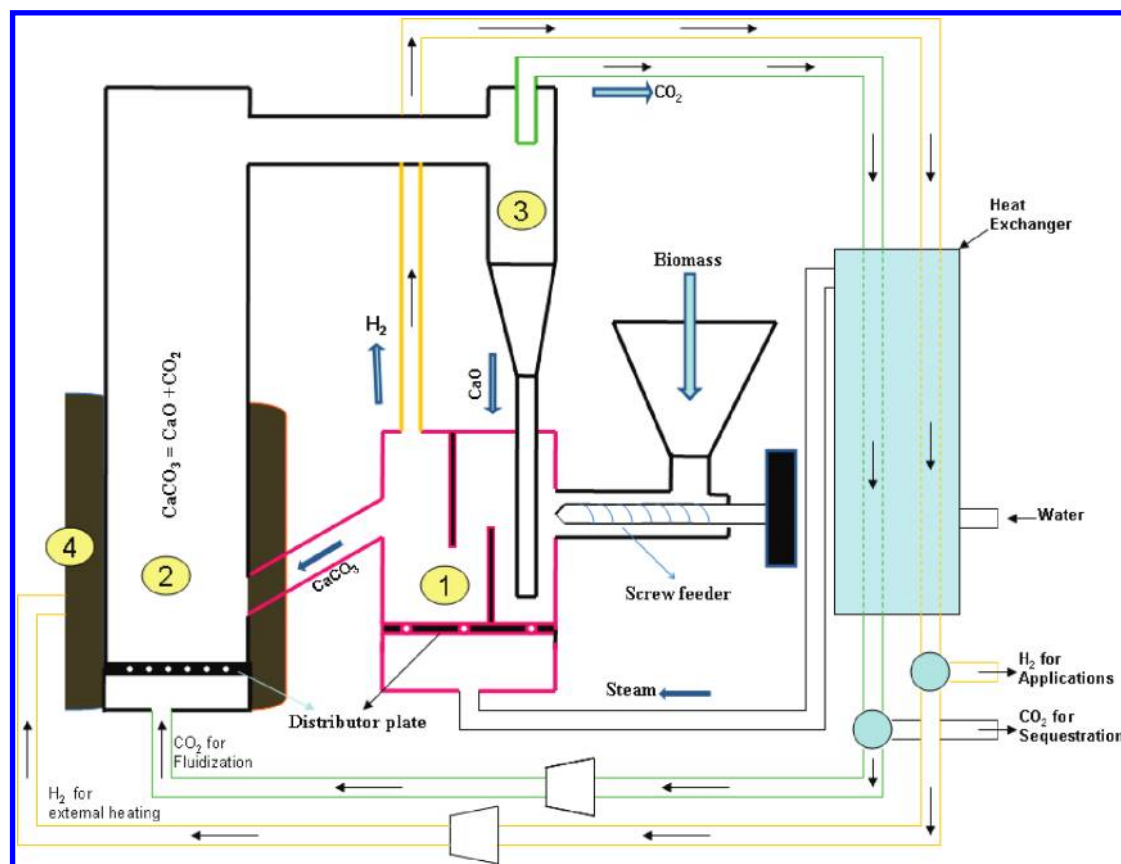
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**Figure 1.** Schematic diagram of the proposed chemical-looping gasification system.

that can produce H<sub>2</sub>-enriched gas from biomass with in-process CO<sub>2</sub> capture and sorbent regeneration.

### Process Details

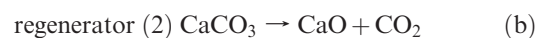
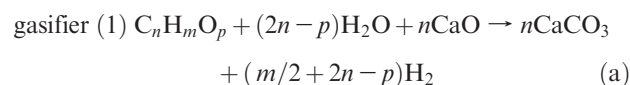
In this research, an innovative concept of continuous H<sub>2</sub>-enriched gas production from biomass using fluidized-bed technology with in-process CO<sub>2</sub> capture is proposed. A custom-designed circulating fluidized-bed (CFB) reactor would be the center piece of this research. The coupled gasification/CO<sub>2</sub> capture proposed in this research is illustrated in the following schematic diagram (Figure 1). It would be in a loop with end–end configuration composed of a bubbling fluidized bed (BFB) as a gasifier (1), a CFB as a regenerator (2), and a cyclone (3). The regenerator would be connected to the gasifier through the cyclone. The riser section of the proposed CFB would act as a regenerator, where the sorbent, CaCO<sub>3</sub>, would be converted into CaO and CO<sub>2</sub> by the application of external heat, typically at about 900 °C. The products CaO and CO<sub>2</sub> would be separated in the cyclone. CaO would be fed to the loop seal (gasifier) through the standpipe, and CO<sub>2</sub> would be collected and supplied to the riser (regenerator) after filtration for continuous fluidization. The loop seal would act as a BFB gasification system, where biomass and steam would be supplied and CaO would be fed from the cyclone. The loop seal is expected to be operated at 650 °C, where gasification with in-process CO<sub>2</sub> capture is expected. After completion of the reaction, mostly H<sub>2</sub>-enriched gas would be produced and collected from the BFB gasifier (loop seal) and CaO once converted to CaCO<sub>3</sub> by absorbing CO<sub>2</sub> produced during the gasification process would be fed back to the regenerator to continue the cycle.

