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COMPARISON OF SODIUM AND POTASSIUM CARBONATES AS LITHIUM ZIRCONATE MODIFIERS FOR HIGH-TEMPERATURE CARBON DIOXIDE CAPTURE FROM BIOMASS-DERIVED SYNTHESIS GAS

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ABSTRACT

The process of gasification converts biomass into synthesis gas (syngas), which can be used to produce biofuels. Solid-phase sorbents were investigated for the removal of CO_2 from a N_2/CO_2 gas stream using a CO_2 concentration similar to that found in a biomass gasification process. During the gasifying process, large amounts of carbon dioxide (CO_2) are created along with the syngas. The produced CO_2 must be removed before the syngas can be used for fuel synthesis and to avoid the possible formation of unwanted byproducts. A thermogravimetric analyzer was used to test the CO_2 absorption rates of sorbents composed of lithium zirconate (Li_2ZrO_3), as well as mixtures of Li_2ZrO_3 with potassium carbonate (K_2CO_3) and sodium carbonate (Na_2CO_3). The experimental results show that Li_2ZrO_3 has a low absorption rate, but sorbents containing combinations of Li_2ZrO_3 and the K_2CO_3 and Na_2CO_3 additives have high uptake rates. Using different proportions of K_2CO_3 and Na_2CO_3 produces varying uptake rates, so an optimization experiment was performed to obtain an improved sorbent. The CO_2 absorption and regeneration stability of the solid-phase sorbents were also examined. A sorbent composed of Li_2ZrO_3 and 12.1 weight % Na_2CO_3 was shown to be stable, based on the consistent CO_2 uptake rates. Sorbents prepared with Li_2ZrO_3, 17.6 weight % K_2CO_3 and 18.1 weight % Na_2CO_3 showed instability during regeneration cycles in air at 800 °C. Sorbent stability improved during regeneration cycles at 700 °C. Further testing of the Li_2ZrO_3 sorbent under actual syngas conditions, including higher pressure and composition, should be done. Once the optimum sorbent has been found, a suitable support will be needed to use the sorbent in an actual reactor.

INTRODUCTION

High energy and transportation costs have increased interest in the thermochemical conversion of biomass into biofuels. Biomass is converted through the processes of gasification, the water-gas shift reaction ($CO+H_2O \leftrightarrow CO_2+H_2$), and synthesis reactions to liquid fuels. Each of these processes produces carbon dioxide (CO_2) which can negatively impact the system operation. The surplus CO_2 continues through such processes, requiring additional equipment and energy to process. For some synthesis catalysts, excess CO_2 affects the fuel synthesis chemistry. High levels of CO_2 can be an inhibitor to certain synthesis catalysts, reducing the rate of reaction and producing unwanted byproducts. Therefore, it is usually necessary to remove CO_2 from the process to achieve acceptable concentrations of desirable products in the syngas [1].

A common method for removing CO_2 is the use of an aqueous amine scrubbing system. Although the amine absorption system is typical, it is quite expensive. The chemical absorption process requires the alkanolamine absorbent to be in a liquid phase aqueous solution; the amine liquids are mixed with water to produce specific concentrations that work best under different operating conditions. Once the CO_2 is absorbed into the aqueous amine mixture, it is released in another location by increasing the temperature and decreasing the pressure. This process is energy intensive because the aqueous amine must undergo a phase change from liquid to vapor. Due to water's large heat of vaporization, a significant amount of heat is required for it to boil [2]. This energy expense is the source of a large penalty on process efficiency.

In recent years, there has been an increase in research of solid-phase sorbents for CO_2 capture from flue gases. Researchers have done experiments on numerous types of sorbents to determine whether using solid sorbents is a plausible and economical way of removing CO_2 from fossil fuel plants' emissions. However, the syngas stream in a syngas-to-fuel process is significantly different than combustion flue gases; syngas has essentially no oxygen (O_2) and very little nitrogen (N_2), and may be at a higher pressure depending on the location in the process from which it is removed. Thus, sorbents shown to be appropriate in flue gas studies may not be effective under syngas conditions.

