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Enhanced Hydrogen Production Integrated with CO$_2$ Separation in a Single-Stage Reactor

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ABSTRACT

Hydrogen production from coal gasification can be enhanced by driving the equilibrium limited Water Gas Shift reaction forward by incessantly removing the CO_2 by-product via the carbonation of calcium oxide. This project uses the high-reactivity mesoporous precipitated calcium carbonate sorbent for removing the CO_2 product to enhance H_2 production. Preliminary experiments demonstrate the show the superior performance of the PCC sorbent over other naturally occurring calcium sorbents. It was observed that the CO_2 released during the in-situ calcination causes the deactivation of the iron oxide WGS catalyst by changing the active phase of the catalyst from magnetite (F_3O_4). Detailed understanding of the iron oxide phase diagram helped in developing a catalyst pretreatment procedure using a H_2/H_2O system. Intermediate catalyst pretreatment helps prevent its deactivation by reducing the catalyst back to its active magnetite (Fe_3O_4) form. Multicyclic runs which consist of combined WGS/carbonation reaction followed by in-situ calcination with a subsequent catalyst pretreatment procedure sustains the catalytic activity and prevents deactivation. The water gas shift reaction was studied at different temperatures, different steam to carbon monoxide ratios (S/C) 3:1, 2:1, 1:1 and different total pressures ranging from 0 - 300 psig. The CO conversion was found to have an optimal value with increasing pressure, S/C ratio and temperatures. The combined water gas shift and carbonation reaction was investigated at 650 C, S/C ratio of 3:1and at different pressures of 0-300 psig.

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EXECUTIVE SUMMARY

The performance of the high temperature shift (HTS) and calcium oxide system to produce hydrogen deteriorates over multiple WGS-carbonation and calcination cycles. This is due to the deactivation of the HTS catalyst (iron oxide) by the CO_2 gas that is evolved during the calcination phase. Hence, it is imperative to understand the HTS catalyst composition through an iron oxide phase diagram. Iron oxide occurs in three different phases: Hematite (Fe_2O_3), Magnetite (Fe_3O_4) and Wustite (FeO). The active phase of the HTS catalyst is Magnetite (Fe_3O_4). However, in the presence of an oxidizing atmosphere, like pure CO_2, the Magnetite phase gets oxidized to Hematite (Fe_2O_3). This is evident from the iron oxide phase diagram for CO-CO_2 system as illustrated in Figure 2. Thus, a pretreatment procedure was developed which reduces the oxidized form to the required phase. This step consists of treating the oxidized catalyst to a 20% H_2 in 80% H_2O stream at 600 ^{o}C which reduces the Hematite (Fe_2O_3) form to Magnetite (Fe_3O_4) form. This fact was confirmed by X-ray diffraction analyses of the HTS catalyst before and after the pretreatment procedure. The HTS catalyst as obtained contains comprises of Fe_2O_3 (hematite) phase. The catalyst when subsequently subjected to the pretreatment procedure changes its phase to the active magnetite (Fe_3O_4). Multicyclic runs which consist of combined WGS/carbonation reaction followed by in-situ calcination with a subsequent catalyst pretreatment procedure sustains the catalytic activity and prevents deactivation.

The water gas shift reaction was investigated at different temperatures ranging from 450 – 750°C, different steam to carbon monoxide ratios (S/C) 3:1, 2:1, 1:1 and different total pressures ranging from 0 - 300 psig. These experiments were conducted as base line experiments to determine the optimum conditions for maximum WGSR catalytic activity at different temperatures and pressures. The catalyst used for these tests was the high temperature shift catalyst consisting of iron oxide on chromia support procured from Sud Chemie. It was found that the CO conversion increases with increasing temperature up to a critical temperature (550-650 ^{o}C) beyond which it begins decreasing monotonically. This optimum temperature was one at which both the kinetics and the reaction equilibrium favored the formation of the products. It was also found that with an increase in the S/C ratio and pressure there was an increase in the CO conversion. Besides this, the optimum temperature decreases with an increase in the both the pressure and the S/C ratio. At high pressures the temperature dependence on CO conversion decreases and the optimum temperature remains constant with an increase in the S/C ratio. The partial pressure ratios of the products to the reactants were computed for each case of S/C ratio and on comparison with the equilibrium values were found to lie well within the equilibrium partial pressure ratios (equilibrium constants). With an increase in the temperature and pressure the partial pressure ratios were found to approach equilibrium more closely but with an increase in the S/C ratio they moved away from equilibrium.

After gaining a deep insight into the trends exhibited by the water gas shift reaction at various conditions and obtaining the optimum conditions for maximum CO conversion the combined water gas shift and carbonation reaction was investigated at high pressures. In order to enhance the purity of the hydrogen produced from the water gas shift reaction our proprietary calcium based sorbent (PCC) was used insitu to remove the carbon dioxide from

the product gas and thereby further enhance the water gas shift reaction. The combined reactions were studied at 650 C and an S/C ratio of 3:1 at various pressures ranging from 0 to 300 psig. It was found that the CO conversion for the combined reactions increases with an increase in the total pressure resulting in an increase in the purity of the hydrogen produced. At 0 psig a 95.6 % hydrogen stream is produced for the first 265 seconds while at 150 psig 99.7% pure hydrogen stream is obtained for the first 1168 seconds and at 300 psig a 99.8% pure hydrogen stream is produced for the first 1477 seconds. Hence the CO conversion increased with an increase in the pressure resulting in the production of high purity hydrogen at high pressures.

INTRODUCTION

The water gas shift reaction (WGSR) plays a major role in increasing the hydrogen production from fossil fuels. However, the enhanced hydrogen production is limited by thermodynamic constraint posed by the equilibrium limitation of the WGSR. However, this constraint can be overcome by concurrent water-gas shift (WGS) and carbonation reactions to enhance H_2 production by incessantly driving the equilibrium-limited WGSR forward and by in-situ CO_2 removal from the product gas mixture. This process can effectively and economically produce a pure H_2 stream by coal gasification with integrated capture of CO_2 emissions, for its subsequent sequestration. The reaction schemes involved are as follows:

$$\text{WGSR:} \quad CO + H_2O \Longleftrightarrow CO_2 + H_2 \quad\quad (1)$$

$$\text{Carbonation Reaction:} \quad CaO + CO_2 \rightarrow CaCO_3 \quad (2)$$

$$\text{Calcination Reaction:} \quad CaCO_3 \rightarrow CaO + CO_2 \quad (3)$$
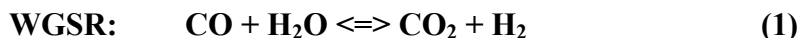
While various calcium oxide precursors were tested for CO_2 capture, naturally occurring limestones were unable to react completely due to pore pluggage and pore-mouth closure (Gupta and Fan, 2002). However, the highly reactive mesoporous precipitated calcium carbonate (PCC) particles, synthesized by a novel wet precipitation technique using surface modifiers, can achieve up to 70 wt% capture during carbonation. Life cycle testing of the sorbent over multiple cycles of carbonation-calcination reactions showed that PCC sorbent attains a capture capacity of 40-36 wt% over 50-100 cycles, which is significantly higher than most of the other high temperature sorbents reported in literature (Iyer et al., 2004). In contrast, naturally occurring limestone (LC) shows poor performance.

The enhanced water gas shift reaction for H_2 production with *in-situ* carbonation was studied using High Temperature Iron Oxide Shift (HTS) catalyst and calcium sorbents. Experimental evidence clearly shows that the PCC sorbent demonstrates superior performance over that of naturally occurring limestone sorbents. Gas composition analyses show the formation of pure hydrogen stream during the initial part of the breakthrough curve, thus demonstrating the synthesis of pure hydrogen. To date, in this project, the reactions were investigated over reaction temperatures ranging from 500-750 ^{o}C at ambient pressures. The current focus is to conduct these experiments at high pressures varying from 1-20 atm. In addition the effects of varying the steam to carbon monoxide ratios is also investigated. The

incessant removal of CO_2 from the water gas shift reaction not only enhances the hydrogen production process but it also reduces the requirement for excess steam to drive the WGSR forward. Thus, operating at conditions involving near-stoichiometric steam requirements augments the H_2S removal by CaO.

WGS iron oxide catalyst: phase diagram and deactivation

It is evident from previous reports (Annual report, Sept 2004) that the performance of the HTS-CaO system deteriorates over multiple WGS-carbonation and calcination cycles. This is due to the deactivation of the HTS catalyst by the CO_2 gas that is evolved during the calcination phase. In our previous report (Semi-Annual Technical Progress report, March 2005) we had designed a novel multi-fixed bed reactor system which avoids the contact of CO_2 with the WGS catalyst system during the calcination phase. Hence in this quarter, a novel approach to understand the WGS catalyst phases and its deactivation was undertaken.

It has been suggested in literature that exposing the commercial iron oxide/chromium oxide catalyst to high operating temperatures leads to a decrease in the kinetics of the high temperature shift catalyst (Bohlbro, 1969; Newsome, 1980). The deactivation of the catalyst is a result from different phenomena occurring during the operation of the commercial catalyst under the water-gas shift conditions. Keiski and Salmi (1992) found that operating close to industrial temperature of 575-723 K led to a decrease in catalytic activity due to a sintering process. The deactivation of the catalyst was most active during the first 150 hours and the decay of the catalyst was linked to a decrease of the surface area and to an increase of the mean pore size of the catalyst.

The commercial catalyst of iron oxide/chromium oxide is a catalyst that can undergo bulk phase conditions when exposed to different atmospheres. The active phase of the catalyst is magnetite (Fe_3O_4). However, during the calcination step of the WGS-carbonation and calcination process, pure CO_2 is released from the calcium carbonate and the water gas shift catalyst is exposed to an oxidizing atmosphere of 100% CO_2 at 700°C. According to the thermodynamics of iron oxide under various gas compositions and temperatures, the iron oxide catalyst is oxidized from magnetite to hematite (Fe_2O_3), an oxidized form of iron oxide. Since the active bulk phase of the catalyst is magnetite, the iron oxide catalyst needs to be reduced from hematite to magnetite. According to the thermodynamic plot of iron oxide

in a hydrogen-steam system, iron oxide becomes magnetite when exposed to a reducing atmosphere of 20% H_2 and 80% H_2O at 600°C.