The regenerator would be heated by either an external heat source (4) or using a part of H<sub>2</sub> produced (5). External heating of the fluidized bed could be accomplished by the insertion of heat-transfer tubes into the bed. Direct burning of fuel inside the regenerator would be a more efficient way of supplying the heat but would require downstream separation of CO<sub>2</sub> unless H<sub>2</sub> is burned with pure O<sub>2</sub>. To avoid separation, processes downstream captured CO<sub>2</sub> (as shown in Figure 1) and/or H<sub>2</sub>O can be used as the fluidizing gas in the regenerator, thus eliminating the need for an expensive oxygen plant.

Biomass fuel would be continuously fed to the gasifier (1), and sorbent material would continually circulate from the gasifier in the form of CaCO<sub>3</sub> to the regenerator (2) and from the regenerator in the form of CaO back to the gasifier. The delivery of the hot CaO to the gasifier/carbonator would provide additional heat for the gasifier/carbonator vessel. In addition, heat release by the exothermic carbonization reactions would supply most of the heat required by the endothermic gasification reactions. Also, CO<sub>2</sub> from the regenerator (2) and product gas produced from the gasifier (1), leaving at high temperature, would be used to produce high-temperature steam required for the gasifier (1).

Furthermore, controlling the rate of solids circulation allows for the regulation of heat delivered to the gasifier. A makeup stream of fresh sorbent (CaCO<sub>3</sub>) would be supplied to maintain capture capacity.

The reactions associated with this process could be summarized as follows:



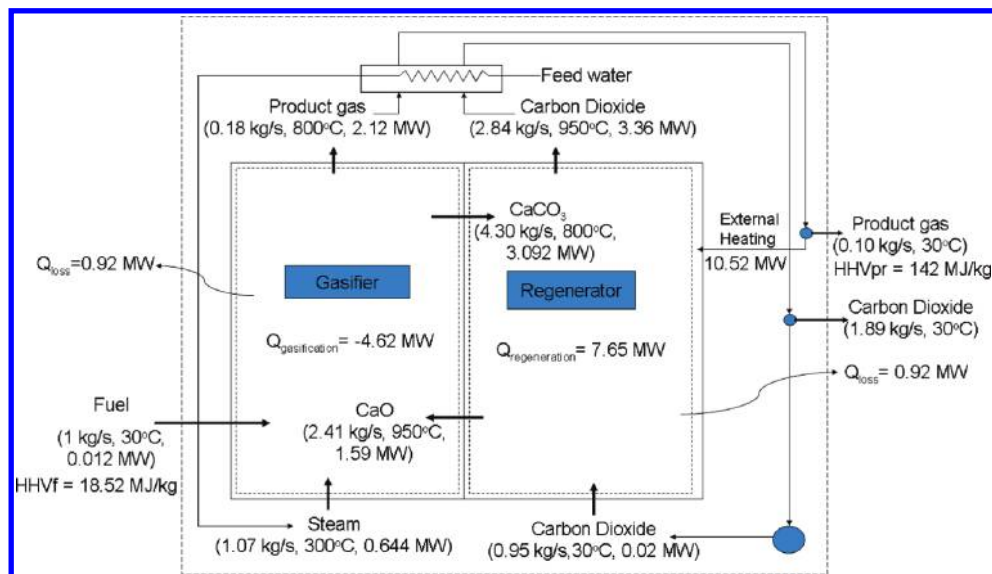
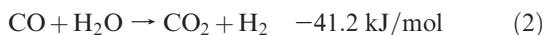
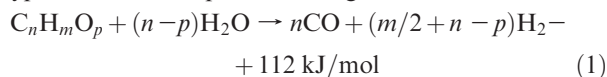


Figure 2. Mass and energy balance for chemical-looping gasification.