The use of lithium zirconate (Li_2ZrO_3) as a CO_2 sorbent is becoming increasingly popular. This is due to the high selectivity between CO_2 and N_2, as well as the relatively low regeneration temperature. Ida, et al. [3] obtained positive results after testing several Li_2ZrO_3-based variations under diverse flue gas conditions. It was found that a mixture of Li_2ZrO_3 and potassium carbonate (K_2CO_3) had better sorption properties than Li_2ZrO_3. They concluded that the formation of a lithium carbonate (Li_2CO_3)/K_2CO_3 eutectic liquid improved the diffusion rate of CO_2 from the particle surface to an inner core of Li_2ZrO_3 that becomes increasingly separated from the surface by a shell of ZrO_2 that forms concomitantly with Li_2CO_3 formation.

In our study, several pure and modified Li_2ZrO_3-based sorbents were prepared to test CO_2 sorption performance under typical syngas conditions (excluding higher pressures). The sorption experiments were conducted in a thermogravimetric analyzer at diverse conditions, depending on the sorbent. The performance of each sorbent was based on the rate of sorption for the first 20 minutes of an uptake cycle.

MATERIALS AND METHODS

Each sorbent's ability to uptake CO_2 was tested using a Cahn TG-131 thermogravimetric analyzer (TGA). Each sorbent was placed in the TGA and tested at distinct conditions which influence the overall uptake or release of CO_2 within the sample. The uptake of CO_2 was based on the change in mass of the sample during the experiment. The mass changes were assumed to only be the gain or loss of CO_2 from the sample and the uptake rates for the first 20 minutes of an uptake cycle were reported.

The sorbents that were tested were Li_2ZrO_3, Li_2ZrO_3 doped with potassium carbonate (K_2CO_3), Li_2ZrO_3 doped with sodium carbonate (Na_2CO_3) and Li_2ZrO_3 doped with varying ratios of both additives.

Sorbent Preparation

The following sorbent preparations were based on procedures discussed by Pannocchia et al. [4]. Li_2ZrO_3 was made by combining 99+% A.C.S. reagent grade Li_2CO_3 (from Sigma-Aldrich), and 99% metals basis ZrO_2 (from Aldrich), in a 1:1 molar ratio in accordance with the equation:

$$Li_2CO_3 + ZrO_2 \leftrightarrow Li_2ZrO_3 + CO_2 \tag{1}$$

Enough acetone to make a slurry was mixed in to allow for a more even distribution of the compounds; the mixture was then calcined in air for 6 hours at 850 °C. The temperature increase and decrease rates were 1 °C/min. After calcination, the mixture was ground into a powder and collected for later use.

Two methods were used to dope Li_2ZrO_3 with K_2CO_3.

Method 1: anhydrous K_2CO_3 (from J.T. Baker) was ground into a powder using an agate mortar. The K_2CO_3 was mixed with specified amounts of Li_2CO_3 and ZrO_2. The molar ratios used were taken from the following equation.

$$\begin{aligned}1.1Li_2CO_3 + 1.0ZrO_2 + 0.2K_2CO_3 \leftrightarrow 1.0Li_2ZrO_3 \\ + 0.1Li_2CO_3 + 0.2K_2CO_3 + CO_2\end{aligned} \tag{2}$$

The doped mixture was prepared using the same procedure as described for Li_2ZrO_3.

Method 2: Li_2ZrO_3 was made using the initial method, but with the molar ratio changed to 1.1:1.0 moles of Li_2CO_3 to ZrO_2. After the calcination process, the Li_2ZrO_3 was ground and weighed. The quantity of K_2CO_3 needed to give 1.1:1.0:0.2 molar ratio was calculated, and the correct amount of K_2CO_3 was mixed in with the Li_2ZrO_3.

The sample of Li_2ZrO_3 doped with Na_2CO_3 was prepared via method 2, exchanging K_2CO_3 with Na_2CO_3.

The samples containing both K_2CO_3 and Na_2CO_3 were made using method 2. The foundation of each sample was 1 g of Li_2ZrO_3, and the relative amounts of each additive were based on weight ratios rather than molar ratios.