Rethwisch et al. (1985) studied the water-gas shift reaction at 660 K on both unsupported magnetite and magnetite particles supported on graphitic materials. They found that exposing the catalyst to a 15% CO/85% CO_2 gas mixture at 660 K for 22 hours could restore high catalytic activity, but no significant increases were found in a 40% H_2/60% H_2O gas mixture for 22 hours. The CO/CO_2 treatment step resulted in a 200-300% increase in activity through a water-gas shift condition of 64% H_2O, 32% CO, and 4% CO_2.

High Pressure Hydrogen Production

To obtain high purity H_2, the WGS reaction is generally carried out in two stages (Gerhartz, 1993; Bohlbro, 1969): (1) high temperature shift (250-500 ^{o}C) using iron catalysts and (2) low temperature shift (210-270 ^{o}C) using copper-based catalysts. Copper based catalysts are extremely intolerant to small quantities of sulfur (< 0.1ppm) and hence the fuel gases need to be desulfurized upstream of the WGS reactor. A high steam:CO ratio is required to enhance CO conversion and the consequent hydrogen production. The steam to CO ratio at 550 ^{o}C can be as high as 50 in a single-stage operation or 7.5 for a more expensive dual-stage process to obtain 99.5 % pure H_2 (Newsome, 1980). For example, to lower the CO content of the typical fuel gas from 45 % (inlet) to 3% (outlet) a total steam addition of 1.18 kg/m^3 of the gas is required, at a total pressure of 60 bars and 410 ^{o}C (Gerhartz, 1993). While higher temperature enhances the kinetics of the WGSR, thermodynamics adversely affects the hydrogen production due to the equilibrium limitation of the WGSR with the H_2 yield falling with rising temperature.

Enhancing the Water gas Shift Reaction and Hydrogen Purification

An effective technique to shift the WGSR to the right for enhanced hydrogen generation has been to remove hydrogen from the reaction mixture. This premise has lead to the development of hydrogen separation membranes. However, membranes cannot completely remove hydrogen from the mixture and there is also the effect of a considerable pressure drop across them (Roark, et al 2002). In addition, any remaining hydrogen in the main stream would dilute CO_2 and would lead to poor process economics.

The other option is to remove the CO_2 from the reaction gas mixture. Various solvents such as amines, Selexol, Rectisol etc have been used to scrub the CO_2 from the WGS reaction gas mixture (Steigel and Ramezan, 2006) between two stages. However, these solvents operate at ambient temperatures and consequently this method involves severe energy penalties due to cooling and reheating of the reaction gas mixture. Hence, high temperature CO_2 membranes were developed (US DOE, 2005) which operate in the same temperature range as that of the WGSR. Thus the development of these membranes has led to the concept of membrane reactors. However, the use of these membranes leads to the development of a pressure drop and the costs associates with these membranes make the overall process expensive.

Calcium Assisted Hydrogen production

There are several processes that enhance hydrogen production using limestone sorbents such as the ZECA process and the HyPr-RING Process (Lin et al., 2002; Ziock et al., 2001). However, these processes operate at very high pressures (12-100 MPa) to produce H_2, which is not economically viable. On the other hand processes such as HyPr-RING result in the gasification of coal with in-situ CO_2 capture using $CaO/Ca(OH)_2$ systems (Lin et al., 2005). However, these systems operate at very high pressures (70 bar) and require excess steam and produce only 91% pure hydrogen. In addition, there have been several reports on sorption enhanced hydrogen production by coupling SMR and in-situ CO_2 capture using a sorbent (Hufton et al., 1999; Akiti 2004; Balasubramanian et al., 1999; Lopez Ortiz and Harrison, 2001). Calcium oxide assisted steam methane reforming (SMR) was attempted in earlier studies (Balasubramanian et al., 1999; Lopez Ortiz and Harrison, 2001). They detailed the performance of a single-step sorption-enhanced process using a Ni-based catalyst to produce hydrogen. However they also mixed dolomite-CaO powder with the Ni-based catalyst to separate CO_2 and enhance H_2 concentration to 97%.

Our proposed process under consideration involves removing CO_2 from the gas mixture by reacting it with CaO (carbonation), which can be conducted at high operating pressures. Albeit, higher pressures and temperatures lead to thermodynamic equilibrium, the constant removal of CO_2 drives the reaction forward, resulting in enhanced kinetics and improved H_2 yield.

EXPERIMENTAL

Modification of integral fixed bed reactor system for high-pressure operation

The existing reactor setup (described earlier in Annual report, Sept 2005) was modified to handle high pressures of up to 20 atmospheres. A back-pressure regulator procured from Swagelok (KPB series) was installed in the setup to build pressure within the reactor. This back pressure regulator is capable of building pressures of upto 68.9 atm (1000 psig). The valve seat material is made of PEEK which is corrosion resistant to acidic hydrogen sulfide vapors, which makes it capable of conducting H_2S experiments. As shown in Figure 1 below, the inlet of the backpressure regulator is connected to the reactor rod and the outlet is connected to a heat exchanger. Since the entire section of the equipment setup upstream of the backpressure regulator will be exposed to high pressures various components were replaced to make the setup capable of handling pressures of as high as 20 atms. Flow meters previously used to adjust the flow rates of the reactant gases were replaced by mass flow controllers procured from Brooks Instruments (model 5850E). Teflon pipes used for carrying the reactant gases to the reactor and the water from the pump to the steam generation unit were replaced by flexible stainless steel tubes. The reactant gases from the cylinder are made to flow through the steel tubes to the mass flow controllers where their flow rates are accurately metered. The mass flow controllers can handle a pressure of about 21 atms. From the mass flow controllers the reactant gases flow through a steel tube to the steam generating unit. The steam generating unit is maintained at a temperature of 200 ^{o}C and contains a packing of quartz chips which provide a large surface area of contact between the reactant gases and the water. The steam generating unit not only facilitates the complete evaporation on the water being pumped into the steam generating unit but it also serves to preheat the reactant gases entering the reactor. The reactor has been provided with a pressure gauge and a thermocouple to monitor the temperature and pressure within. The reactant gases leaving the reactor enter the back pressure regulator which builds pressure by regulating the flow rate of the gases flowing through it. The pressure regulator is very sensitive and the pressure within the reactor can be changed quickly without any fluctuations by just turning the knob. The back pressure regulator is also capable of maintaining a constant pressure for a long period of time thereby increasing the accuracy of the experiments conducted.
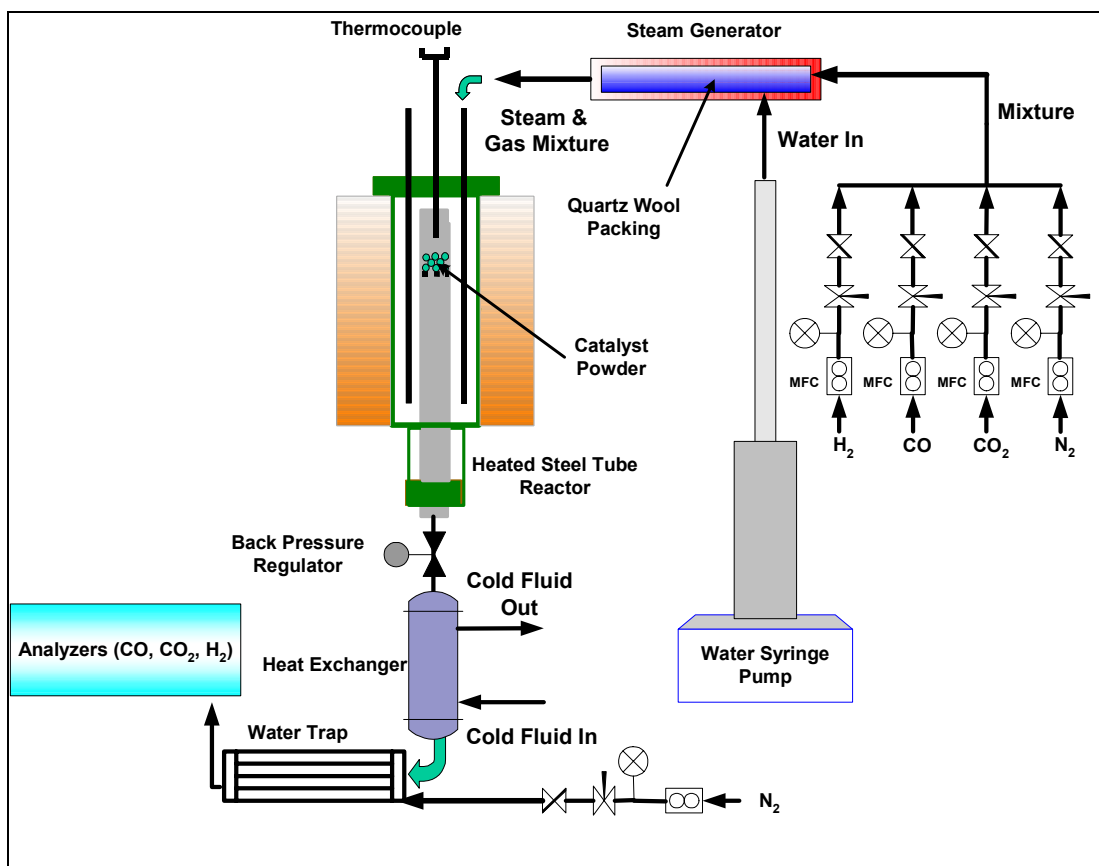
Figure 1: Modified integral fixed-bed reactor setup for conducting high pressure WGS and carbonation reactions

Reactor Setup troubleshooting and shakedown

Initial problems were encountered during the catalyst and the catalyst and sorbent runs while conducting high pressure experiments. The pressure in the reactor could not be built beyond 100psig. Occasionally, in a few experiments huge fluctuations in the gas flow were also obtained. These problems were traced back to the same cause wherein the powder in the reactor rod was being blown out into reactor and into the tubes connected to the reactor. Thi was due to the backpressure developed in the reactor rod. The pressure could not be built in the reactor due to the sorbent powder clogging the orifice of the pressure regulator, preventing the regulator to be completely closed. Also, the powder that had entered the tube connecting the steam generating unit to the reactor began collecting there and reducing the cross section of the tube causing a huge localized pressure drop. This pressure drop caused the condensation of the steam entering the reactor which results in the formation of water droplets thereby leading to large fluctuations in the flow rate of the gases. This problem was

solved by restricting the flow of the powder from the reactor tube by placing a small amount of quartz wool in the form of a thin layer over the powder bed. This method of preventing the entrainment of the powder along with regular cleaning and maintenance of the reactor solved both the problems mentioned above.