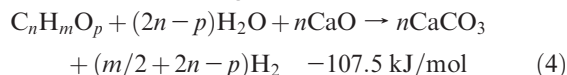
### Energy Balance of the System

The overall energy balance of the system is shown in Figure 2. For the analysis, the chemical-looping gasification is divided into two subsystems: gasifier and regenerator. The energy moving in and out and the energy required for each of the subsystems are accounted for, and the system efficiency is calculated here.

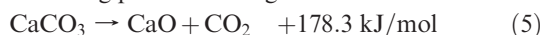
Typical reactions expected in the gasifier are



Thus, the overall reaction in gasifier could be written as



The reaction taking place in the regenerator would be



Calculations are based on biomass with a composition of C, 51.13%; H, 6.10%; and O, 41.96%. This composition was taken from the experimental work of Mahishi and Goswami.<sup>9</sup> Using eqs 4 and 5, the flow of different streams are calculated and the values in kg/s are shown in Figure 2 along with the temperature and energy at which it is entering and leaving each subsystem.

In an ideal scenario, heat produced during the carbonation reaction (eq 3) provides the energy necessary for the gasification reaction; thus, the gasifier does not need any external heating under steady state. The rate of heating for the regenerator is estimated as 10.52 MW. Heat required for steam generation is 3.08 MW. The product gas leaving the gasifier and the carbon dioxide leaving the regenerator are above 800 °C; therefore, its sensible energy is proposed to be used for the steam production. Thus, accounting for all of these energy flows, the theoretical thermal efficiency of the system is found to be 87.49%.

To have a better understanding of the process, a sensitivity study is carried out to examine the effect of carbon-dioxide-

capture and regeneration efficiencies on the overall system efficiency. This study has been conducted following two scenarios.

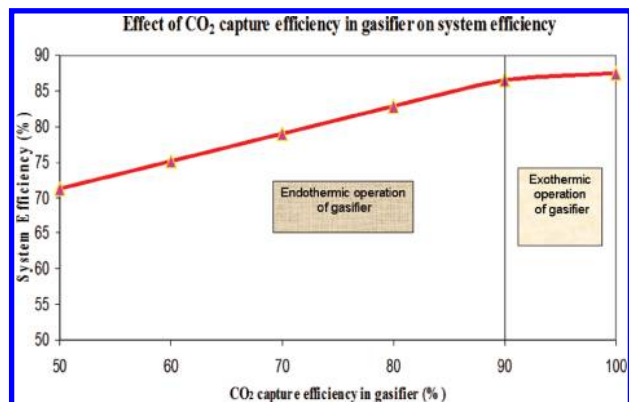
**Scenario 1: Carbon-Dioxide-Capture Efficiency in the Gasifier Varies, but the Regenerator Efficiency Remains Constant at 100%.** The following assumptions are made for this scenario: (1) The energy balance in the regenerator remains the same with the ideal scenario. (2) The energy generated during the carbonation reaction in the gasifier changes with the CO<sub>2</sub>-capture efficiency. (3) The product gas contains mainly hydrogen and a fraction of carbon dioxide not captured by CaO in the gasifier. (4) The sensible heat of the carbon dioxide is added to that of hydrogen to calculate the total enthalpy of the product gas.

With the reduction in the capture of carbon dioxide by calcium oxide, the energy released during the carbonation reaction will be lower; thus, the overall energy balance for the gasifier will be endothermic. Thus, an external heating source is required. If it comes from the combustion of a part of the product gas, then the efficiency of the system will drop. As from Figure 3, it can be seen that, when the CO<sub>2</sub> capture is 100%, the overall system efficiency is 87.49%, while it reduces to 71% for 50% CO<sub>2</sub> capture. The calculation shows that around 90% capture efficiency should be maintained if the gasifier operates under autothermal conditions.

