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MULTICYCLE PERFORMANCE OF A SINGLE-STEP PROCESS FOR H_2 PRODUCTION

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ABSTRACT

Combining the chemical reaction and product separation steps in a single processing vessel is currently of great interest. In this study, reaction and separation are combined by carrying out the water-gas shift reaction in the presence of a calcium-based CO_2 acceptor. The continuous removal of CO_2 from the gas phase alters the shift reaction equilibrium and permits almost complete CO conversion and CO_2 removal. The reaction temperature is significantly higher than employed in the traditional shift process, and, as a consequence, no shift catalyst is required.

Previously reported results showed that greater than 99% removal of total carbon oxides could be achieved over a range of experimental conditions with greater than 99.9% removal achieved at the most favorable conditions. Total carbon oxide content of the product gas in the latter case was approximately 30 ppmv (dry basis). However, for the process to be economical, it is necessary that the CO_2 acceptor retain its activity and capacity through a number of carbonation-calcination cycles. Results of multicycle tests in which dolomite precursor was cycled between the fully calcined (CaO + MgO) and half-calcined ($CaCO_3$ + MgO) forms are presented in this paper. Tests were carried out to investigate the effects of temperature, gas composition, and space velocity on multicycle performance. Greater than 99% carbon oxide removal was achieved in each cycle of an eleven-cycle test with only moderate deterioration in acceptor performance.

INTRODUCTION

In an effort to simplify chemical processing, the concept of combining the reaction and separation steps has received a great deal of recent emphasis. A number of approaches involving the selective removal of a product of a reversible reaction have been proposed. This selective product removal upsets the "normal" equilibrium and permits effectively complete conversion of the limiting reactant. Recent examples include the use of semi-permeable membranes for H_2

removal in the dehydrogenation of ethylbenzene(1), ethane(2), and methylcyclohexane(3), and the water-gas shift reaction(4). Similar results can be achieved, for example, by the preferential removal of product toluene during the dehydrogenation of methylcyclohexane via pressure swing adsorption(5).

Combining the water-gas shift reaction with continuous removal of CO_2 from the gas phase using a CO_2 acceptor provides an alternate method for producing H_2 in which effectively complete CO conversion is achieved in a single reaction step. At a temperature equal to or greater than 500°C, which is at least 150°C higher than normally used, a catalyst is not required for the shift reaction, and CO_2 will react rapidly with CaO as the acceptor. The important reactions are:

$$CO(g) + H_2O(g) \leftrightarrow CO_2(g) + H_2(g) \qquad (1)$$

$$CO_2(g) + CaO(s) \leftrightarrow CaCO_3(s) \qquad (2)$$

This basic concept was first described more than 60 years ago(6) and was later revised by Squires(7) but not pursued. In a recent study(8), a laboratory-scale fixed-bed reactor containing a calcium-based CO_2 acceptor was used to study the combined reactions as a function of shift/carbonation temperature and pressure, synthesis gas composition, space velocity, and the composition and properties of the acceptor. At 15 atm in the temperature range of 500 - 600°C and at space velocities as high as 3400 hr^{-1} (STP), equilibrium for the combined reactions was closely approached. Greater than 99.5% conversion of CO and removal of CO_2 was achieved, and the total carbon oxide concentration in the product gas was 400 ppm (dry basis) or less. At the most favorable conditions, the total carbon oxide concentration was reduced to about 30 ppm (dry basis). Even though calcined dolomite, the favored CO_2 acceptor, is widely available at low cost, it will be necessary for the acceptor to retain structural integrity and activity through numerous calcination-carbonation cycles if the process is to be economical. This paper examines the effect of reaction conditions on the multicycle behavior of the combined shift and carbonation reactions.

BACKGROUND

The potential advantages of the combined shift-carbonation process may be illustrated by thermochemical equilibrium analysis. For example, if a standard shift reactor is operated at 550°C with the synthesis gas feed containing 22% H_2, 8% CO_2,30% CO, and 40% H_2O, only about 56% of the CO may be reacted at equilibrium to yield a product which, after removal of CO_2 and excess H_2O, contains about 75% H_2. When the shift and carbonation reactions are combined at 550°C and 1 bar, the equilibrium conversion of CO increases to greater than 99%, and, if the combined reactions are carried out at 550°C and 25 bar, essentially 100% conversion of CO is possible, and the equilibrium concentrations of CO and CO_2 are reduced to about 80 and 50 ppm, respectively (both, dry basis). In current practice, the shift process is carried out at lower temperature and using a higher steam-to-CO ratio in order to achieve the higher fractional CO conversion required to produce high-purity hydrogen. Thus, the combined reactions offer the potential for reduced steam consumption in addition to process simplification.