High Pressure Water Gas Shift Reaction Testing

The water gas shift reaction was conducted using the high temperature shift (HTS) catalyst (iron oxide on chromia) obtained from Süd-Chemie. These experiments were conducted as base line experiments to determine the optimum conditions for maximum WGSR catalytic activity at different temperatures and pressures. Catalyst fines were used in a fixed bed reactor setup for all the experiments. The total flow rate of the gases through the reactor was maintained a constant at 725 sccm for all the experiments and the concentration of carbon monoxide in the reaction mixture was maintained at 10.3 %. 0.25 g of the catalyst was loaded into the reactor and the pressure, temperature and gas flow rates were adjusted for each run. The steam free gas compositions at the outlet of the reactor were monitored continuously using the CO, CO_2 and H_2 gas analyzer system described earlier (Annual Technical Progress Report, September 2005). The reactions were conducted at different temperatures ranging from 450 – 750°C, different steam to carbon monoxide ratios (S/C) 3:1, 2:1, 1:1 and different total pressures ranging from 0 - 300 psig.

Simultaneous WGS and carbonation at High Pressures

In this quarter, the combined water gas shift and carbonation reaction was conducted using the same experimental setup described earlier. A sorbent (calcium oxide) to catalyst ratio of 10:1 was used for all the experiments conducted. The combined water gas shift and carbonation reaction experiments were conducted at 650°C with an S/C ratio of 3:1 at various pressures. 650°C was chosen as the optimum temperature for the first set of experiments as carbonation occurs at a rapid rate at this temperature and the water gas shift reaction gives a conversion of 0.8028 at 0 psig, 0.8138 at 150 psig and 0.8221at 300 psig. 5 g of PCC sorbent is mixed with .25 g of HTS catalyst and packed into the reactor rod. The PCC is calcined in-situ at 700C in a stream of nitrogen until the carbon dioxide analyzer confirms the absence of CO_2 in the outlet stream. The catalyst is then pretreated in an atmosphere of steam and

hydrogen to convert it to the magnetite phase, which is the active form for the water gas shift reaction. The combined reaction is then performed at 650 C in the presence of 10 % of CO and 30% steam, the rest of the reaction mixture consisting of nitrogen. This being an unsteady state experiment the data collection is started exactly when the carbon monoxide and steam are allowed to flow into the reactor and the time taken for the gases to reach the analyzers is accounted for by the incorporation of the residence time calculation.

RESULTS AND DISCUSSIONS

WGS iron oxide catalyst deactivation, phase transformation, and pre-treatment,

It is imperative to understand the HTS catalyst composition through an iron oxide phase diagram (Figures 2 and 3). Iron oxide occurs in three different phases: Hematite (Fe_2O_3), Magnetite (Fe_3O_4) and Wustite (FeO). The active phase of the HTS catalyst is Magnetite (Fe_3O_4). However, in the presence of an oxidizing atmosphere, like pure CO_2, the Magnetite phase gets oxidized to Hematite (Fe_2O_3). This is evident from the iron oxide phase diagram for CO-CO_2 system as illustrated in Figure 2. Thus, a pretreatment procedure was developed which reduces the oxidized form to the required phase. This step consists of treating the oxidized catalyst to a 20% H_2 in 80% H_2O stream at 600 ^{o}C which reduces the Hematite (Fe_2O_3) form to Magnetite (Fe_3O_4) form. This is clear from Figure 3. This fact was confirmed by X-ray diffraction analyses of the HTS catalyst before and after the pretreatment procedure. The HTS catalyst as obtained contains comprises of Fe_2O_3 (hematite) phase as shown in Figure 4 (a). The catalyst is subsequently subjected to the pretreatment procedure described earlier which changes its phase to the active magnetite (Fe_3O_4) form as shown in Figure 4 (b).
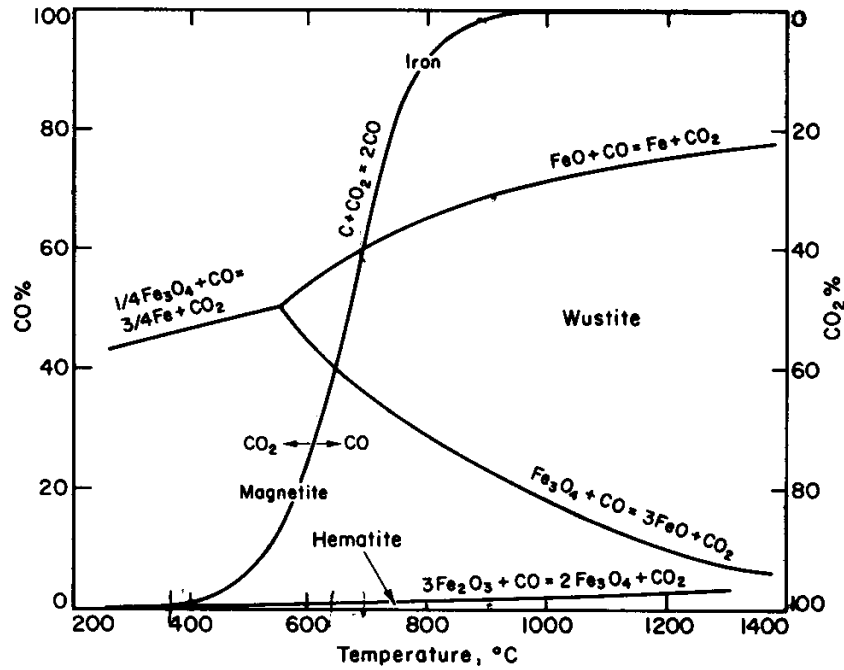
Figure 2: Equilibrium phase diagram for iron oxide system for various CO-CO_2 gas compositions and temperatures (adapted from Ross, 1980)
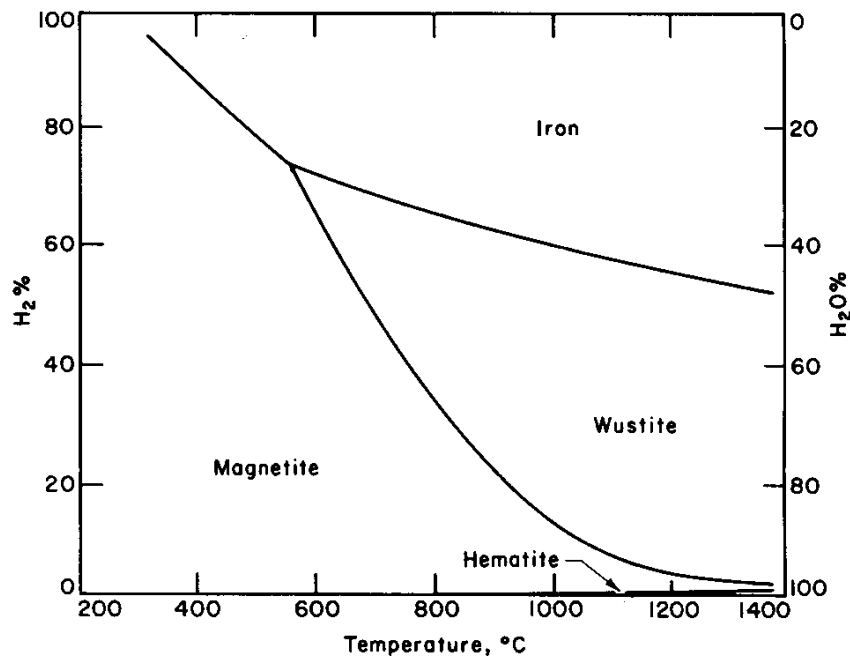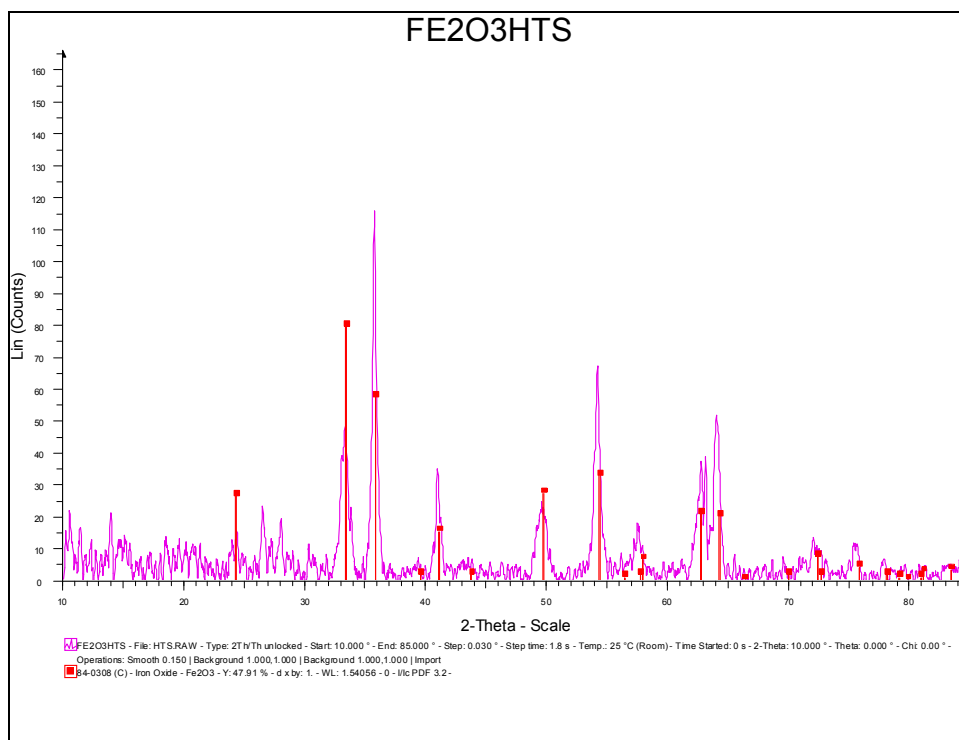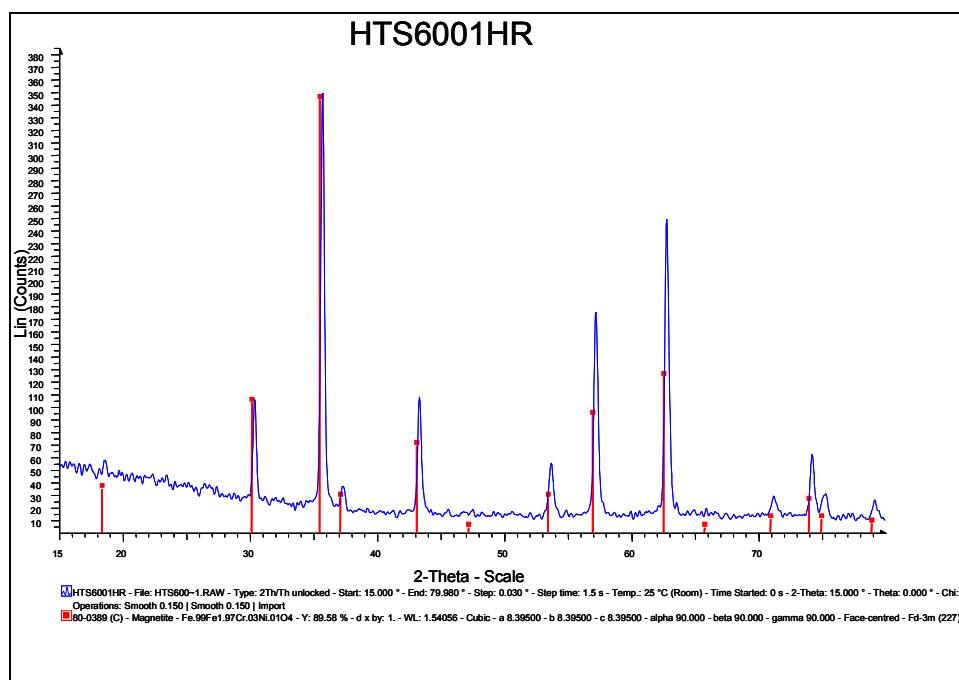