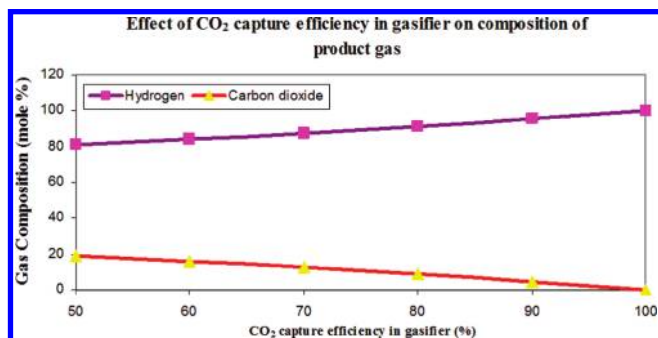
The reduction in the effectiveness of CaO to capture CO<sub>2</sub> can occur because of several reasons: (1) Tar, which is formed during gasification, may deposit on the CaO, thus reducing its surface availability for CO<sub>2</sub> capture. (2) With a repeated number of carbonation and calcination cycles for the sorbent, its properties may change that results in a lower CO<sub>2</sub> capture. (3) The sintering and agglomeration problem involves CaO, Ca(OH)<sub>2</sub>, and CaCO<sub>3</sub>.

Because carbon dioxide produced during the gasification process is not captured, the composition of gases will also change. Figure 4 shows the composition of gases at different CO<sub>2</sub>-capture efficiencies. At 50% CO<sub>2</sub> capture, the hydrogen fraction is estimated up to 80% in the product gas, while 20% will be carbon dioxide. This analysis clearly shows the importance to ensure a higher capture of carbon dioxide during the gasification process. To maintain that, one option is to have a higher CaO/biomass ratio in the gasifier.





**Figure 3.** Effect of the carbon-dioxide-capture efficiency in the gasifier by CaO on the overall system efficiency.

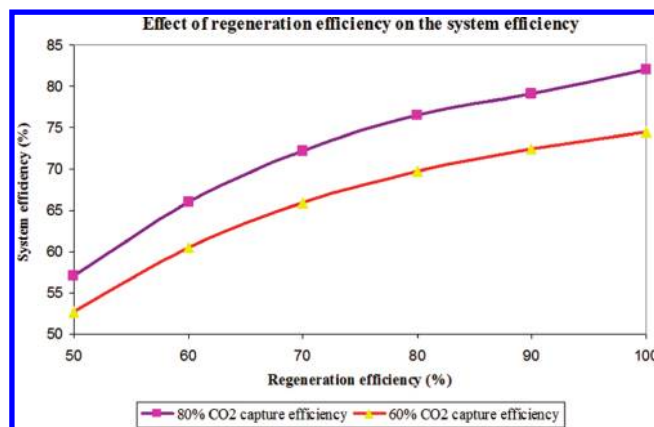


**Figure 4.** Effect of the CO<sub>2</sub>-capture efficiency on the composition of product gas.

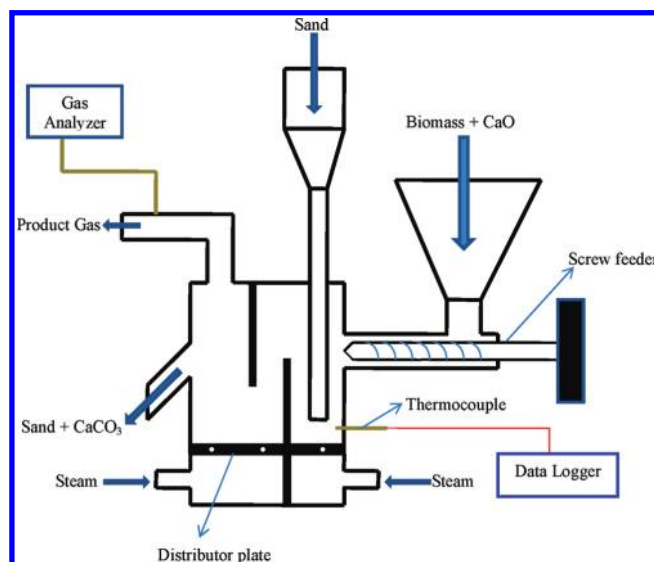
This may help to increase the carbon dioxide capture on one hand but, on other hand, also increases the size of the gasifier and regenerator and the heat requirement of the regenerator.

