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STUDY OF CALCINATION-CARBONATION OF CALCIUM CARBONATE IN DIFFERENT FLUIDIZING MEDIUMS FOR CHEMICAL LOOPING GASIFICATION IN CIRCULATING FLUIDIZED BEDS

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ABSTRACT

Chemical looping gasification (CLG) of biomass in a circulating fluidized bed is an excellent option for production of separate streams of hydrogen rich and carbon dioxide rich gases. This process uses H₂O (steam) instead of air or oxygen for gasification, and thereby produces high value nitrogen free product gas. An important feature of this process is in-process removal of carbon dioxide from the reaction site by CaO. This allows the reaction to move towards higher yield of hydrogen. Circulating fluidized bed (CFB) provides an ideal reactor configuration for such a looping reaction. A CFB based CLG unit operates somewhat similar to the FCC reactor except that the bubbling bed in the loopseal serves as the gasifier where calcined limestone absorbs carbon dioxide forming calcium carbonate. The riser works as the regenerator of CaCO₃, the CO₂ sorbent. Thus, the sorbent particles move back and forth between the riser calciner and loopseal carbonizer. To study this process closely and to determine how well the sorbent retains its reactivity through such a cyclical process, an experiment was carried out in a Quartz wool matrix reactor (QWM), which closely simulates the highly expanded ambience of a fast-fluidized bed. An empirical relation was developed for the conversion of calcium carbonate (CaCO₃) as a function of temperature and residence time. A simple reaction kinetic model for calcination in presence of N₂, CO₂ and H₂O has been developed and compared. Loss in effectiveness of the sorbent has been studied and another empirical relation was developed for the estimation of extent of carbonation with the number of cycle.

INTRODUCTION

Chemical looping gasification (CLG) is an innovative approach for production of hydrogen-rich gas with in-process capture and regeneration of carbon dioxide. It consists of two fluidized bed reactors, one operating as a gasifier in bubbling bed mode, and another as a regenerator in fast fluidized bed regime, together forming a circulating fluidized bed reactor. Calcium oxide (CaO) is used as the sorbent in the gasifier. It absorbs the carbon dioxide produced during gasification and is subsequently regenerated in the regenerator. Thus, from the gasifier a CO₂ free hydrogen-rich gas is obtained while from the regenerator, a relatively pure stream of carbon dioxide is produced that can be taken directly for sequestration or other value added use thus avoiding the cost and efficiency penalty for post capture. The main focus of this paper will be on the study of regeneration behaviour of calcium carbonate.

The calcination reaction ($\text{CaCO}_3 = \text{CaO} + \text{CO}_2 + 183 \text{ kJ/mol}$) is highly endothermic in nature. Also its capacity for regeneration of CaO depends on the fluidizing medium in the fast fluidized bed. The fluidizing medium in the riser for the study was chosen to

be carbon dioxide because the CFB riser is to use a part of the CO_2 produced (Acharya et al, 2009). The partial pressure of carbon dioxide in this case will naturally be very high, and it might be above the equilibrium pressure of CO_2 for calcination. Therefore, one would expect a very low regeneration of the sorbent, CaO . This necessitates an alternative medium that could not be air due to potential nitrogen-dilution of the product gas from the nitrogen in air. So, steam is identified as the next best and yet inexpensive fluidizing medium.

The main objective of this research is to determine the level of regeneration with nitrogen (N_2), carbon dioxide (CO_2) and steam (H_2O) as the fluidizing medium and compare them. Ideally the work should be done in a fast-fluidized bed, but it is extremely difficult to follow the calcination process while the particles are constantly moving around the CFB loop. Standard Thermo Gravimetric (TGA) test is more representative of a fixed bed than of a fast bed reactor. Fast bed reactor is characterized by it is highly expanded bed, where reacting particles are widely apart. For this reason experiments were done in the quartz wool matrix reactor developed by Wu and Basu (1993), where particles were dispersed on a quartz wool matrix with a voidage similar to that of a fast bed. The gas velocity was adjusted to represent the gas-solid slip velocity in a fast bed. Thus, this closely simulates the reaction in the riser of a CFB. A reaction kinetic model was developed for calcination in three different mediums. The comparisons of different medium were made on the basis of activation energy and the reaction rate constant. The results obtained could provide a basis for the choice of fluidizing medium for the regenerator in a chemical looping gasification system. In a CFB-CLG reactor the sorbent will continuously move back and forth between the gasifier and the regenerator undergoing calcination and carbonation. So, the calcination-carbonation cycle was studied to identify the loss in activity of sorbent over different cycle. This will help to identify the requirement of fresh sorbent into the system.