Experimental Procedure

Each initial sorbent sample was tested at various conditions (Table 1). This allowed for the observation of varying affects that each set of conditions would have on the sorbent and established a set method for future testing.

To determine the optimum ratio of K_2CO_3 and Na_2CO_3 for CO_2 absorption, a fixed method was used (Table 2). The sorbent samples tested had a mass of approximately 95 mg. The sorbents were heated in a CO_2/N_2 gas mixture to 800 °C at a ramp of 15 °C per minute, and held there for ten minutes. The gas mixture consisted of 15% CO_2 and 85% N_2 by volume, flowing at a rate of 80 sccm. This initial heating in CO_2/N_2 ensured that the creation of a eutectic phase was achieved for each mixture, as will be discussed later. After ten minutes, the gas was switched to air for 20 minutes. The sorbent was cooled at a rate of 15 °C per minute to 550 °C. At 550 °C the CO_2/N_2 mixture was turned back on, and the sample was held isothermal for 30 minutes. At this point, the air replaced the CO_2/N_2 mixture and the sample was heated back to 800 °C at a rate of 10 °C per minute where it was held for 30 minutes. At

	Initial Ramp to 800 °C	Ramp to 550 °C	Isothermal 550 °C	Ramp to 800 °C	Cool to Room Temp
pure Li_2ZrO_3	air	N_2	CO_2/N_2	N_2	N_2
Li_2ZrO_3 w/calcined K_2CO_3	N/A	N_2	CO_2/N_2	N_2	N_2
Li_2ZrO_3 w/mixed K_2CO_3	N/A	N_2	CO_2/N_2	CO_2/N_2	N_2
Li_2ZrO_3 w/mixed Na_2CO_3	CO_2/N_2	CO_2/N_2	CO_2/N_2	CO_2/N_2	CO_2/N_2

Table 1. Gas flows used during each segment during the initial sorbent sample testing. n/a: Not available

	Description	Gas Mixture	Ramp rate (°C/min)	Final Temp (°C)	Time (min)
1	sorbent heated	CO_2/N_2	15	800	N/A
2	sorbent held at isothermal temp	CO_2/N_2	N/A	800	10
3	sorbent held at isothermal temp	air	N/A	800	20
4*	sorbent cooled	air	15	550	N/A
5*	sorbent held at isothermal temp	CO_2/N_2	N/A	550	30
6*	sorbent heated	air	10	800	N/A
7*	sorbent held at isothermal temp	air	N/A	800	30
8*	sorbent cooled	air	10	550	N/A
9	sorbent cooled	air	10	room temp	N/A

Table 2. Method segments for testing the optimization samples. n/a: Not available *Segment repeated 3 times

the end of 30 minutes the sample was cooled to 550 °C at a rate of 10 °C per minute. This cycle was repeated three times (not including the initial heating to 800 °C in the CO_2/N_2 mixture). After the final period at 800 °C, the sample was cooled in air to room temperature.

Several experiments were run to test the stability of the sorbents during continuous CO_2 absorption and regeneration (Tables 3 and 4). The Li_2ZrO_3+Na_2CO_3 sample underwent multiple cycles of CO_2 absorption and desorption. The sorbent was heated in air at a rate of 10 °C per minute to a temperature of 700 °C, where it was held in air for 60 minutes. It was then cooled at 10 °C per minute to 550 °C. At this point, the CO_2/N_2 gas mixture replaced air and the sorbent was held isothermally for one hour. The sample was then heated in air to 700 °C and was held there for 1.5 hours; after which time, it was cooled to 550 °C. This cycle was repeated fourteen times (excluding the initial temperature ramp), and after the final cycle, the sorbent was cooled to room temperature.