The experimental study used a laboratory-scale fixed-bed reactor shown in Figure 1. A full description of the reactor and analytical systems has been published(8), and only a brief summary is presented here. Gaseous components of the synthesis gas feed were obtained from high-pressure cylinders, and flow rate was controlled using mass flow controllers. Water was added as a liquid using a high-pressure syringe pump; feed lines were heat traced to insure complete vaporization. Preheated synthesis gas flowed downward over the packed bed of CO_2 acceptor and exited through a condenser and back pressure regulator to the analytical train. Product gas composition was determined by gas chromatography using argon carrier gas and both thermal conductivity (TCD) and flame ionization (FID) detectors. The TCD was used for the analysis of N_2, H_2 and high concentrations ($\geq$ 0.5%) of CO and CO_2. When the concentrations of CO and CO_2 were below the TCD detection limit, these compounds were converted to CH_4 using a ruthenium-catalyzed methanator, and analysis was completed using the more sensitive FID. This system permitted the analysis of CO and CO_2 from low-ppm levels through several percent.

Ten to fifteen grams of dolomite acceptor precursor were used in each test. First-cycle calcination was achieved by heating the dolomite to 750°C in N_2. Shift-carbonation conditions were such that CaO, but not MgO, would react with CO_2 so that, after the first cycle, the acceptor was alternately in the fully calcined (CaO + MgO) and half-calcined ($CaCO_3$ + MgO) forms. Composition and selected structural properties of the as-received and fully calcined dolomite are presented in Table 1. The diameters of pores created during calcination were in the range of 10^{-2} to 10^{-1} μm, with a peak in the distribution curve at about 7 x 10^{-2} μm.

The response of the semi-batch reactor for a typical run is shown in Figure 2. Dimensionless time, t*, is defined by

$$t^* = \frac{n_f\, y_{(CO + CO_2)}\, t}{n_{CaO}} \qquad (3)$$

where n_f is the molar gas feed rate, $y_{(CO + CO_2)}$ is the mol fraction of CO plus CO_2 in the feed gas, n_{CaO} is the mols of CaO in the reactor, and t is the reactor time; t* = 1 corresponds to the

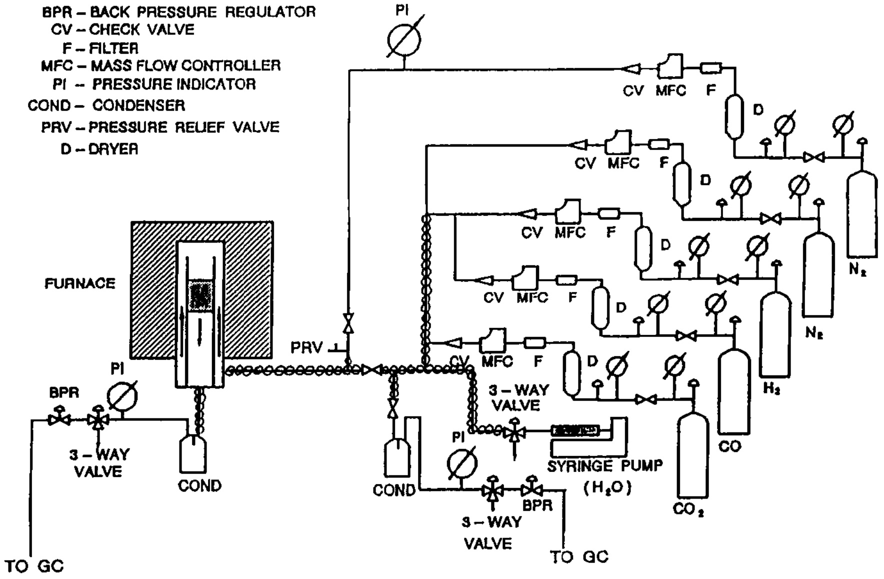

FIGURE 1. Schematic of the reactor system.

TABLE 1. CHEMICAL COMPOSITION AND STRUCTURAL PROPERTIES OF THE DOLOMITE ACCEPTOR

a) Chemical Analysis (as reported by National Lime Co.)

Component	Wt %
$CaCO_3$	54.5
$MgCO_3$	45.0
SiO_2	0.2
Fe_2O_3	0.07
Al_2O_3	0.08
S	0.03
Other	0.12

Loss on ignition at 1800°F - 47.7%

b) Structural Properties (measured at LSU)

	Surface Area (m^2/g)	Pore Volume (cm^3/g)
Dolomite	1.6	0.012
Calcined at 750°C in N_2	21.3	0.36