EXPERIMENTAL SETUP

The quartz wool matrix reactor comprises a stainless steel reactor of 50 mm internal diameter heated externally by electric heaters (Fig 1). A precision electronic balance sits at the top of the reactor. Temperature was measured at three different locations of the reactor with K type thermocouple. Data from the balance, thermocouple and all flow meters were recorded by a data acquisition system. Reactor was heated to the desired temperature and then the gas was supplied from the bottom of the reactor. Flow of gas, (or gas mixtures) going into the reactor was measured by electronic regulating type flow meters. A measured weight of calcium carbonate of size 45 micron was sprinkled over and inside the quartz wool that was placed inside a wire basket suspended on the balance. The particle size was deliberately chosen small to reduce the mass transfer effect as well as to make sure that the particle size was significantly smaller than the reactor size. Once the system was stabilized and a constant temperature in the reactor was noted, the basket with quartz wool and calcium carbonate was lowered into the reactor. The change in mass of the sample was measured continuously. After allowing the reaction (calcination and carbonation) for 30 minutes it was taken out, cooled and was weighted.

After calcination for 30 min, the sample was moved out into a cooler ambient to quench the calcination reaction. Thereafter, the medium in the QWM was changed to carbon dioxide and the temperature of reactor was reduced to 650°C. Once the temperature drops to 650°C, the previously calcined sample was lowered into the reactor, and was left there for another 30 min for carbonation. Thus the sample undergoes alternative calcination and carbonation. It is repeated for 5 cycles of calcination and carbonation.

The calcination reaction ($\text{CaCO}_3 = \text{CaO} + \text{CO}_2$) was studied at four temperatures: 800°C, 900°C, 950°C and 1000°C for each of the three media, CO_2 , H_2O and N_2 . The carbonation reaction ($\text{CaO} + \text{CO}_2 = \text{CaCO}_3$) in a biomass gasifier generally takes place at a relatively lower temperature in a CLG. So, in QWM reactor, the carbonation was studied at 650°C with CO_2 alone. Experiments in CO_2 alone ensure that complete conversion of calcium oxide. Any loss in conversion over consecutive cycle could occur due to sintering of the particle.

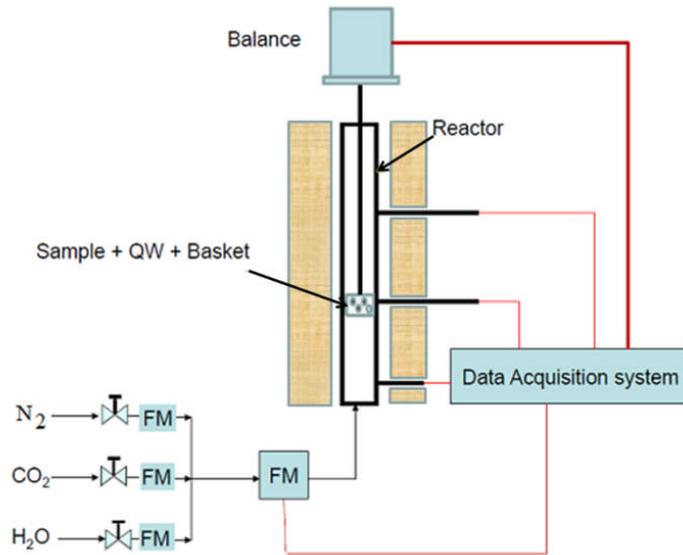


Figure 1: Schematic of QWM experimental setup

To examine the kinetics of calcination as well as to compare the rate for three media a first order reaction kinetic model was used.

$$\frac{dX}{dt} = K \frac{(1-X)(P_{eq} - P_{CO_2})}{P_{eq}} \quad (1)$$

$$K = k_0 e^{-\frac{E_a}{RT}}$$

$$X = \left(\frac{W_u - W_t}{W_o} \right) \times \left(\frac{100}{44} \right)$$

$$P_{eq} = 4.137 \times 10^7 e^{-\frac{23474}{T}} \quad (\text{Stanmore and Gilot, 2005})$$

Where, K = intrinsic rate constant (s^{-1}), X = conversion (-), P_{eq} = equilibrium decomposition pressure (atm), P_{CO_2} = partial pressure of CO_2 (atm), k_0 = reaction rate constant (s^{-1}), E_a = activation energy (kJ/mol), R = universal gas constant

(kJ/mol K), T = temperature (K), W_o = initial weight of calcium carbonate (gm), W_t = weight of calcium carbonate after time t (gm).