The method for testing sorbent regenerability was generally the same as the method for testing optimization (Table 2). All of the gas flows and holding times remained constant, however the

	Description	Gas Mixture	Ramp rate (°C/min)	Final Temp (°C)	Time (min)
1	sorbent heated	air	10	700	N/A
2	sorbent held at isothermal temp	air	N/A	700	60
3*	sorbent cooled	air	10	550	N/A
4*	sorbent held at isothermal temp	CO_2/N_2	N/A	550	60
5*	sorbent heated	air	10	700	N/A
6*	sorbent held at isothermal temp	air	N/A	700	90
7*	sorbent cooled	air	10	550	N/A
8	sorbent cooled	air	10	room temp	N/A

Table 3. Method segments for testing Li_2ZrO_3+Na_2CO_3 regenerability. n/a: Not available *Segment repeated 14 times

	Description	Gas Mixture	Ramp Rate (°C/min)	Final Temp (°C)	Time (min)
1	sorbent heated	CO_2/N_2	15	800	N/A
2	sorbent held at isothermal temp	CO_2/N_2	N/A	800	30
3*	sorbent cooled	air	15	550	N/A
4*	sorbent held at isothermal temp	CO_2/N_2	N/A	550	30
5*	sorbent heated	air	10	750	N/A
6*	sorbent held at isothermal temp	air	N/A	750	30
23**	sorbent cooled	air	10	550	N/A
24**	sorbent held at isothermal temp	CO_2/N_2	N/A	550	30
25**	sorbent heated	air	10	800	N/A
26**	sorbent held at isothermal temp	air	N/A	800	30
27**	sorbent cooled	air	10	550	N/A
28	sorbent cooled	air	10	room temp	N/A

Table 4. Method segments for testing sorbent regenerability. n/a: Not available *Segment repeated at the respective regeneration temperatures: 760, 770, 780, 790 **Segment repeated 6 times

different regeneration temperatures were used and the number of cycles was increased to 11. After the initial heating to 800 °C, the regeneration temperatures were 750 °C, 760 °C, 770 °C, 780 °C, 790 °C and 800 °C respectively. The remainder of the experiment retained 800 °C as the regeneration temperature.

Results and Discussion

Preliminary Samples

Figure 1a shows the CO_2 uptake curve for Li_2ZrO_3. The CO_2 uptake over the first 20 minutes of sorption is quite low, the rate being 7.08×10^{-3} mg CO_2/mg sorbent·h. These results are consistent with values reported by Pannocchia et al. In that study, it was shown that Li_2ZrO_3 had a low uptake rate, and the CO_2 uptake decreased significantly as time progressed [4].

Figure 1b shows the CO_2 uptake curve for the sorbent Li_2ZrO_3+K_2CO_3 sample made via method 1. The CO_2 uptake was 2.18×10^{-3} mg CO_2/mg sorbent·h. There is no definitive conclusion for why the uptake rate was lower for this sample, but it is known from catalyst synthesis that the method of preparation can affect catalyst performance [5].

The CO_2 uptake curve for the sorbent sample of Li_2ZrO_3+K_2CO_3 that was prepared using method 2 is shown in Figure 1c. The CO_2 uptake rate for this sorbent is 7.24×10^{-2} mg CO_2/mg sorbent·h for the first 20 minutes of absorption. This rate is an order of magnitude larger than that of Li_2ZrO_3 and can be attributed to Li_2CO_3 and K_2CO_3 forming a eutectic liquid. These results can also be seen in other research [3].

Since a combination of Li_2CO_3 and K_2CO_3 increased the CO_2 absorption rate, it was decided that Na_2CO_3 should be tested as an additive to Li_2ZrO_3. This Li_2ZrO_3+Na_2CO_3 sorbent sample was prepared using method 2 as this was the method that had given better results with K_2CO_3. The uptake curve can be seen in Figure 1d. The CO_2 uptake rate was 1.70×10^{-1} mg CO_2/mg sorbent·h. This uptake rate was two orders of magnitude higher than that of the Li_2ZrO_3. For a comparison of the rates, see Figure 2.