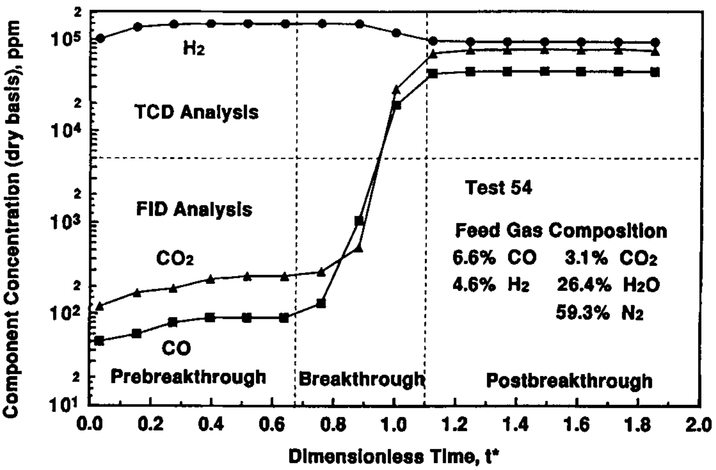

FIGURE 2. Typical reactor response curve showing product concentrations as a function of dimensionless time.

time at which all of the acceptor would be reacted if both the shift and carbonation reactions go to completion with infinitely fast global rates. During the early stages of the shift-carbonation phase, referred to in Figure 2 as the prebreakthrough period, both reactions were fully effective and the CO and CO_2 concentrations (dry basis) of the product gas were effectively constant at about 80 and 300 ppm, respectively. Both reactions are sufficiently fast to permit equilibrium concentrations, which at these reaction conditions are 20 ppm CO and 110 ppm CO_2, to be closely approached. Hydrogen concentration was at its maximum during this prebreakthrough period. CO and CO_2 breakthrough began at $t^* \sim 0.7$ when the leading edge of the carbonation reaction front reached the end of the fixed bed of CO_2 acceptor. CO and CO_2 concentrations increased rapidly while H_2 concentration decreased during the active breakthrough period. CO_2 acceptor was effectively exhausted at $t^* \sim 1.1$, after which a second steady state was reached where only the shift reaction occurred.

The concentration data were used to calculate the fractional removal of total carbon oxides, FCOX, and the fractional conversion of acceptor, X*, as a function of time. These results are shown in Figure 3. During the prebreakthrough period, the fractional removal of carbon oxides was 0.998 and the fractional acceptor conversion was directly proportional to time. The beginning of breakthrough corresponded to a rapid decrease in carbon oxide removal and in the rate of acceptor conversion. At the conclusion of the test, the fractional acceptor

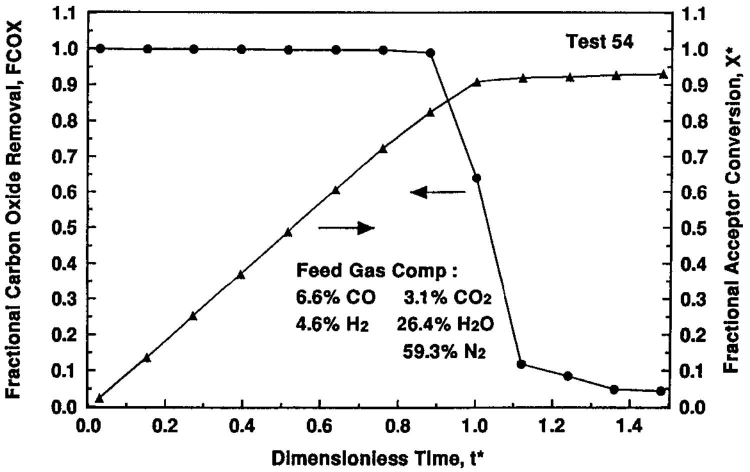

FIGURE 3. Typical reactor response curve showing fractional carbon oxide removal and fractional acceptor conversion as a function of dimensionless time.

conversion was 0.93 and carbonation was still occurring at a low rate. Note that during the steady-state postbreakthrough period, the conversion of CO to CO_2 via the shift reaction continued but there was little or no CO_2 removal.

Results similar to those illustrated in Figures 2 and 3 were achieved over a range of shift-carbonation temperatures, space velocities, and feed gas compositions. Combined shift-carbonation equilibrium during the prebreakthrough period was closely approached at all temperatures in the range of 500 to 650°C, and fractional carbon oxide removal during the prebreakthrough period exceeded 0.98 at all temperatures between 400 and 600°C. Final fractional conversion of the CO_2 acceptor was generally greater than 0.90. Complete results of these single-cycle tests have been published(8).

MULTICYCLE TEST PROGRAM

A number of five-cycle tests and one eleven-cycle test were carried out to obtain preliminary information on sorbent durability. The dolomite acceptor precursor, whose composition and structural properties are shown in Table 1, was used in all tests.