**Scenario 2: The Regeneration Efficiency in the Regenerator Changes, while the Carbon-Dioxide-Capture Efficiency in the Gasifier Remains Steady at 60 and 80%.** To study the combined effect of change in regeneration efficiency as well as carbon-dioxide-capture efficiency on the overall system efficiency, the following assumptions are made: (1) The solid leaving the regenerator to the gasifier is only calcium oxide. (2) The total amount of fresh calcium carbonate to be fed into the regenerator will be equal to [CaCO<sub>3</sub> required for producing CaO (CaO for 100% CO<sub>2</sub> capture in the gasifier + CaO recirculating inside the regenerator – unreacted CaO coming from the gasifier + CaO leaving from the regenerator with bed drain)]/regeneration efficiency – [CaCO<sub>3</sub> coming from the gasifier – non-calcinated CaCO<sub>3</sub> leaving the regenerator as bed drain]. (3) An amount (5%) of the solids is drained from the regenerator. (4) Energy loss because of the drainage of solid, energy retained by solid recirculation within the regenerator, and energy generated during the carbonation reaction in the gasifier changing with the capture efficiency are considered. (5) The product gas contains mainly hydrogen and a fraction of carbon dioxide not captured by CaO in the gasifier. (6) The sensible energy with the carbon dioxide is added with the hydrogen sensible energy to calculate the total product gas sensible energy.

Figure 5 shows the effect of the regeneration efficiency on the overall system efficiency for 80 and 60% carbon dioxide capture in gasifier. This study gives more of a realistic system efficiency that can be obtained practically. For 80% CO<sub>2</sub>-capture efficiency, the system efficiency varies from 57 to



**Figure 5.** Effect of the regeneration efficiency on the overall system efficiency for 80 and 60% carbon dioxide capture in the gasifier.



**Figure 6.** Experimental setup of the fluidized-bed steam gasifier.

82% by changing the regeneration efficiency from 50 to 100%. Similarly, for 60% CO<sub>2</sub>-capture efficiency, the system efficiency varies from 53 to 74.5% for the similar regeneration efficiency.

### Experimental Setup

The proposed concept is tested at batch mode. Two experimental units were built for studying eqs a and b. Figure 6 shows the schematic diagram of the experimental system to study the hydrogen-enriched gas production from biomass gasification with in-process carbon dioxide capture. The reactor was a bubbling fluidized bed. Steam was used as the fluidizing medium. The reactor was 10 × 10 cm in cross-section and 15 cm in height. Biomass (sawdust) and CaO were mixed in a known proportion and fed into the reactor by a screw feeder. Biomass was supplied at rate of 0.5 kg/h. Sand (0.15–0.3 mm) was used as an inert bed material. The bed temperature was measured by a thermocouple, and data were recorded in a data logger. For gas sampling, the online gas analyzer, Fisher–Rosemount NGA 2000 MLT, was fitted to measure the gas composition and shows the percentages by volume of CO, CO<sub>2</sub>, H<sub>2</sub>, and CH<sub>4</sub>. The gas analyzer was calibrated using standard gases, in which the concentration of each species is known. Nitrogen gas, 99.99% pure, was used to set zero condition. Before moving to the gas analyzer, the producer gas was made to pass a condenser coil to remove the water vapor and tar. After this, it was cleaned again with a fiber filter.

To start, the reactor was heated externally until the bed temperature reaches the desired temperature. Once it reaches the desired temperature, the external heating was cut off and the mixture of biomass and CaO was supplied to start the reaction (a), which was a combination of gasification and carbonization reactions.

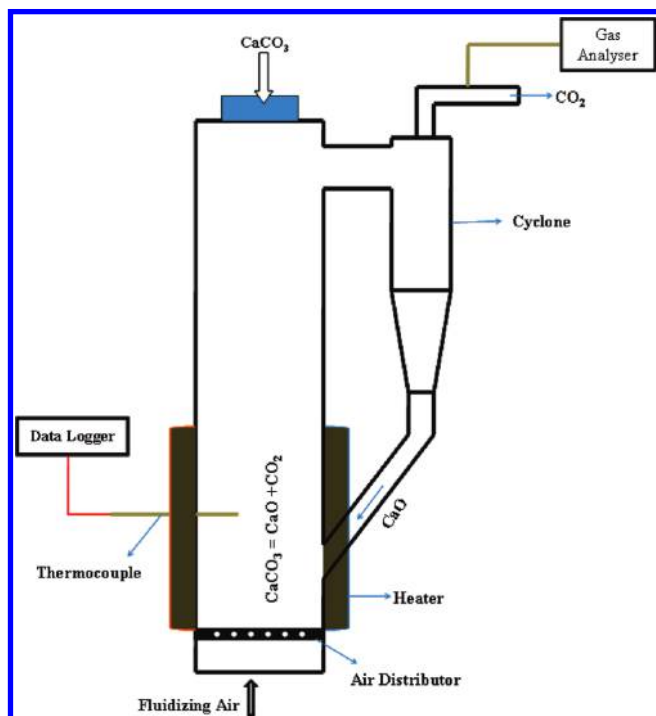


Figure 7. Experimental setup to study the regeneration of CaCO<sub>3</sub>.