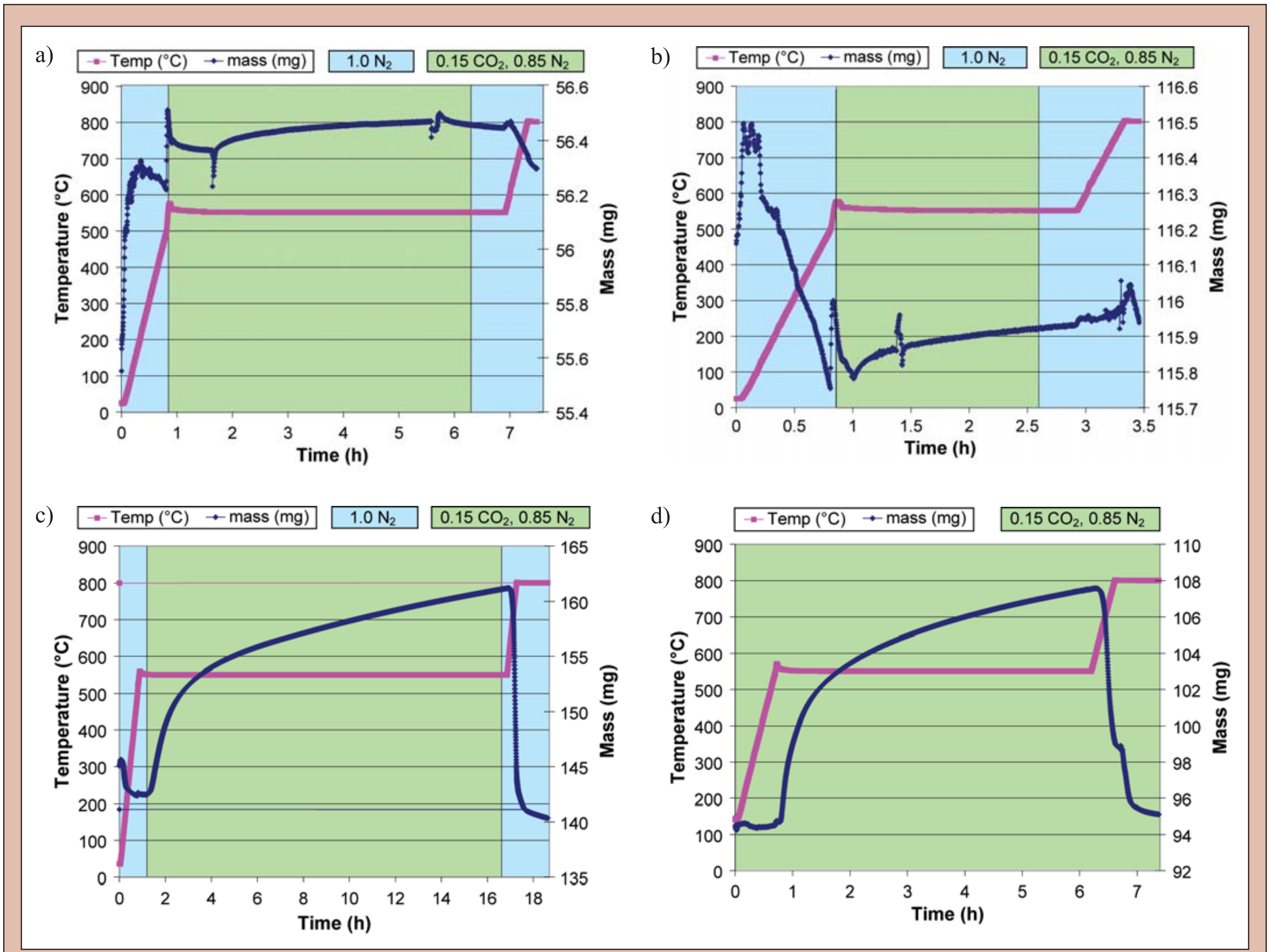

Figure 1. CO_2 uptake profiles from various Li_2ZrO_3 and additive combinations. Note that the gas compositions are given in fractions. a) Representative graph of mass and temperature versus time for CO_2 uptake for Li_2ZrO_3 without additives; b) representative graph of mass and temperature versus time for CO_2 uptake with Li_2ZrO_3 and K_2CO_3 mixture prepared by method 1; c) representative graph of mass and temperature versus time for CO_2 uptake with Li_2ZrO_3 and K_2CO_3 mixture prepared by method 2; d) representative graph of mass and temperature versus time for CO_2 uptake with Li_2ZrO_3 and Na_2CO_3 mixture prepared by method 2.