Reference-case reaction conditions are identified in Table 2. These conditions were selected on the basis of results from the previous study(8), and the effect of individual reaction

TABLE 2. REFERENCE-CASE CALCINATION AND SHIFT/CARBONATION REACTION CONDITIONS FOR MULTICYCLE TESTS

Sorbent Precursor	Dolomite
Initial Mass, g	13.2
Particle Size Range, μm	149-210
Calcination Conditions	
Temp., °C	750
Pressure, atm	3.3
Gas Comp., % N_2	100
Flow Rate, sccm	700
Shift/Carbonation Conditions	
Temp., °C	550
Pressure, atm	15
Gas Comp., % CO	5.6
% H_2O	20.0
% N_2	74.4
Flow Rate, sccm	250
Space Velocity (hr^{-1}), stp	1425

parameters was evaluated by comparison with the reference-case results. Note that the reference-case shift-carbonation feed gas contained only CO, H_2O, and N_2. Although little, if any, N_2 would be expected in an actual process, significant quantities were included because of the unique requirements of the laboratory apparatus. The omission of H_2 and CO_2 from the reference case feed composition was a matter of convenience. The presence of H_2, and the absence of significant CO_2 in the reactor product, was a sure indication that the shift and carbonation reactions were occurring. More complex feeds containing the four major components of synthesis gas -- CO, CO_2, H_2, and H_2O -- such as used in Figures 2 and 3 were tested subsequently. In all tests, reference values were used for all reaction parameters except where otherwise noted.

Reference-Case Results

Figure 4 compares the CO and CO_2 breakthrough curves from the first and fifth cycles of a five-cycle test using reference-case reaction conditions. In the first cycle, CO concentration was equal to or less than 10 ppm (dry basis) for $t^* < 0.3$. Breakthrough began at $t^* \sim 0.65$, and the CO concentration increased to 26,000 ppm (2.6%) at the end of the test. CO

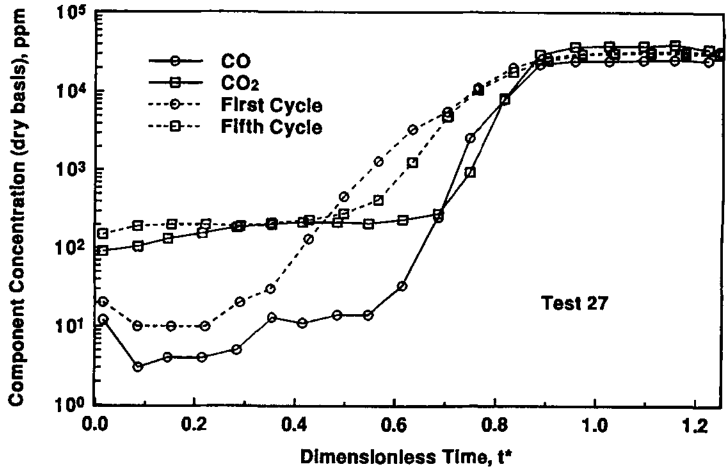

FIGURE 4. CO and CO_2 breakthrough curves in the first and fifth cycles: reaction conditions - Table 2.

concentrations during the early stages of cycle 5 were also near the 10 ppm level, but breakthrough began at t* ~ 0.45. The slope of the breakthrough curve in the fifth cycle was somewhat smaller, indicating a slower global reaction rate. Prebreakthrough CO_2 concentrations were also similar in the first and fifth cycles, in the general range of 90 to 220 ppm. CO_2 breakthrough in the fifth cycle occurred at an earlier time, and the slope of the breakthrough curve was also lower. Fractional removal of total carbon oxides in the prebreakthrough period was 0.996 in each of the five cycles, and the final fractional conversion of CaO decreased from 0.84 after cycle 1 to 0.80 after cycle 5.

An alternate method of evaluating sorbent durability is shown in Figure 5 where the dimensionless CO and CO_2 breakthrough times are plotted versus cycle number. The breakthrough times are arbitrarily defined as the times corresponding to product gas concentrations of 100 ppm CO and 500 ppm CO_2. Over the five cycles, the CO_2 breakthrough time decreased from t* = 0.71 to t* = 0.58 while the CO breakthrough time decreased from t* = 0.64 to t* = 0.41. The largest decrease occurred between cycles 1 and 2, with a smaller decrease between subsequent cycles. These numbers represent an average decrease in breakthrough time of about 4% and 7% per cycle for CO_2 and CO, respectively.

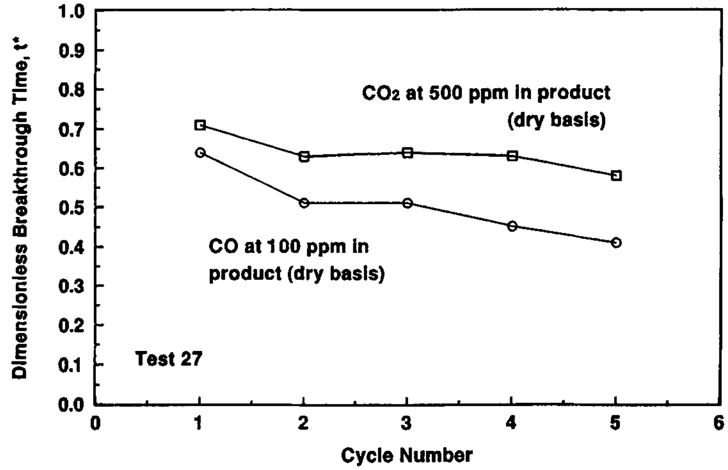

FIGURE 5. Decrease in the duration of the prebreakthrough period as a function of cycle number: reference conditions - Table 2.