Figure 3: Equilibrium phase diagram for iron oxide systems for various H_2-H_2O gas compositions and temperatures (adapted from Ross, 1980)

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(a) before pretreatment (hematite)

(b) after pretreatment (magnetite)

Figure 4: X-ray diffraction patters of the high temperature shift (HTS) iron oxide catalyst

Combined WGS-carbonation reactions over multiple reaction-regeneration cycles, which include intermediate catalyst activation after every cycle, were performed using PCC-HTS system. Typically about 1.77 g of PCC-CaO was loaded in the reactor and the temperature was ramped to 700° in flowing N_2 to ensure the calcination of calcium carbonate to calcium oxide. After completion of the calcination, the reactor was cooled down to room temperature and 0.25 g of HTS catalyst was mixed into the reactor. The reaction temperature was then raised to 600°C and the catalyst pretreatment gas mixture consisting of a steam to H_2 ratio of 4:1 in N_2 for one hour. This pretreatment step activates the catalyst by reducing the HTS catalyst from Fe_2O_3 (hematite) to Fe_3O_4 (magnetite). The reaction gas mixture of 10.3% CO and 31% H_2O, and the balance being 5.0 grade N_2 was then sent into the reactor. The total gas flow-rate was maintained at 0.725 slpm and the steam/CO ratio was set at ~3. After the calcium oxide sorbent reaches its maximum loading capacity and the system reaches steady state and the reactor temperature was subsequently ramped to 700° C in flowing N_2 to effect the calcination of the carbonated sorbent. Subsequent to the calcination step the catalyst pretreatment is performed and the combined WGS-carbonation reaction is then conducted in the flowing reaction gas mixture. Thus, the sequence of operation is (a) combined WGS-carbonation reaction, (b) catalyst pretreatment, (c) calcination. This three step procedure was repeated for five continuous cycles.

The details of the CO conversion breakthrough curve for all the 5 cycles are depicted in Figure 5. The system gives 100% conversion for 90 seconds through the first cycle and the sorbent reached its breakthrough loading at 1091 seconds (18.2 min). Beyond this the CO conversion of 80 % corresponds to that obtained with only the catalyst at 600° C. For the second reaction cycle the system gave almost 100% conversion for 64 seconds and the sorbent reached its breakthrough loading at 787 seconds (13.1 min). The final CO conversion for the second cycle was 80 %. The third reaction cycle resulted in almost 100% conversion for 79 seconds and the sorbent reached its breakthrough in 818 seconds. The final CO conversion for the third cycle was 78%. In the fourth cycle the system did not achieve 100% CO conversion and the sorbent reached its breakthrough in 891 seconds. The final CO conversion for the fourth cycle was 69%. The fifth reaction cycle also did not result in 100% CO conversion and the time for the sorbent to reach its maximum loading capacity was 719 seconds. The final CO conversion for the fifth cycle was 69%. Thus the final steady

state CO conversion of the system, after it has reached the breakthrough, varies from 80% to 69% over five cycles. This depicts a drop in the catalyst activity of only 11% while the catalyst is exposed to 5 cycles. This is in sharp contrast to the significant drop in the catalyst activity when the catalyst pretreatment was not conducted. This can be observed by the drop in the catalytic activity from 80% in the first cycle to 40% in the second cycle as illustrated in Figure 5. Thus, the intermediate catalyst pretreatment helps prevent catalyst deactivation by reducing the catalyst to its active magnetite (Fe_3O_4) form.
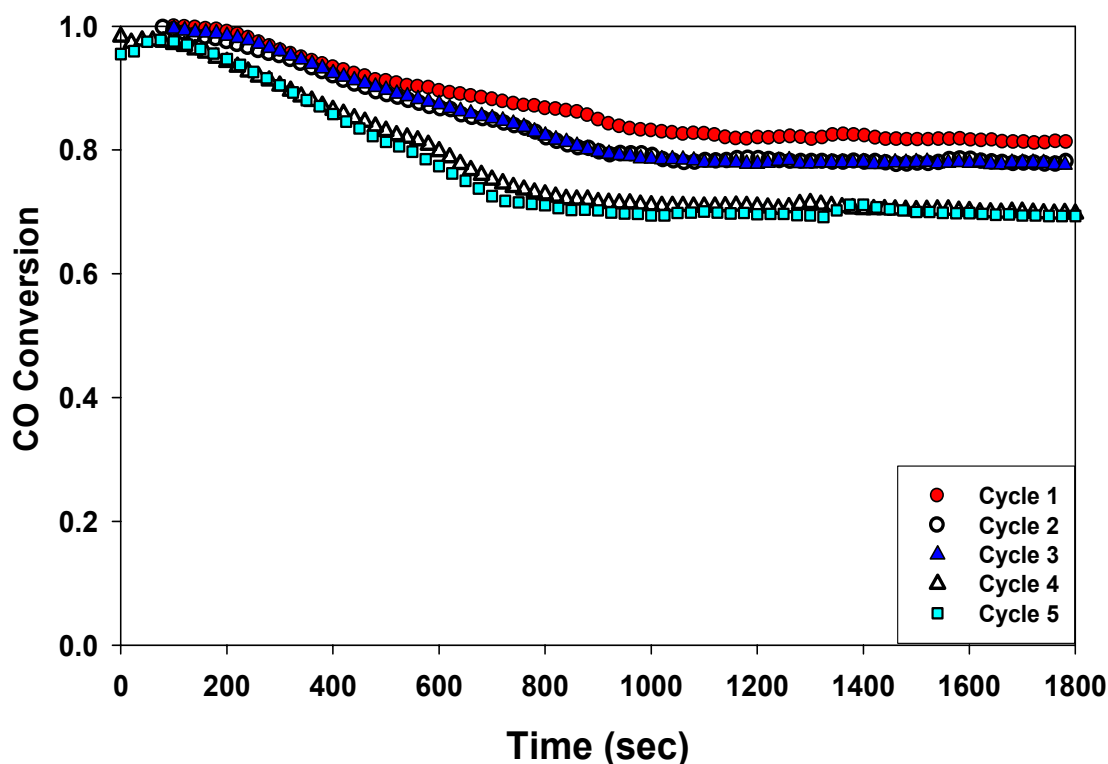

Figure 5: Breakthrough curve depicting the CO conversion for PCC-HTS catalyst system for five cycles (T = 600 ^{o}C, 10.3% CO, 31% H_2O, Total flow = 0.725 slpm)

High Pressure Water Gas Shift Reaction Testing

Figure 1 shows the CO conversion profiles for increasing reaction temperatures as well as the S/C ratios at ambient pressures. The CO conversion increases with increasing temperature up to a critical temperature (550-650 ^{o}C) beyond which it begins decreasing monotonically. It can be seen from Figure 1 that at 0 psig and a S/C ratio of 3: 1 the conversion increases from 45.8 % at 450C to 83.2 % at 600°C. It is well known that the rate of the reaction increases as temperature increases. Beyond 600 ^{o}C the conversion decreases and at 800 C it is 69.4%. This is observed due to the opposing trends of the reaction kinetics and thermodynamic