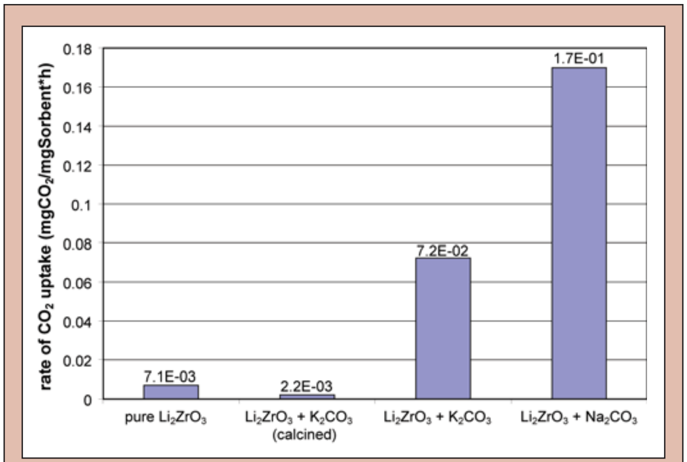

Figure 2. CO_2 uptake rates of the preliminary sorbent samples at conditions shown in Table 1.

Optimization Experiments

The addition of both K_2CO_3 and Na_2CO_3 resulted in an increase in the uptake rate of CO_2. It was decided that experiments should be run to see if there is a ratio of K_2CO_3 to Na_2CO_3 that would give a maximum uptake rate. The foundation for each sorbent sample was 1 g of Li_2ZrO_3, and varying quantities of K_2CO_3 and Na_2CO_3 were added. The quantity of either additive was determined using a sequential simplex optimization method [6]. The optimization was based on the weights of each additive and the objective function was the average uptake rate over the first 20 minutes of absorption. The preliminary experiments showed that a small amount of either additive would increase the uptake rate of CO_2. To set a basis for the optimization experiment, two samples were made using either K_2CO_3 or Na_2CO_3 only, both of which were large quantities when compared to the preliminary samples. Sample 1, containing approximately 0.5 g of K_2CO_3, had a CO_2 uptake rate of 9.72×10^{-3} mg CO_2/mg sorbent·h. Sample 2, containing approximately 0.5 g of Na_2CO_3, had a CO_2 uptake rate of 2.17×10^{-2} mg CO_2/mg sorbent·h. A total of 17 mixtures were tested with results shown in Figure 3a. Sample 13, composed of 0.9998 g Li_2ZrO_3, 0.1887 g K_2CO_3 and 0.1742 g Na_2CO_3, gave the best results, with an uptake rate of 1.956×10^{-1} mg CO_2/mg sorbent·h. Unfortunately, the optimization study had to be terminated prematurely due to time constraints, so further testing needs to be done in order to determine if this is the best possible mixture.

Note that both samples 1 and 2 have lower uptake rates than the preliminary test samples containing lesser amount of K_2CO_3 or Na_2CO_3 added to Li_2ZrO_3, demonstrating that the quantity of each compound added to the Li_2ZrO_3 base has a direct affect on the uptake rate. Figure 3b shows weight fractions of each additive contained in the optimization samples and the respective rates of CO_2 uptake.

A significant loss of mass from the sorbent was seen during some of the tests. During the regeneration cycles, the sorbent lost more mass than it gained during the absorption of CO_2; this can be seen in Figure 4. Pannocchia et al. hypothesized that at high temperatures, potassium in the sorbent is oxidized while in air and is released from the sample [4]. Regeneration in N_2 showed no weight loss at 800 °C.