Effect of Shift/Carbonation Temperature

Five-cycle tests were also conducted at shift/carbonation temperatures of 600°C and 650°C, with all other reaction conditions at reference values. Average fractional removal of total carbon oxides during the prebreakthrough period of each cycle is shown in Figure 6, with results at the 550°C reference temperature included for comparison. Prebreakthrough concentrations increased and fractional carbon oxide removal decreased because of the adverse effect of higher temperature on the combined shift-carbonation reaction equilibrium. Fractional carbon oxide removal at 600°C was reasonably constant at about 0.985. At 650°C, the prebreakthrough performance actually improved with increasing cycle number, from about 0.90 in cycle 1 to 0.94 in cycle 5.

In spite of the constant fractional removal of carbon oxides with cycle number at 600°C and the improved performance at 650°C, sorbent deterioration, measured in terms of duration of the prebreakthrough period, did occur. This is illustrated in Figure 7 where fractional carbon oxide removal as a function of dimensionless time for the first and fifth cycles of the 600°C test is compared. In cycle 1, the active breakthrough period corresponded approximately to $0.9 < t^* < 1.1$. In cycle 5, breakthrough began at $t^* \sim 0.8$, and the reaction was effectively complete by $t^* = 1.0$. Fractional conversion of CaO to $CaCO_3$ was essentially complete at the

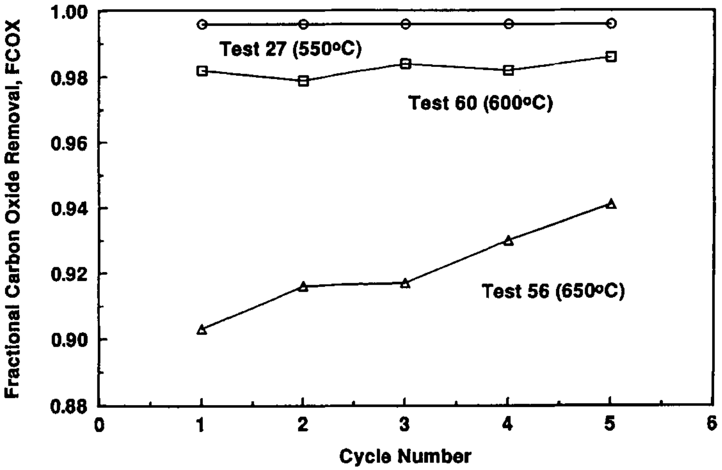

FIGURE 6. Fractional carbon oxide removal during the prebreakthrough period as a function of cycle number and shift/carbonation temperature: other reaction conditions - Table 2.

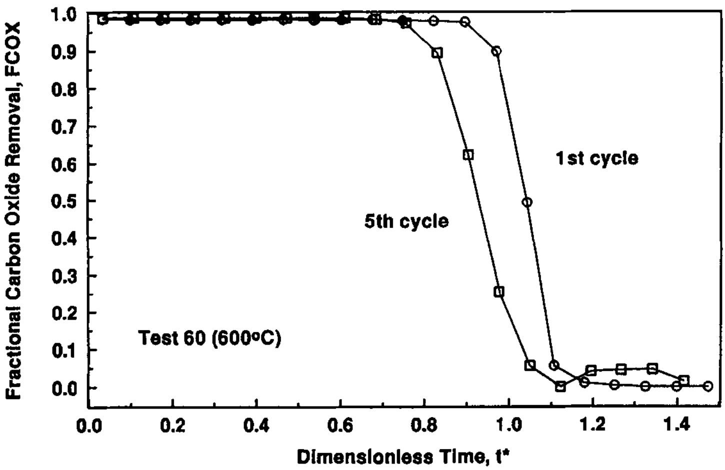

FIGURE 7. Fractional carbon oxide removal as a function of dimensionless time during the first and fifth cycles: 600°C shift-carbonation temperature, other reaction conditions - Table 2.

end of cycle 1 and decreased to 0.89 after cycle 5. The rate of acceptor deterioration increased slightly as the shift-carbonation temperature increased.