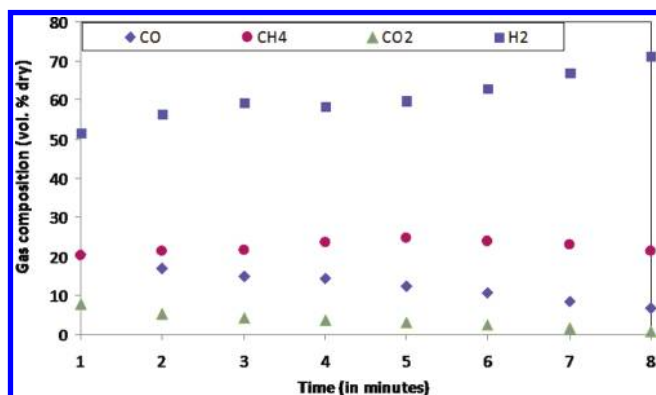


Figure 8. Composition of the product gas.

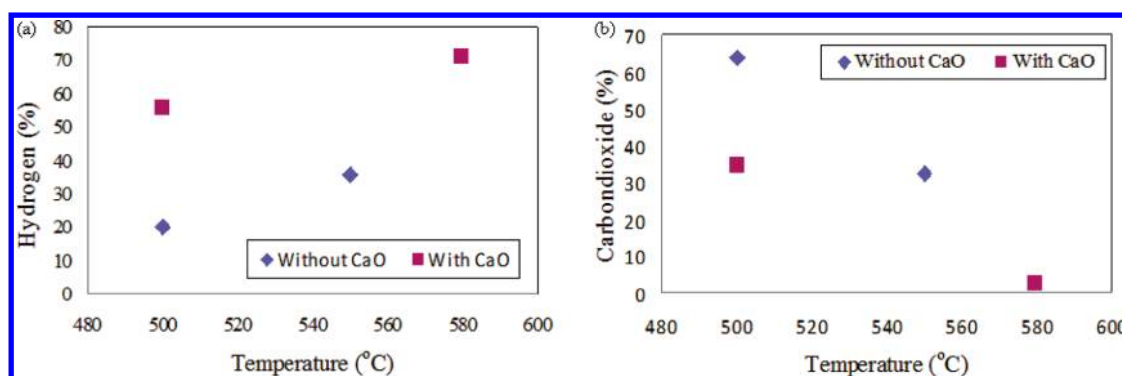


Figure 9. Effect of the temperature and use of CaO on the (a) hydrogen and (b) carbon dioxide concentrations.

The schematic of the experimental setup to study the regeneration of CaO from calcium carbonate is shown in Figure 7. This is a CFB reactor that was expected to act as the regenerator of the process proposed in the Process Details. The reactor was a cylindrical pipe of 7.5 cm in diameter. The calcium carbonate (CaCO<sub>3</sub>) was fed into the reactor from the top. In this case, air was supplied as the fluidizing medium. In the proposed process, either CO<sub>2</sub> or H<sub>2</sub>O would be supplied. Because the reaction is highly endothermic, a significant amount of energy was required for maintaining a temperature of 850 °C and higher. However, in this case, we could achieve 800 °C by supplying external heat using charcoal. The temperature inside the reactor was measured using a thermocouple, and data were recorded in a data logger. The concentration of carbon dioxide at the outlet is measured by the same gas analyzer.

## Results and Discussion

The experiments were conducted at steam/biomass [S/B] = 1.5 and [Ca/C] = 1. Figure 8 shows the composition of the product gas with time at a temperature of 580 °C. The hydrogen concentration up to a maximum of 71% was obtained. The carbon dioxide was nearly zero at that condition. The methane concentration remains more or less constant, while carbon monoxide reduces with time.