RESULTS AND DISCUSSION

Effect of Temperature and Residence Time on Calcination

Table 1 shows the results of calcination at different temperatures in presence of three different media. A conversion greater than 99% was obtained at 900°C in a N₂ environment in 12.5 min. The same level of conversion was obtained in a shorter time if the temperature increased to 950°C. In CO₂ environment this conversion at 900°C was only 72.89%. Even at 1000°C the maximum conversion was 92.95% in 30 min. A higher partial pressure of CO₂, close to the equilibrium decomposition pressure would inhibit the calcination reaction. Therefore at such high CO₂ partial pressure the conversion is much lower even at very high temperatures. With steam, complete conversion was obtained in shorter residence time of 10 min at a temperature of 1000°C.

Table 1: Calcination obtained during calcination under three different mediums

Temperature (°C)	N ₂		CO ₂		H ₂ O	
	Conversion (%)	Time (mins)	Conversion (%)	Time (mins)	Conversion (%)	Time (mins)
600					8.78	30
700	52.29	30			73.22	30
800	96.32	25.50	7.58	30	96.94	30
900	99.39	12.5	20	30	100	25
950	99.31	10	72.89	30	100	19.16
1000	100	10	92.95	30	100	10

Supply of N₂ and steam quickly removes carbon dioxide from the system, thus lowering its partial pressure resulting in higher conversion. However, steam offers higher conversion than N₂. At 700°C, 73.22% conversion was obtained which was 28% more than that obtained with N₂ at the same temperature. Steam seems to have a catalytic effect that lowers the equilibrium decomposition temperature for calcination reaction to occur, thus conversion has been complete even at very low temperature. Wang and Thompson (1995) found that the surface adsorption of H₂O molecules weakens the CaO-CO₂ bond resulting in enhanced calcination rates. Iyer et al (2005) attributed this phenomenon to higher gas-solid heat transfer properties of steam. Therefore the calcination obtained was much higher with steam.

The calcination with steam can occur at a lower temperature, but it needs longer residence time. As shown in Fig 6, it will take a long time to achieve full conversion with CO₂ as medium, while it takes 10 min with N₂ and 19 min with steam at 950°C. Therefore, to study the combined effect of temperature and residence time, a linear regression model was developed.

The fractional conversion of CaCO₃, X is expressed empirically as a function of temperature θ and time τ .

For H₂O:

$$X = -1627 + 1.68 \theta + 46.1 \tau - 0.0416 \theta \tau \quad [R^2 = 88.8\%] \quad (2)$$

For CO₂:

$$X = -359 + 0.446 \theta \quad [R^2 = 79.3\%] \quad (3)$$

For N₂:

$$X = 186 - 0.126 \theta - 14.6 \tau + 0.0188 \theta \tau \quad [R^2 = 99.1\%] \quad (4)$$

Here, θ = Temperature (°C), τ = time (min) and X = conversion of CaCO₃ (%).

From Table 1 it is apparent that the conversion of CaCO₃ in presence of H₂O reduces with reduction in temperature, but there was a sharp order of magnitude drop in conversion when the temperature drops from 700°C to 600°C. Reasons for this large reduction below 700°C could not be explained at this time.

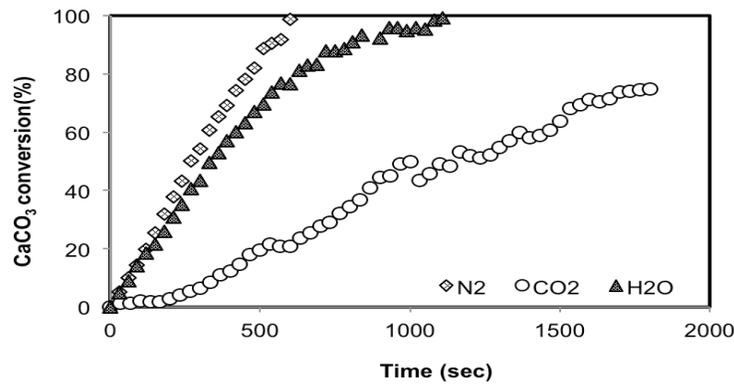


Figure 2: Calcination obtained with time at T = 950°C for three different media

Kinetics of Calcination

The intrinsic rate constant (Eq. 1) for calcination was calculated at each temperature and by the use of the Arrhenius plot; the activation energy was determined. The activation energy and the reaction rate constant for the calcination reaction occurring in presence of three media is shown in Table 2.