Effect of Space Velocity

Increasing space velocity decreases the contact time between gas and acceptor, but exposes the acceptor to a greater quantity of gas per unit time. Consequently, a five-cycle test at 3000 hr^{-1} (stp) was carried out to determine if space velocity had a significant effect on acceptor durability. CO breakthrough curves for each of the five cycles are shown in Figure 8. Because of the increased space velocity, the duration of the prebreakthrough period and the slope of the breakthrough curve were significantly reduced. CO concentrations during the early stages were in the range of 10 to 20 ppm in cycle 1, and increased to about 40 ppm in the remaining cycles. These concentrations were only marginally larger than the prebreakthrough concentrations at the reference space velocity of 1425 hr^{-1} (stp). Although there was a considerable decline in performance between cycles 1 and 2, little or no further deterioration occurred during the remainder of the test. CO_2 breakthrough curves (not shown) were similar to those of CO, leading to the conclusion that, on a five-cycle average basis, there was essentially no effect of space velocity on the rate of acceptor deterioration.

Feed Gas Composition

As previously noted, the reference feed gas contained only CO, H_2O, and N_2. H_2 and CO_2 were added to produce a feed gas consisting of 6.6% CO, 3.1% CO_2, 4.6% H_2, 26.4% H_2O, and balance N_2 to determine the possible effect of the more complex feed gas on acceptor performance. The total carbon oxide content of 9.7% was 73% greater than that of the reference gas, while the steam-to-CO ratio was increased only a small amount from 3.6 to 4.0. As a consequence, prebreakthrough CO and CO_2 concentrations were somewhat larger, and the duration of the prebreakthrough period was decreased. Acceptor durability, however, did not suffer.

Prebreakthrough CO and CO_2 concentrations and fractional removal of total carbon oxides are plotted as a function of cycle number in Figure 9. Prebreakthrough CO concentrations ranged from 46 to 135 ppm, with an average of 101 ppm (dry basis), while the corresponding range for CO_2 concentrations was from 225 to 262 ppm, with an average of 240 ppm (dry basis). Although the prebreakthrough CO concentrations were appreciably larger than those using the reference gas composition, the fractional removal of total carbon oxides remained quite high and was either 0.997 or 0.998 for each of the five cycles.

Acceptor durability when the feed gas contained all major synthesis gas components is compared in Figure 10 where fractional carbon oxide removal and fractional CaO conversion

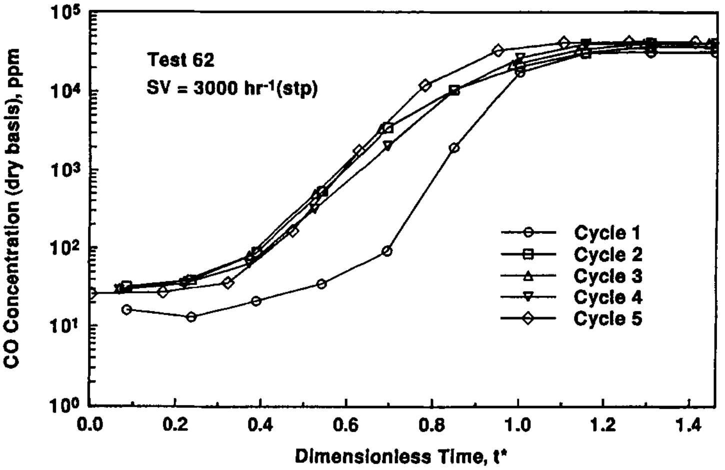

FIGURE 8. CO breakthrough curves during each of the five cycles: space velocity = 3000 hr^{-1} (stp), other reaction conditions - Table 2.

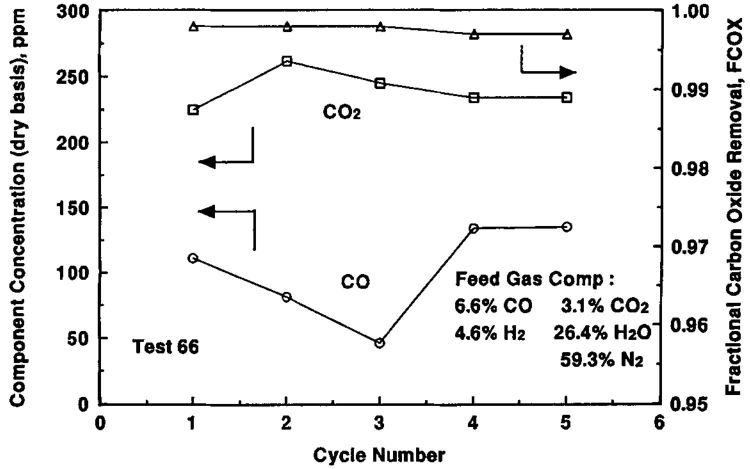

FIGURE 9. Prebreakthrough CO and CO_2 concentrations and fractional removal of carbon oxides as a function of cycle number: feed gas containing all major components of synthesis gas, other reaction conditions - Table 2.