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equilibrium with increasing temperature. As the temperature increases the reaction rate increases while the equilibrium constant decreases. Thus at lower temperatures although the equilibrium constant is high the reaction rate is very low and at high temperatures the reaction is very fast but the equilibrium constant is very low. Consequently maximum conversion is reached at an optimum temperature at which both the kinetics and the reaction equilibrium are favorable. From Figure 1 it can be seen that the conversion increases with an increase in the S/C ratio. At a temperature of 650°C the conversion is 63.5% for a S/C ratio of 1:1 while it is 71.6% for 2:1 and 80.28% for 3:1. This is in accordance with the Le Chatelier's principle where, as the reactant composition increases the equilibrium will be shifted in the forward direction and will favor the formation of the products. It can also be seen from Figure 6 that as the S/C ratio increases the temperature at which maximum conversion is reached decreases. While for 1:1 the maximum conversion is reached at 650°C for 3:1 it is reached at 550°C. This can be explained based on the previous trends. As the steam concentration is increased the equilibrium is shifted in the forward direction and hence the maximum conversion that can be obtained according to thermodynamics is achieved at a lower temperature. As the temperature increases beyond this point the conversion remains almost the same until thermodynamics dictates a lowering in the conversion at high temperatures.
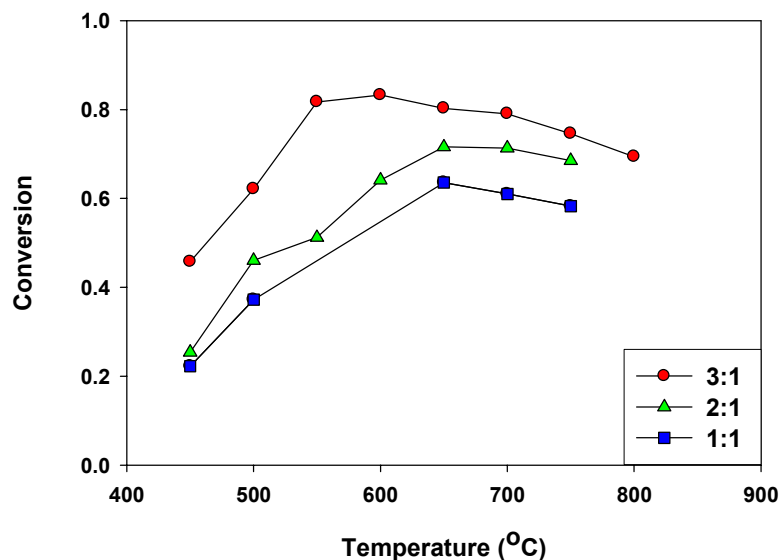

Figure 6: Effect of reaction temperature on CO conversions for various steam: CO ratios at 0 psig (0.25g HTS, Total flow = 0.725 slpm)

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The water gas shift reaction conducted at 150 psig follows the same trend as the 0 psig experiments as evident from Figure 7 below. The CO conversion trend shows the presence of an optimal value for varying temperature. For a steam: CO ratio of 1:1 the conversion is 46.2 % at 450C reaches a maximum at 550 C with a conversion of 69.2 % and then decreases to 62.7 % at 650°C. At 550C a conversion of 69.2 % is reached for a S/C ratio of 1:1, 84.2 % for 2:1, and 86.3% for 3:1. On comparing Figure 6 with Figure 7 it is evident that at any temperature the conversion is always higher at 150 psig when compared to 0 psig. Also the curves for conversion are flatter at 150 psig when compared to 0 psig, which shows that the temperature dependence on the conversion decreases with an increase in the pressure.
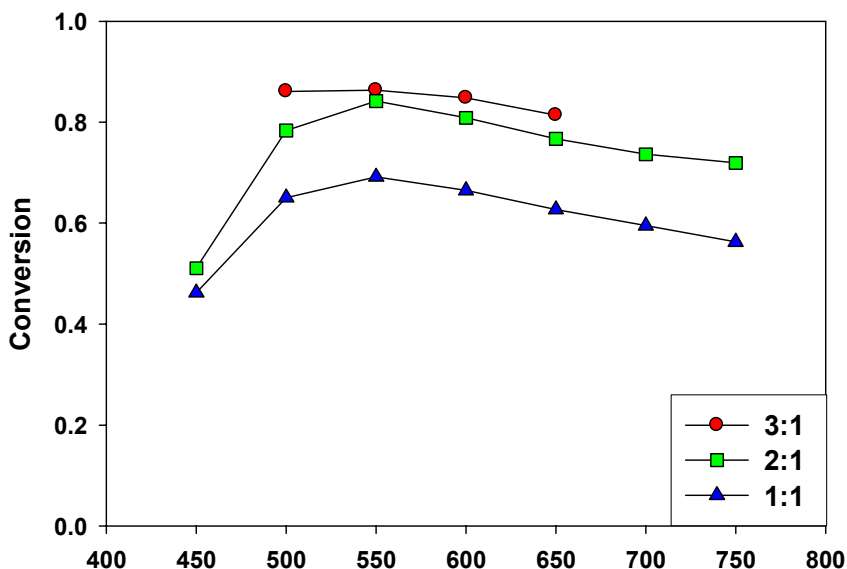

Figure 7: Effect of reaction temperature on CO conversions for various steam: CO ratios at 150 psig (0.25g HTS, Total flow = 0.725 slpm)

The effect of reaction temperatures and S/C ratios on CO conversion at 300 psig follows exactly the same trend as that for 150 psig and 0 psig. In addition, at any temperature the conversion at 300 psig is always greater than at 150 psig or 0 psig. For a temperature range of 450 C to 750 C the conversion varies over a smaller range for 300 psig when compared to either 150 psig or 0 psig showing that the dependence of conversion on temperature decreases with an increase in the total reaction pressure.
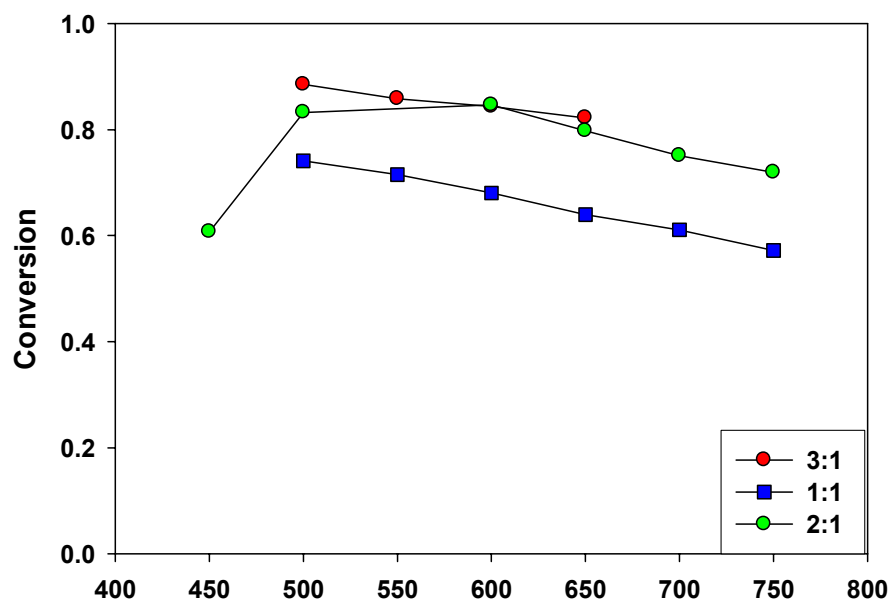
Figure 8: Effect of reaction temperature on CO conversions for various steam: CO ratios at 300 psig (0.25g HTS, Total flow = 0.725 slpm)

From Figure 9 it can be seen that for a S/C ratio of 1:1, the conversion increases with an increase in the pressure. At 500°C the conversion is 0.3890 for 0 psig, 0.6506 for 150 psig and 0.7411 for 300 psig. As the total pressure increases there is an increase in the partial pressure of the reactants that results in an increase in the overall rate of the reaction. From Figure 9 it can also be seen that the maximum conversion is reached at lower temperatures as the pressure increases. At 0 psig 600°C gives the maximum conversion, at 150 psig 550°C gives maximum conversion and at 300 psig a temperature lower than 500 C gives maximum conversion. This is because as the pressure increases the rate of the reaction increases and hence maximum conversion is reached at lower temperatures.
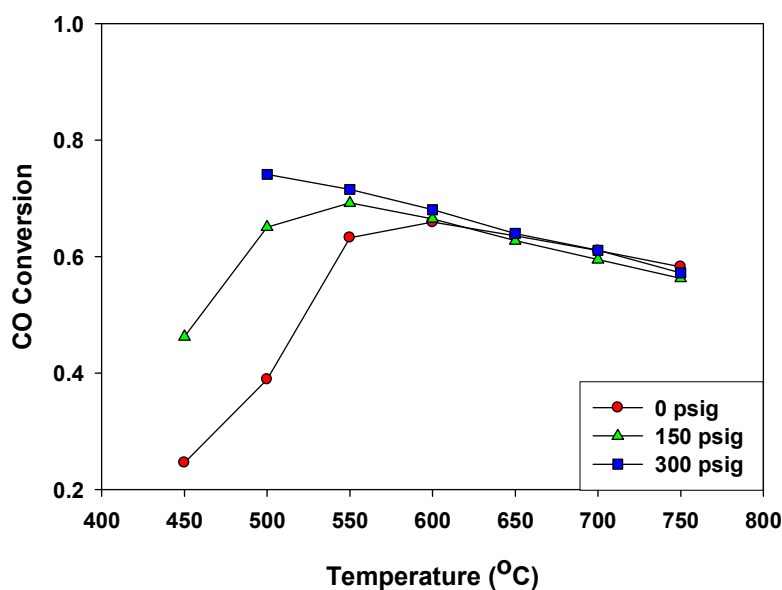
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Figure 9: Effect of reaction temperature on CO conversions for various pressures
(S/C ratio = 1:1; Total flow = 0.725 slpm)

When a steam to CO ratio of 2:1 is used the conversion with respect to temperature and pressure varies in a manner similar to a steam to CO ratio of 1:1. On comparing the Figure 5 and Figure 6 it can be seen that for all temperatures the conversion is always higher for a steam to CO ratio of 2:1. At 0 psig maximum conversion is achieved at a temperature of 650 C while at 300 psig it is achieved at a temperature of $550^{o}C$.