Table 2: Kinetics of calcination under three different media

	N ₂	CO ₂	H ₂ O
E_a (kJ/mol)	257.78	180.56	248.62
k_o (1/s)	4.82×10^{10}	2.12×10^6	3.63×10^{10}

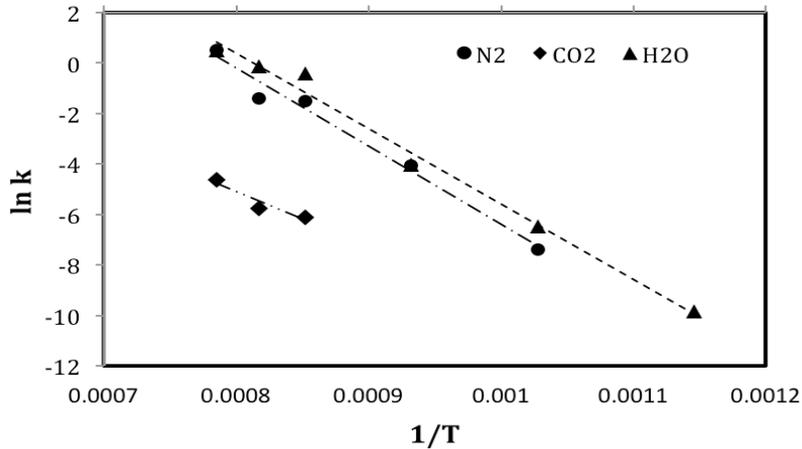


Figure 3: Arrhenius plot for calcination done in presence of three medium

Fig 3 shows the comparison of reaction kinetics in presence of different media. it suggests that the kinetic rate in presence of steam is closer to that in presence of nitrogen. On the other hand for CO₂ the kinetics rates are significantly lower.

Calcination and Carbonation Reaction Cycle

In a chemical looping system, the sorbent (CaO) undergoes through number of calcination-carbonation cycle and with each cycle its performance decrease. This could occur due to sintering and deposition of tar/char on sorbent particles. The change in percentage of CaO in the sorbent particle during calcination-carbonation cycle is plotted against time in Fig 4. Calcination occurred in presence of N₂, CO₂ or H₂O while carbonation in CO₂.