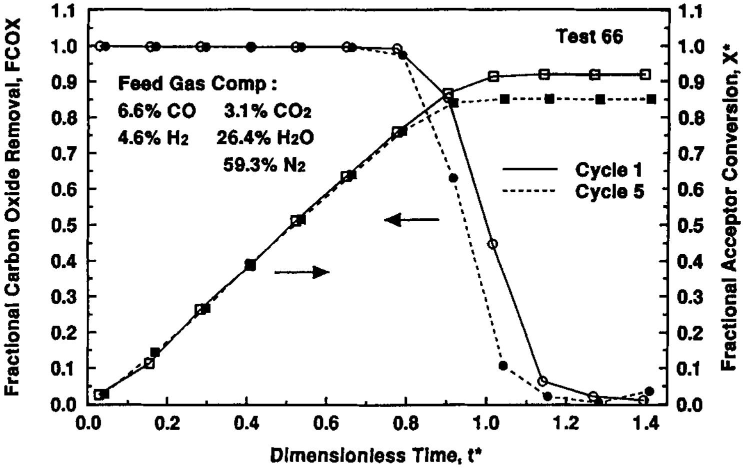

FIGURE 10. Fractional carbon oxide removal and fractional acceptor conversion as a function of dimensionless time during the first and fifth cycles: feed gas containing all major components of synthesis gas, other reaction conditions - Table 2.

are plotted as a function of dimensionless time for the first and fifth cycles. Carbon oxide removal approached completion for t* ≤ 0.75 in both cycles, and the global rate of the combined reactions was approximately equal, as indicated by the similar slopes of the breakthrough curves. The obvious changes over the five cycles were the slightly earlier breakthrough in the fifth cycle and the reduction in final fractional CaO conversion, from 0.91 in cycle 1 to 0.85 in cycle 5.

Calcination Temperature and Atmosphere

Although earlier studies involving the carbonation reaction alone(9) indicated that the minimum calcination temperature which produced a rapid calcination rate resulted in optimum acceptor durability, higher calcination temperature is desirable from the process viewpoint to increase the equilibrium CO_2 partial pressure and reduce the required flow rate of calcination sweep gas. Consequently, five-cycle tests using calcination temperatures of 800°C and 850°C were carried out. The shift-carbonation feed gas contained all major synthesis gas components. One additional test was conducted using 850°C calcination temperature in which 50% H_2O was added to the calcination sweep gas. The familiar pattern of gradual acceptor deterioration was observed, as illustrated in Figure 11. In this figure, t_i/t_1, which is the ratio of the times required

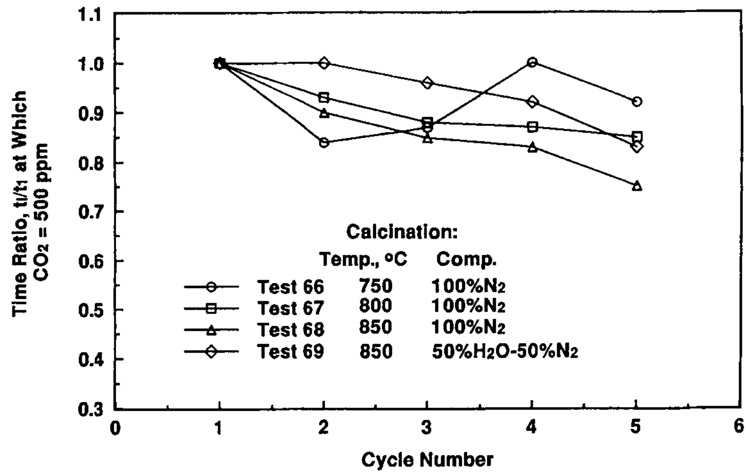

FIGURE 11. Acceptor deterioration in five-cycle tests as a function of calcination temperature and sweep gas composition: other reaction conditions - Table 2.

for the CO_2 product concentration to reach 500 ppm in cycle i to the time required to reach the same concentration in cycle 1, is plotted versus cycle number. This plot forces the value of t_i/t_1 in cycle 1 to be 1.0 for each test, so that the slopes of the curves provide an immediate visual comparison of durability.

Although the results, particularly using reference calcination conditions, are somewhat scattered, the durability clearly decreased as the calcination temperature increased. The addition of 50% H_2O, however, retarded the deterioration rate. Results at 850°C with H_2O were superior to the results at the same temperature without H_2O, and were comparable to results at a lower calcination temperature in dry N_2. The maximum deterioration after five cycles occurred at 850°C in dry N_2, where the final value of t_5/t_1 was 0.75. These(Figure 11)results indicate an average deterioration rate of about 5% per cycle at 850°C in dry N_2, about 2% per cycle at 750°C in dry N_2, and about 3% per cycle at 850°C in the H_2O-N_2 atmosphere. Results based on CO product gas concentrations were similar.