When a S/C ratio of 3:1 is used the conversion with respect to temperature and pressure varies similar to earlier cases of 1:1 and 2:1. On comparing Figures 9-11 it can be seen that for all temperatures the CO conversion is always higher for a S/C ratio of 3:1. At 0 psig maximum conversion is achieved at a temperature of 600º C while at 150 psig it is achieved at a temperature of 550ºC and at 300 psig it is at a temperature lower than 500ºC.
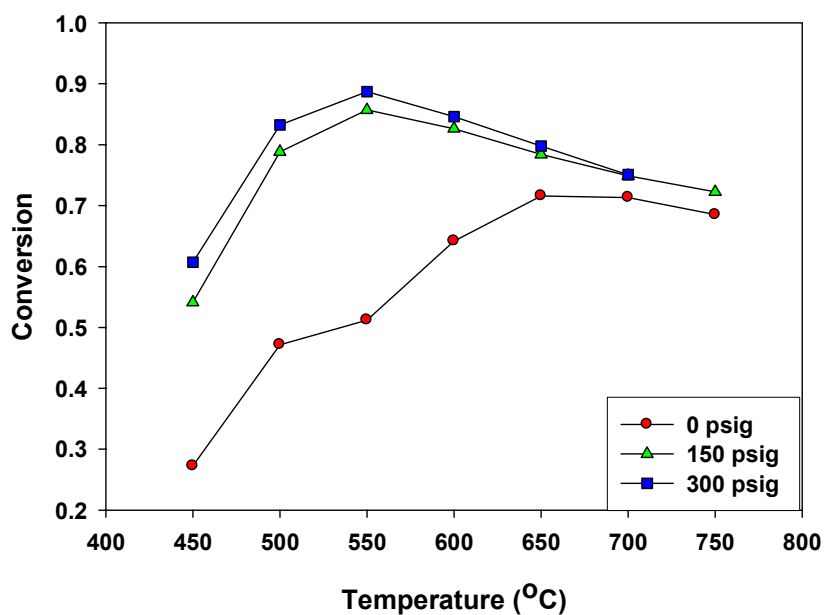
Figure 10: Effect of reaction temperature on CO conversions for various pressures
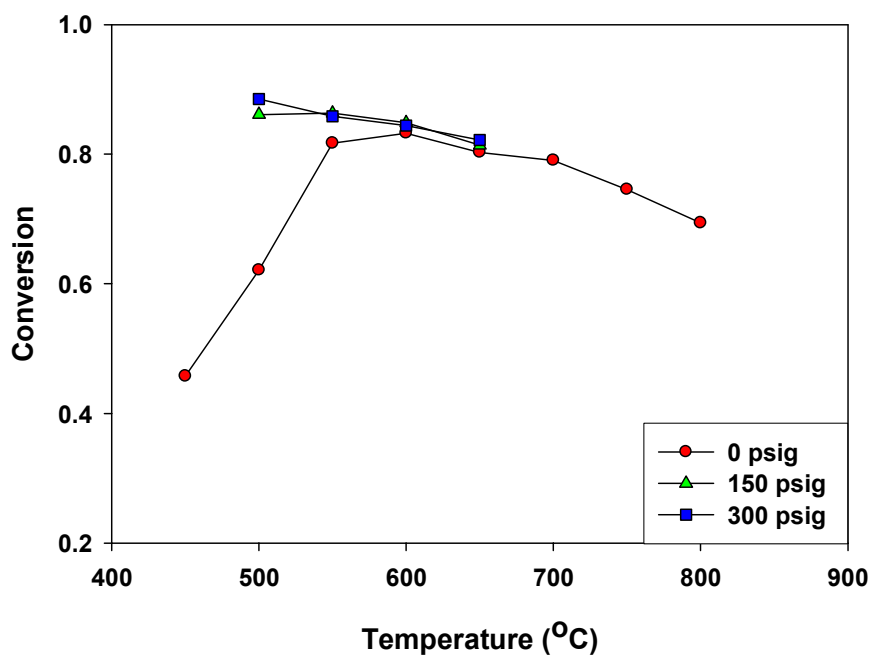(S/C ratio = 2:1; Total flow = 0.725 slpm)

Figure 11: Effect of reaction temperature on CO conversions for various pressures
(S/C ratio = 3:1; Total flow = 0.725 slpm)

Figure 12 depicts the variation in the optimal reaction temperature for maximum CO conversion with increasing total pressure and S/C ratio. It can be seen that maximum conversion is achieved at lower temperatures as the pressure increases. For a S/C ratio of 3:1, at a pressure of 0 psig maximum conversion is achieved at 600C while at 300 psig it is 500 C. This is due to the fact that with increase in the total pressure there is an increase in the rate of reaction and hence higher conversion can be achieved at lower temperatures. Besides, at lower pressures increasing the S/C ratio reduces the optimal temperature for maximum CO conversion. At higher pressures the S/C ratio does not affect the optimal reaction temperature that remains the same for all the ratios.
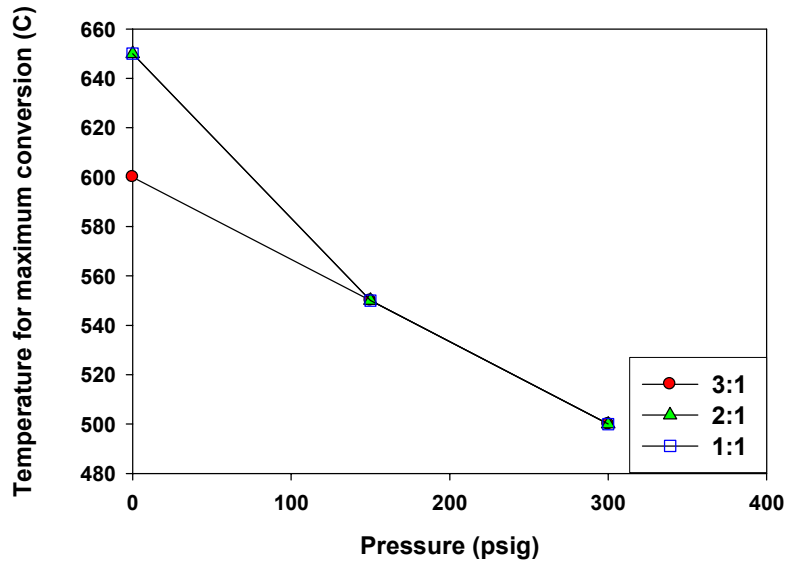

Figure 12: Variation in the optimal temperature with respect to pressure at various S/C ratios

The partial pressure ratios of the products to the reactants were computed for each case of S/C ratio and were compared with the equilibrium values obtained from HSC Chemistry v 5.0 (Outokumpu Research Oy, Finland). The observed partial pressure ratio (K_{obs}) was computed from the experimental data by obtaining the ratio of the partial pressures of the products and the reactants as per the eqn given below:

$$K_{obs} = \frac{P_{H_2}P_{CO_2}}{P_{CO}P_{H_2O}}$$

As shown in Figures 13-15 it was found that each of these values of the observed ratios (K_{obs}) was within the theoretical equilibrium value predicted by thermodynamics. From

Figure 13 it can be seen that for a S/C ratio of 1:1 the partial pressure ratio increases with an increase in the temperature till it approaches equilibrium and then decreases along the equilibrium curve. Besides, as the pressure increases the curves for the partial pressure ratios approach equilibrium more closely and this can be explained by the increase in the rate of the reaction at higher pressures.

From Figures 14-15 it is observed that when S/C ratios of 2:1 and 3:1 are used the exact same trend is observed. A comparison of Figures 13-15 yields that with an increase in the S/C ratios the system moves away from equilibrium. This is justified as an increase in one of the reactants will lead to a lowering in the partial pressure ratio (K_{obs}) and hence the deviation from equilibrium.

Figure 13: Effect of temperature on the partial pressure ratio of the products to the reactants for various pressures (S/C ratio = 1:1; Total flow = 0.725 slpm)
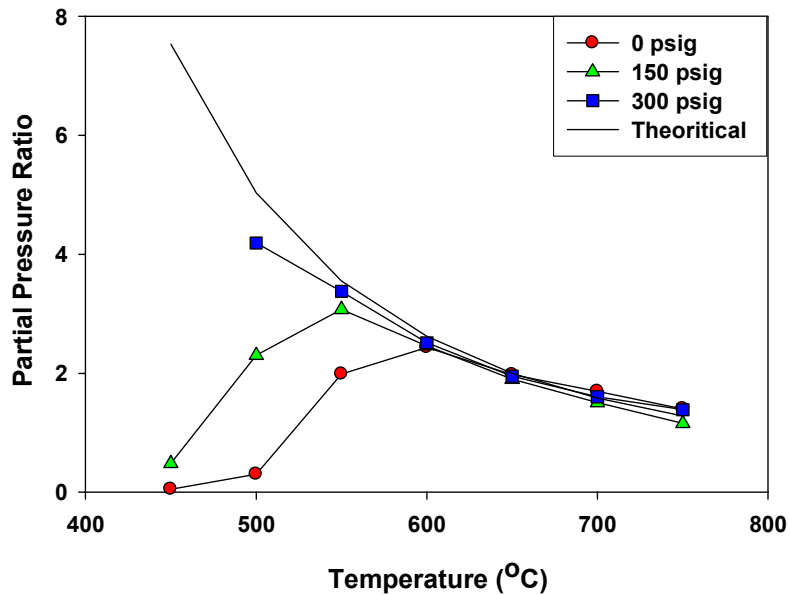
Figure 14: Effect of temperature on the partial pressure ratio of the products to the reactants for various pressures (S/C ratio = 2:1; Total flow = 0.725 slpm)