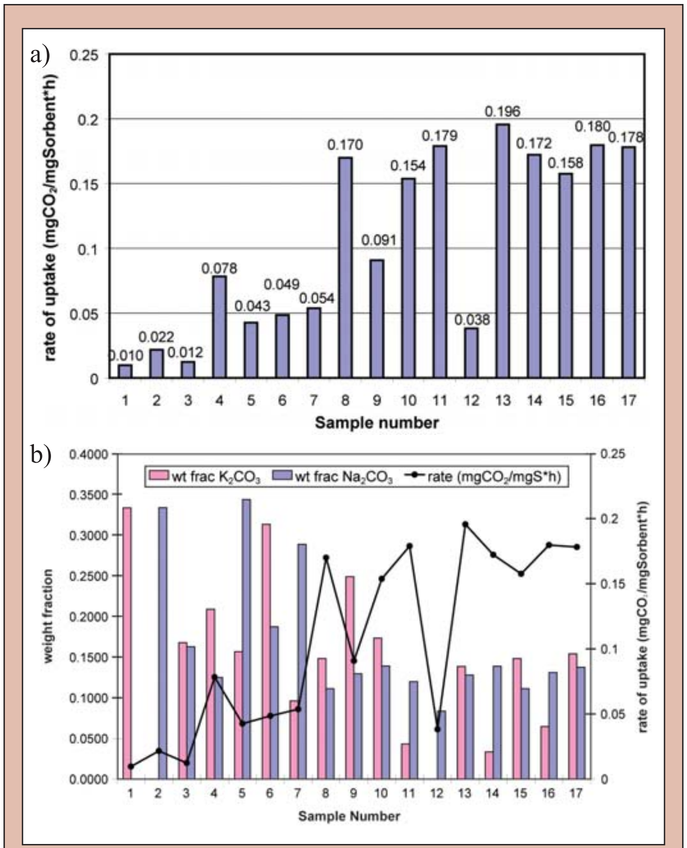

Figure 3. a) CO_2 uptake rates for the optimization samples; b) weight fractions of K_2CO_3 and Na_2CO_3 and the respective CO_2 uptake rates.

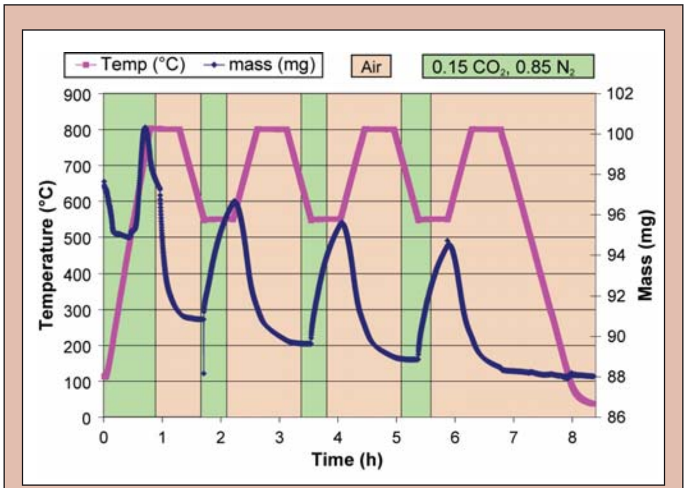

Figure 4. Mass loss during regeneration cycle of optimization sample 10.

Regeneration Experiments

The preliminary sample containing Na_2CO_3 and sample 13 from the optimization samples were tested for CO_2 uptake stability.

Over the course of 14 cycles, the Li_2ZrO_3+Na_2CO_3 sample showed steady CO_2 uptake and release. The uptake rate for the first cycle was 1.37×10^{-1} mg CO_2/mg sorbent·h, and the uptake rate for the final cycle was 1.93×10^{-1} mg CO_2/mg sorbent·h. The final rate was 40% higher than that of the initial cycle. Since the absorption rate increased over time, the sample can be considered stable. See Figure 5 for the regeneration experiment results.

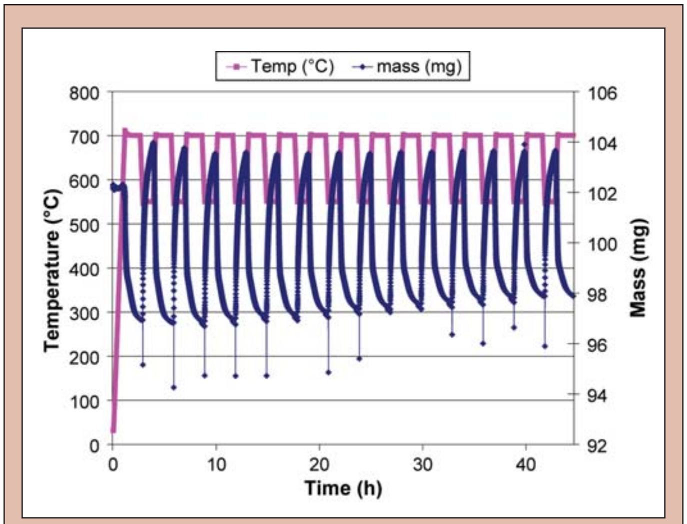

Figure 5. Regeneration experiment for Li_2ZrO_3+Na_2CO_3 sorbent.