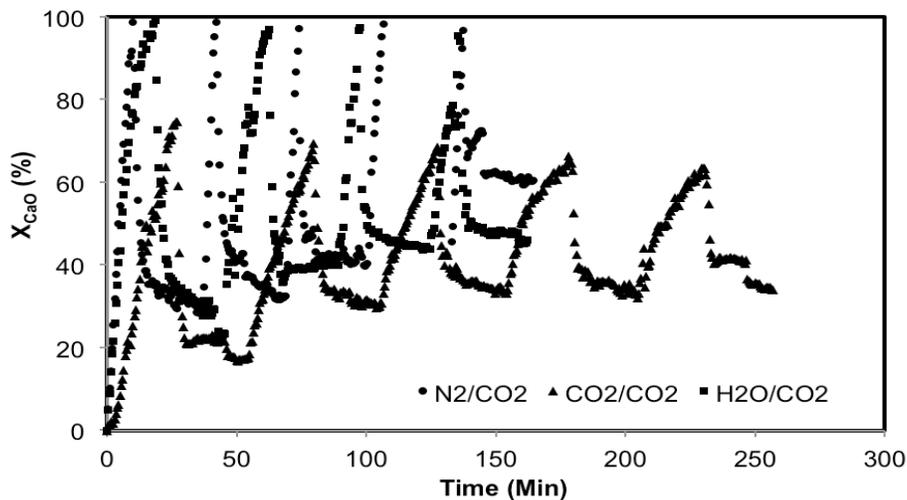


Figure 4: Calcination-carbonation cycle

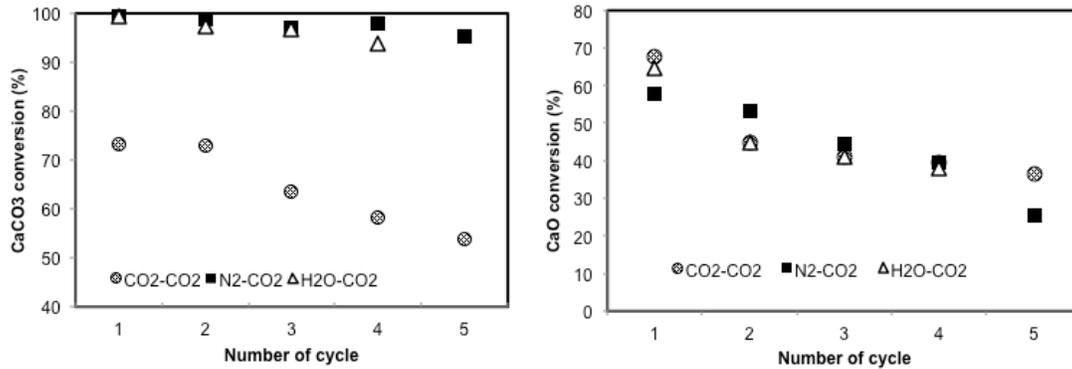


Figure 5: Calcination and carbonation conversion obtained at the end of each cycle

Fig 5 shows the total conversion obtained at end of each calcination and carbonation cycle studied. Calcination in presence of steam and N₂ shows nearly complete conversion at the first cycle studied and then drops slightly for latter cycles. In presence of CO₂, the conversion was only partial even for the first cycle and drops quickly in the subsequent cycle.

The carbonation study shows that irrespective of the medium used for calcination, the ability of the sorbent CaO to capture carbon dioxide decreases with number of cycle. Stanmore and Gilot (2005) inferred that in high temperature calcination, the calcium particles sinters leading to decrease in porosity and surface area compounded by the pore closure due to carbonation (due to difference in molar volume of CaO and CaCO₃) resulting in loss of conversion. Thus to quantify this loss in ability of the sorbent to capture CO₂, an empirical relation was developed between the conversion, X_{CaO} obtained and the number of cycle, N .

$$X_{CaO} = - 18.63 \ln (N) + 62.598 \quad (5)$$

Using this relation one can estimate the frequency at which the fresh sorbent needs to be charged into a CFB based chemical looping gasifier. Limitation of this empirical relation is that it only includes the effect of high temperature sintering phenomenon but does not include other effects that may influence in a commercial chemical looping gasification system. The deposition of tar and carbon on the sorbent are examples of such inhibiting factors. These can only be studied in the real chemical looping gasification system.

CONCLUSION

The study on calcination of CaCO₃ in presence of different media shows that the calcination shown in presence of H₂O is similar to that in N₂. The kinetic of calcination in N₂ and H₂O are much higher than that for CO₂. Compared to other media steam offer higher conversion at a relatively low temperature. Thus steam reduces the energy requirement of calcination, which may partially offset the energy required to produce the additional steam.

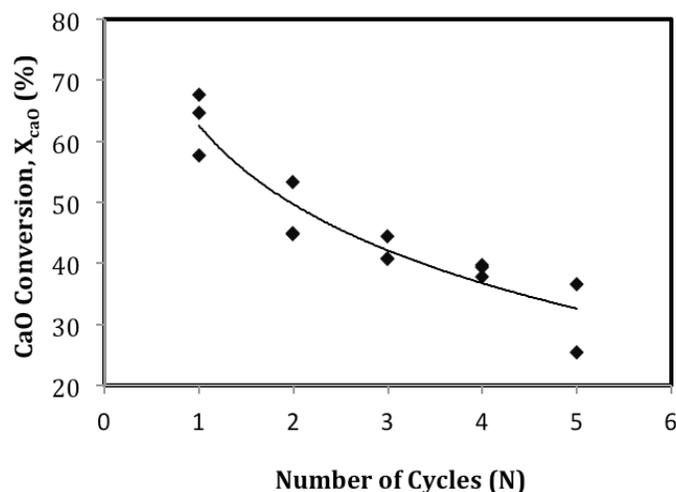


Figure 6: Conversion obtained during carbonation with number of cycles

Considering this and the potential dilution of the product gas with N_2 , steam could be the best medium in the riser in a chemical looping gasification system. However one can expect a lower conversion in a large chemical looping CFB system than that obtained in the present bench scale study. Therefore, a study on calcination-carbonation looping cycle in a pilot lab scale chemical looping gasification plant is underway.

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