Eleven-Cycle Test Results

To conclude the test program, an eleven-cycle test was carried out at the reference reaction conditions shown in Table 2. Prebreakthrough CO and CO_2 concentrations and fractional carbon oxide removal are shown in Figure 12 as a function of cycle number. Results

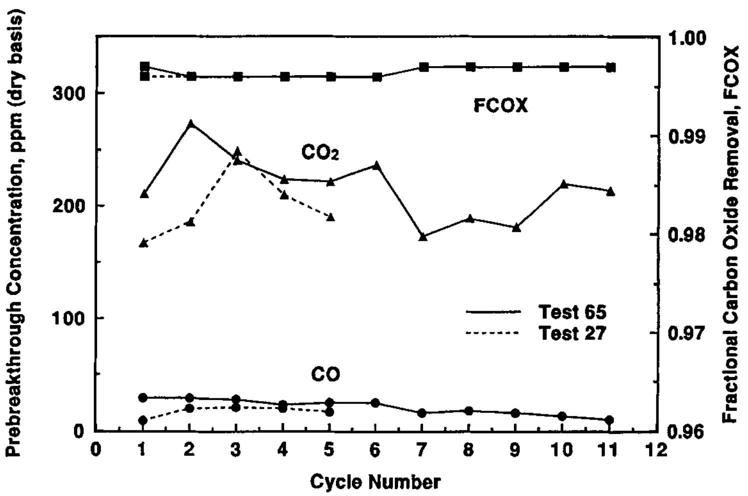

FIGURE 12. Prebreakthrough CO and CO_2 concentrations and fractional removal of carbon oxides: reaction conditions - Table 2.

from the earlier five-cycle test at the same conditions are included for comparison. Prebreakthrough CO_2 concentrations for the sixteen cycles of the two tests ranged from 170 to 280 ppm, while CO prebreakthrough concentrations were in the 10 to 30 ppm range. Fractional removal of carbon oxides was either 0.996 or 0.997 in each of the sixteen cycles. The prebreakthrough concentrations actually decreased slightly with cycle number in the eleven-cycle test.

In spite of the relatively constant prebreakthrough concentrations, acceptor performance continued to deteriorate as shown in Figure 13. For both CO and CO_2, the duration of the prebreakthrough period decreased by an average of about 5% per cycle over the eleven cycles.

CONCLUSIONS

The feasibility of producing hydrogen from synthesis gas in a single-step process by carrying out the water-gas shift reaction in the presence of a regenerable CO_2 acceptor has been proven. Total carbon oxide concentrations in the range of 400 ppm or less and fractional removal of carbon oxides in excess of 0.995 were obtained during the prebreakthrough period of multi-cycle fixed-bed reactor tests over a range of shift-carbonation reaction temperatures, feed gas compositions, and space velocities. In spite of the ready availability and low cost of

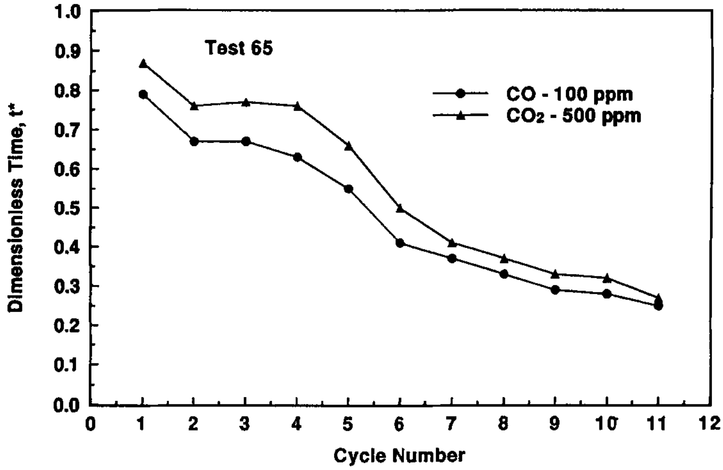

FIGURE 13. Acceptor deterioration as measured by the decrease in the duration of the prebreakthrough period in an eleven-cycle test: reaction conditions - Table 2.

the dolomite acceptor precursor, it is necessary, if the alternate process is to be economical, that the CO_2 acceptor maintain its strength and reactivity through numerous calcination-carbonation cycles.

Concentrations of CO and CO_2 during the prebreakthrough period did not increase as the number of cycles was increased to five and, in one test, eleven. Acceptor deterioration did occur, however, as shown by a gradual decrease in the duration of the prebreakthrough period and a reduction in the global reaction rate during the active breakthrough period. Acceptor durability was effectively independent of shift-carbonation feed gas composition and space velocity, but the rate of acceptor increased with an increase in both the calcination and shift-carbonation temperatures. The addition of steam to the calcination gas appeared to offset the effect of higher calcination temperature. The rate of acceptor deterioration, as measured by the decreased duration of the prebreakthrough period, was from approximately 2% per cycle to 7% per cycle, depending on reaction conditions.

ACKNOWLEDGMENT

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