Figure 9 shows the effect of the temperature on the concentration of hydrogen and carbon dioxide obtained experimentally. The hydrogen concentration was found to be 55.87% at 500 °C. It was increased to 71% at 580 °C. Without calcium oxide, the concentrations of hydrogen at 500 and 550 °C were found to be 20 and 35.83%, respectively. Thus, the use of calcium oxide has been found to increase the hydrogen concentration by 2.8 times more than that without calcium oxide when tests were conducted at 500 °C. According to Le Chatelier's principle, the exothermic reaction moves in the forward direction if the partial pressure of the product is less than the reactant. In the experiments when CaO fed with biomass in the gasifier, CaO absorbed carbon dioxide and formed CaCO<sub>3</sub>, while the partial pressure of carbon dioxide decreased; it accelerated the water–gas shift reaction (eq 2) in the forward direction, forcing more CO to convert into hydrogen and carbon dioxide. Thus, using CaO helped in increasing the hydrogen concentration in the product gas. The concentration of carbon dioxide was found to reduce to nearly zero at 580 °C using CaO. At 500 °C, the concentration of carbon dioxide has been found to reduce by half using CaO as the sorbent. Thus, the presence of CaO not only lowers the carbon dioxide but, at the same time, increases the concentration of hydrogen in the product gas.

Figure 10 shows the temperature inside the gasifier with time for the cases of gasification with and without using CaO.

Gasification with CaO maintains the temperature more or less constant. This is because the carbon-dioxide-capture (carbonization) reaction is an exothermic one; thus, generated heat supplements the heat required for gasification. Therefore, no external heating was required in that case. Whereas in the case

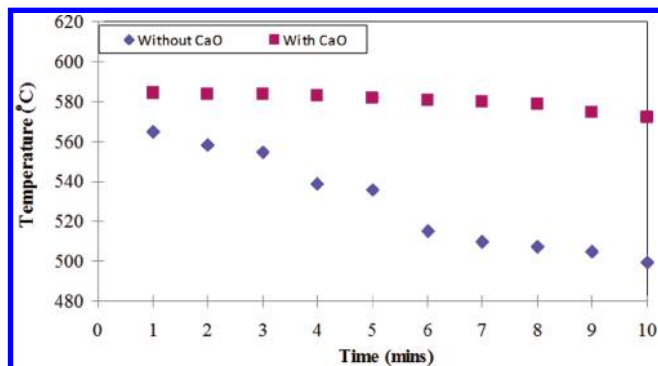


Figure 10. Effect of CaO on the gasifier system temperature.

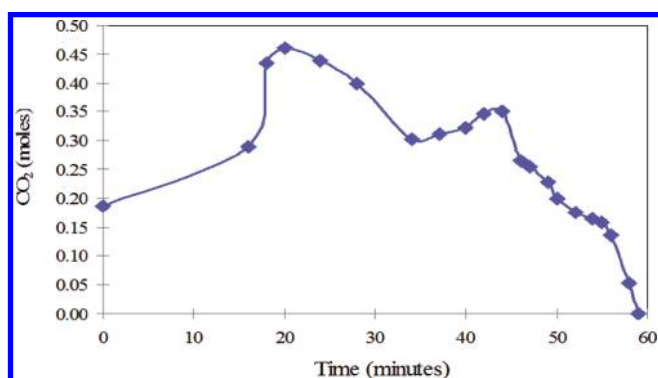


Figure 11. Moles of CO<sub>2</sub> generated with time.

of gasification without CaO, the temperature rapidly drops, requiring external heating for the gasification reaction.

The results of regeneration of CaO from CaCO<sub>3</sub> (reaction b) in the CFB regenerator is shown in Figure 11. From the results, it can be seen that about 40% of calcium carbonate was converted to CaO within the period of 1 h when the reactor is heated at a temperature of 800 °C. Further tests are underway with a temperature at 950 °C. It is expected that the calcination rate would be much higher at a higher temperature.

Figure 12 shows the results of uncertainty analysis to identify the possible variation in measured data because of instrument sensitivity. It shows that hydrogen and carbon monoxide have a lower range of uncertainty, while a higher uncertainty can be seen in the case of carbon dioxide and methane. The used gas analyzer is sensitive to steam or moisture. Because the process uses the steam as a gasifying agent, then there is a high chance that some may escape the dehumidifier, which may result in some deviation in measurement especially for the carbon dioxide concentration. Thus, the range of uncertainty is higher for the carbon dioxide.