As noted before, certain sorbents from the optimization samples lost significant amounts of mass while regenerating. A regeneration test was conducted on sample 13 from the optimization sample set. This test operated at various regeneration temperatures to determine if mass loss occurred at temperatures lower than 800 °C, and whether or not the uptake capacity remained constant. The sorbent lost noticeable amounts of mass despite the lower regeneration temperatures. Throughout the experiment, the absorption rate decreased, and at cycle 6 the absorption rate was significantly reduced. The absorption rate decreased for the remainder of the experiment. The initial uptake rate was 1.57×10^{-1} mg CO_2/mg sorbent·h; the rate at cycle 6 was 1.07×10^{-1} mg CO_2/mg sorbent·h; the final absorption rate was 9.43×10^{-2} mg CO_2/mg sorbent·h. The fluctuations of both the mass and absorption rates deem the sorbent to be unstable as shown in Figure 6. Although it appears to be temperature dependent, the reason for the steady drop in the mass and corresponding absorption rates has not been determined and will be the subject of a future study.

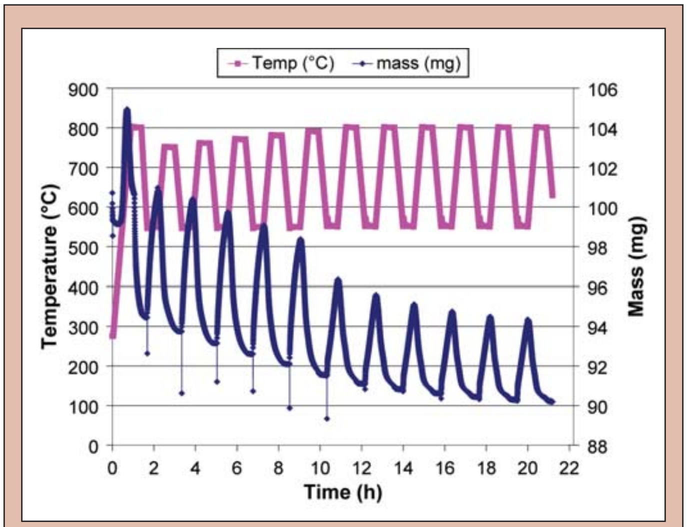

Figure 6. Regeneration experiment for optimum sample 13.

CONCLUSION

The objective of this study was to determine the CO_2 absorption rate of various Li_2ZrO_3-based sorbents. Li_2ZrO_3 has an infinite CO_2/N_2 selectivity, and has the ability to regenerate at relatively low temperatures, making it an excellent sorbent for CO_2 capture from complex gas streams. Li_2ZrO_3 had essentially a zero CO_2 uptake rate, but with the addition of K_2CO_3 and Na_2CO_3, the uptake rate increased significantly. It was also found that a mixture of both K_2CO_3 and Na_2CO_3 with Li_2ZrO_3 results in a larger uptake rate than either sorbent prepared with only one of the additives. Additionally, regenerability tests performed on one sorbent gave favorable results, allowing it to be considered stable. Sample 13 from the optimization study showed extensive mass loss when tested at high regeneration temperatures. Tests done at lower regeneration temperatures showed that significant mass loss still occurred at temperatures higher than 700 °C, but when regenerating at or below 700 °C, the sorbent stability remained constant. Future testing may resolve the mass and absorption rate decreases.

Testing of the Li_2ZrO_3 sorbent under real syngas conditions should be done in the future. These experiments would include testing the sorbent with gases comparable in composition with syngas, as well as introducing the sorbent to higher pressure. Once an optimum sorbent has been found, a support system that would be suitable for an actual reactor will be needed.

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