Figure 15: Effect of temperature on the partial pressure ratio of the products to the reactants for various pressures (S/C ratio = 3:1; Total flow = 0.725 slpm)
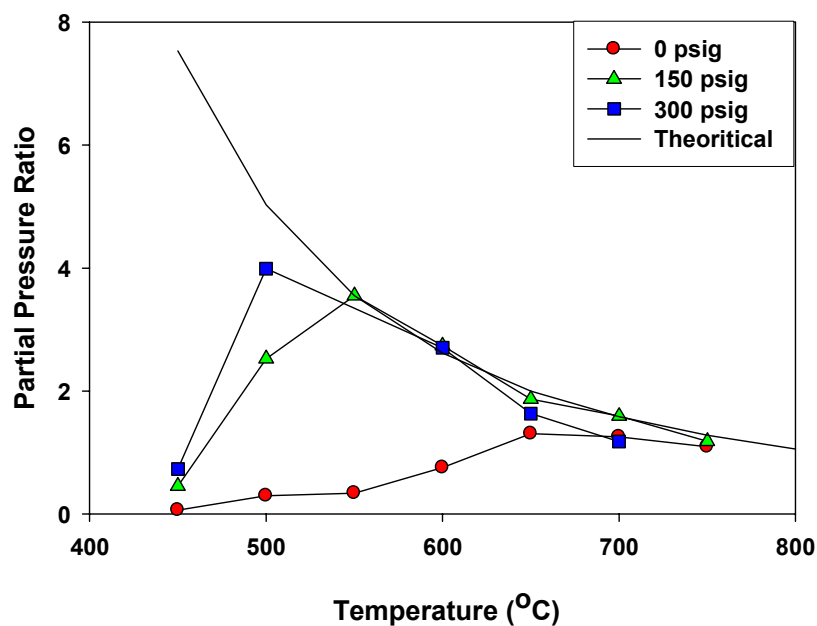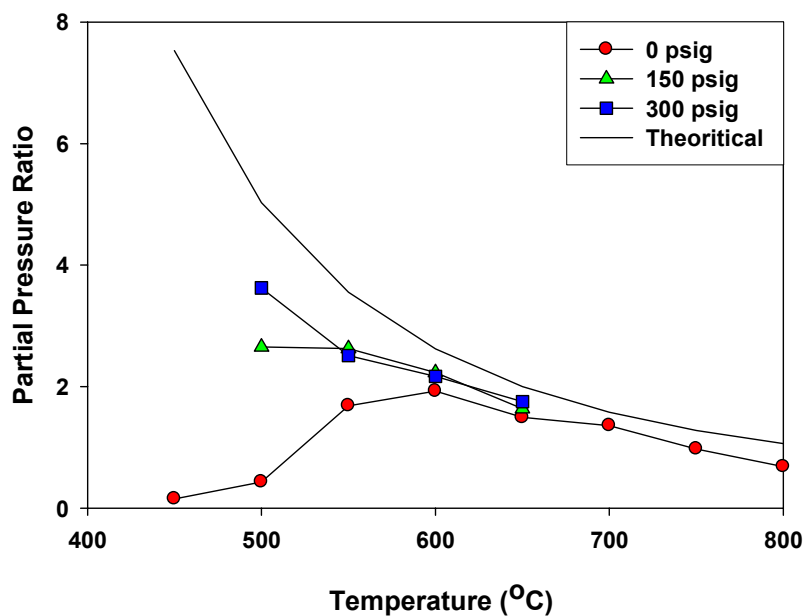
Determination of the residence of the gases through the reactor setup

The residence time of the gases through the entire reactor setup was determined for three different pressures of 0 psig, 150 psig and 300 psig. The residence time was determined by monitoring the time required for the gases to reach the analyzers. This was obtained by flowing CO through the reactor and measuring the time taken for it to reach the analyzer. This test was done at all three pressures. For 0 psig, the residence time was found to be 107 secs, for 150psig it was 300 secs and for 300 psig it was 470 secs. This residence time calculation is very essential while analyzing the data for unsteady state runs in the presence of the sorbent. This residence time for the gases is subtracted from the continuous data obtained through the analyzer based system to give the actual conversion and gas composition data.

Simultaneous WGS and Carbonation at High Pressures

Figures 16-18 illustrate the breakthrough curves for CO conversions with varying total pressure (0-300 psig) and a S/C ratio of 3:1. From Figure 16 it can be seen that at 0 psig a maximum conversion of 96% is obtained for the first 265 seconds after which there is a drop in the conversion due to the consumption of the sorbent which constitutes the breakthrough region of the curve and finally the conversion drops down to about 80% which determines the steady state catalytic activity. From Figure 17 it can be seen that at 150 psig a maximum conversion of 99.78% is obtained for the first 1168 seconds. During this initial pre break through phase both the carbonation and the water gas shift reaction are active and hence the conversion obtained is very high. During the breakthrough phase the conversion for the carbonation reaction decreases due to the progressing consumption of the sorbent which leads to a decrease in the conversion for the water gas shift reaction. In the post break through phase the sorbent has been completely consumed and hence the CO conversion is solely due to the water gas shift reaction. As seen in Figure 18 at 300 psig a maximum conversion of 99.88% is obtained for the first 1477 seconds after which the conversion in the post break through region remains steady at 86%.
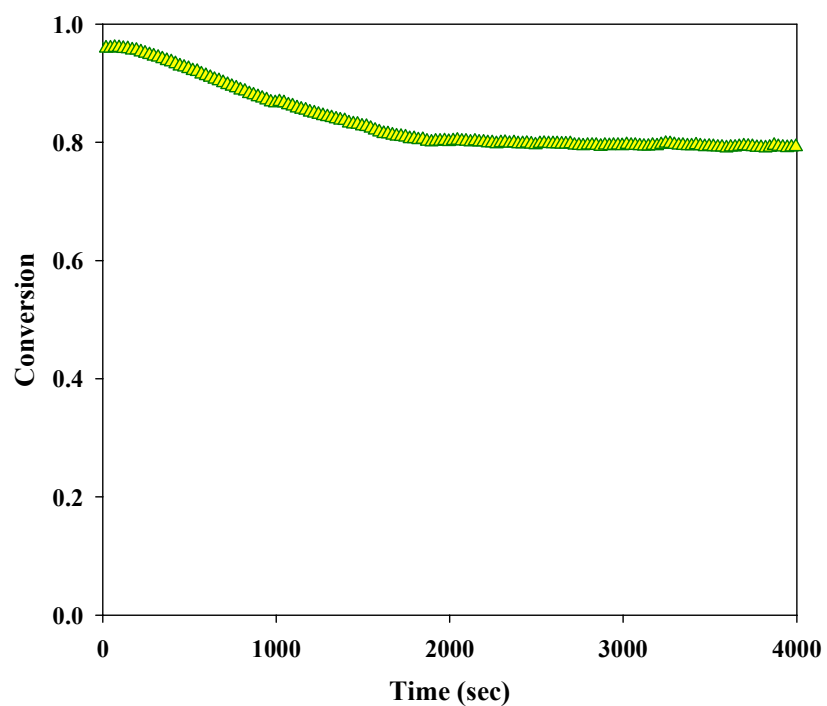
Figure 16: Break through curve for CO conversion at 650C, 0psig and S/C ratio=3:1
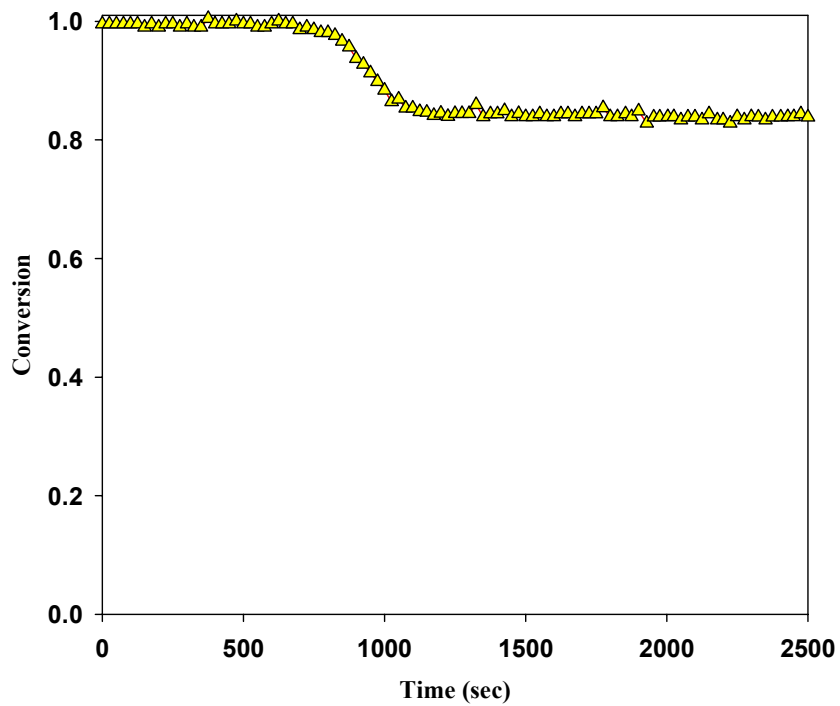

Figure 17: Break through curve for CO conversion at 650C, 150 psig and S/C ratio=3:1
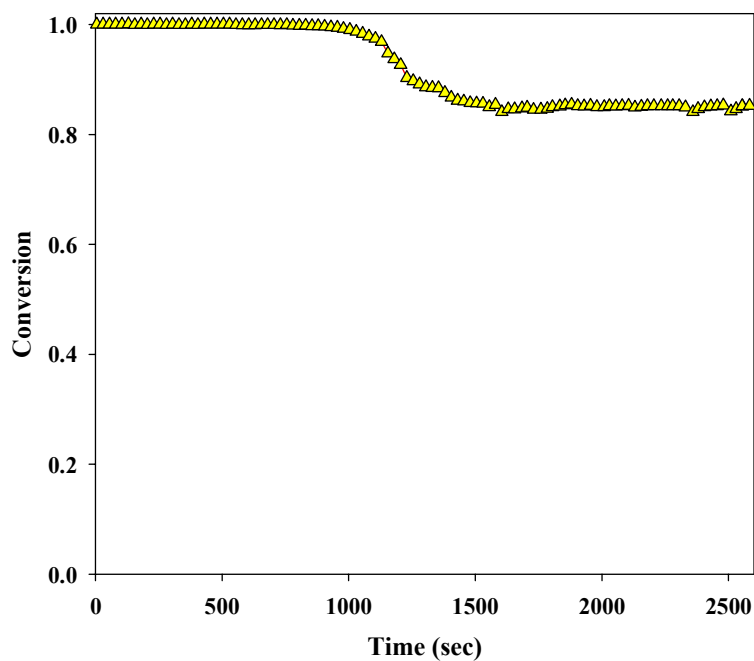
Figure 18: Break through curve for CO conversion at 650C, 300 psig and S/C ratio=3:1