## Conclusion

The research proposes an innovative idea of developing a continuous H<sub>2</sub> production process employing fluidized-bed technology from agricultural biomass with *in situ* CO<sub>2</sub> capture and catalyst regeneration. The novelty of the process lies in the generation of relatively pure H<sub>2</sub> from biomass with CO<sub>2</sub> as a byproduct using steam as the gasifying agent. Another unique feature of the process is internal regeneration of the catalyst, fouled in the gasifier. Thus, the technology will serve the twin purpose of regenerating the catalyst and generation of N<sub>2</sub> free H<sub>2</sub> and CO<sub>2</sub>.

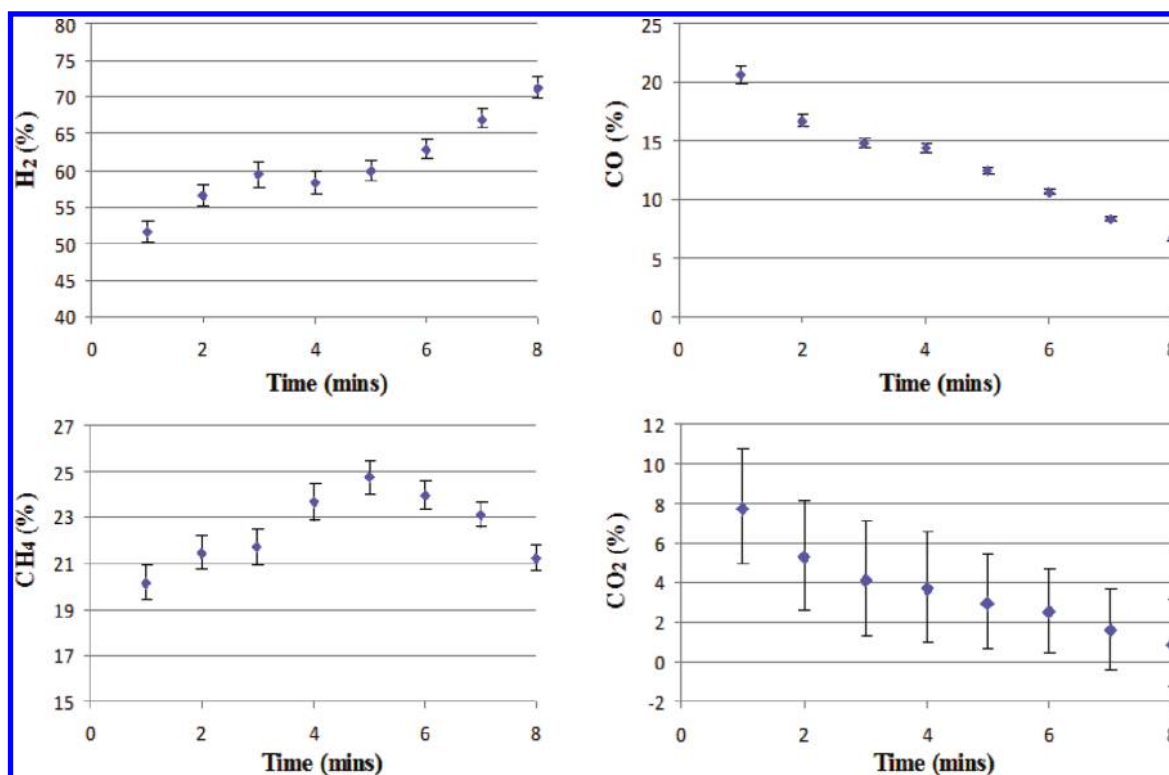


Figure 12. Variation in results obtained because of the sensitivity of measuring equipment.

The theoretical thermal efficiency of the system is found to be 87.49%, while sensitivity analysis shows that efficiency could be as low as 71% if only 50% of the carbon dioxide produced during gasification is captured. Also, while the carbon-dioxide-capture efficiency is kept constant at 80%, changing the regeneration efficiency from 100 to 50% lowers the overall system efficiency from 82 to 57%. Experimental results show that the use of calcium oxide not only helps to reduce the concentration of carbon dioxide to nearly zero but also increases the hydrogen concentration and helps to maintain the gasifier temperature constant,

thus avoiding the additional heat required for the endothermic gasification reaction to take place. At 580 °C gasification temperature, the hydrogen concentration was found to be 71% for [Ca/C] ratio of 1 and S/B ratio of 1.5 and the carbon dioxide concentration was nearly zero. Experimental results on regeneration show that a 40% regeneration of CaO is possible within a 1 h time period when the temperature is maintained at 800 °C. However, this reaction is expected to be much faster at a higher temperature (above 850 °C). Further research on this concept is underway.