Figure 19 compares the H_2 gas production breakthrough curves for increasing pressures at 650^oC and S/C ratio of 3:1. From Figure 19 it can be seen that the H_2 gas purity obtained from the outlet of reactor increases with an increase in the total pressure. At 0 psig a 95.6 % hydrogen stream is produced while at 150 psig 99.7% pure hydrogen stream is obtained for the first 1168 seconds and at 300 psig a 99.8% pure hydrogen stream is produced for the first 1477 seconds.
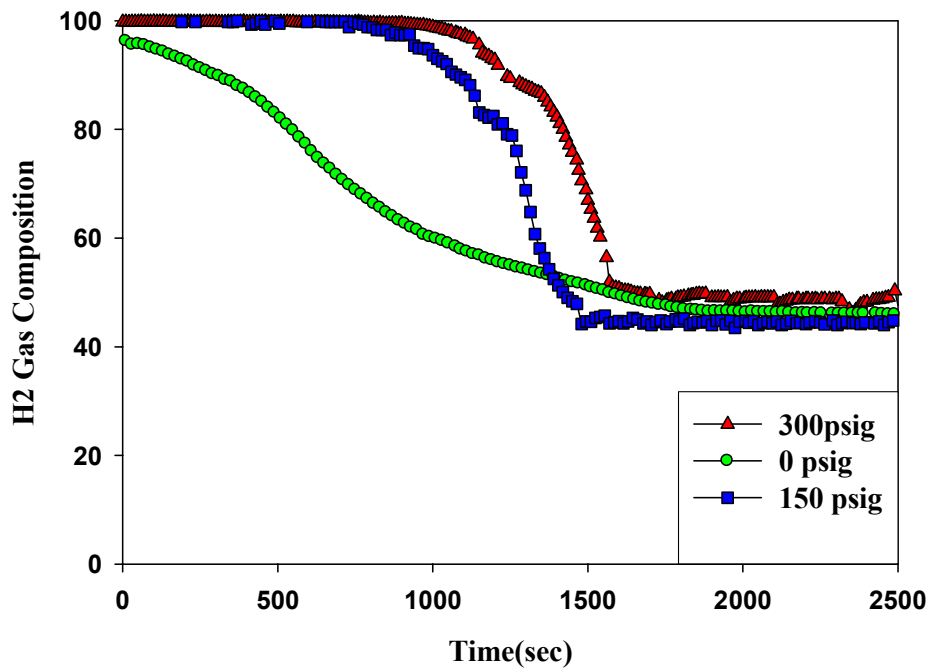
Figure 19: Effect of pressure of the hydrogen gas composition (Temperature=650°C, S/C ratio=3:1)

Figure 20 illustrates the fact that the time for which a pure H_2 stream is produced increases with an increase in the pressure. At 150 psig pure hydrogen is produced for 1167 seconds while at 300 psig pure hydrogen is produced for 1477 seconds. It can also be seen from the curve that an increase in the pressure from 0 to 150 psig results in a steeper increase in the time for which pure hydrogen is produced than when the pressure is increased for 150 psig to 300 psig. Hence it is evident that any further increase in the pressure will increase the time of pure hydrogen production by only a small amount.
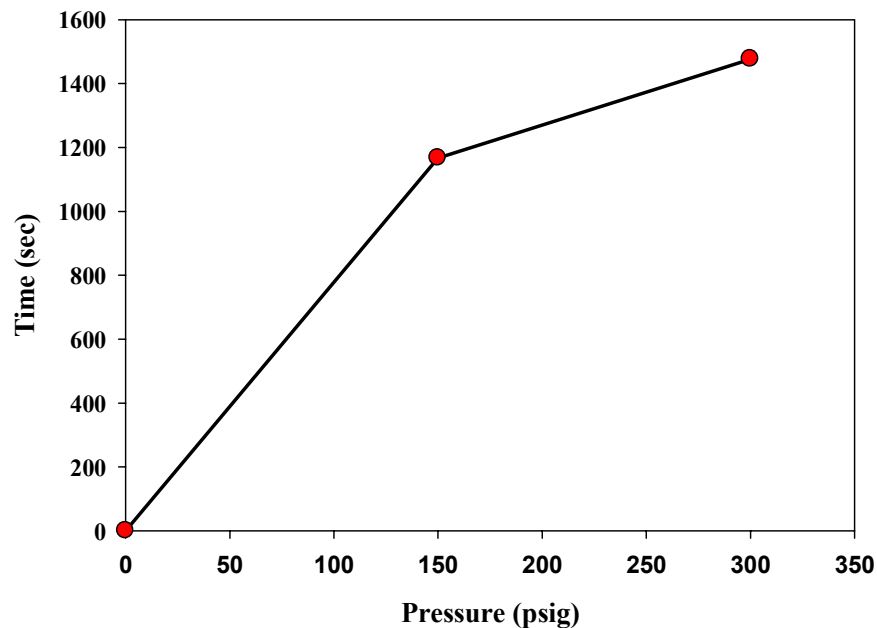
Figure 20: Effect of pressure on the time for which hydrogen production approached 100% purity

CONCLUSIONS

It was observed that the CO_2 released during the in-situ calcination causes the deactivation of the iron oxide WGS catalyst by changing the active phase of the catalyst from magnetite (F_3O_4). Intermediate catalyst pretreatment helps prevent its deactivation by reducing the catalyst back to its active magnetite (Fe_3O_4) form. Multicyclic runs, which consist of combined WGS/carbonation reaction followed by in-situ calcination with a subsequent catalyst pretreatment procedure sustains the catalytic activity and prevents deactivation. The water gas shift reaction was studied at different temperatures, different steam to carbon monoxide ratios (S/C) 3:1, 2:1, 1:1 and different total pressures ranging from 0 - 300 psig. The CO conversion was found to increase with pressure, S/C ratio and temperature upto an optimum temperature. The partial pressure ratios of the products to the reactants were computed and found to lie within the equilibrium values. The combined water gas shift and carbonation reaction was investigated at 650 C, S/C ratio of 3:1and at different pressures of 0-300 psig. At 0 psig a 95.6 % hydrogen stream is produced for the first 265 seconds while at 150 psig 99.7% pure hydrogen stream is obtained for the first 1168 seconds and at 300 psig a

99.8% pure hydrogen stream is produced for the first 1477 seconds. Hence the CO conversion increased with an increase in the pressure resulting in the production of high purity hydrogen at high pressures.

Current Status of the Project and Future Approach

The reactor setup has been suitably modified and high pressure WGSR has been conducted for various temperature, pressure and S/C ratios. Future work will involve a more detailed investigation of the combined water gas shift and carbonation reaction at various S/C ratios (3-1), temperatures (550^oC -700^oC) and pressures (0-300 psig). The reactor setup will be also modified to conduct studies that will include hydrogen sulfide (H_2S) removal during the production of hydrogen through the combined water gas shift and carbonation reactions.

Journal Papers and Patent Applications

This project has resulted in following journal paper and patent application submissions:

- Sakadjian B. S. Iyer M.V., Gupta H., and Fan L.-S. "Kinetics and Structural Characterization of Calcium-based Sorbents under Sub-atmospheric Conditions for High-Temperature CO_2 capture Process" *Ind. Eng. Chem. Res.*, *(under review)*.
- Fan, Liang-Shih; Gupta, Himanshu; and Iyer, Mahesh V. "Separation of Carbon Dioxide (CO_2) from Gas Mixtures by Calcium Based Reaction Separation (Cars-CO_2) Process*". United States Patent Application No. 11/255,099 filed on Oct 20 2005 (Continuation in Parts)*.
- Fan, Liang-Shih; Gupta, Himanshu; and Iyer, Mahesh V. "Regeneration of Calcium Sulfide to Mesoporous Calcium Carbonate using Ionic Dispersants and Selective Reclamation of Unreacted Calcium from Calcium-containing Solid Mixtures to Maximize Calcium Conversion and Prevent Recycling of Inerts" *United States Patent Application No. 60/694,702 filed in June 2005.*

LITERATURE CITED

Balasubramanian, B., Lopez-Ortiz, A., Kaytakoglu, S. and Harrison D. P., "Hydrogen from Methane in a Single-Step Process", *Chem. Engng. Sci.,* **54**, 3543-3552 (1999).

Bohlbro H., "An Investigation on the Kinetics of Conversion of Carbon Monoxide with Water Vapour over Iron Oxide Based Catalysts", second edition, Haldor Topsoe, Denmark (1969).

Gerhartz W., "Ullmann's Encyclopedia of Industrial Chemistry", A12, 5th edn., VCH, New York pp. 179-242 (1993).

Gupta, H.; Fan, L-S. "Carbonation-Calcination Cycle Using High Reactivity Calcium Oxide for Carbon Dioxide Separation from Flue Gas", *Ind. Eng. Chem. Res.* 2002, 41, 4035-4042.

Hufton, J.R.; Mayorga, S.; Sircar, S. "Sorption-Enhanced Reaction Process for Hydrogen Production." *AIChE J.* 1999, 45, 248-256.

Iyer, M. V., Gupta, H., Sakadjian, B. S. and Fan, L.-S. "Multicyclic Study on the Simultaneous Carbonation and Sulfation of High Reactivity CaO", *Ind. Eng. Chem. Res. 43,* 3939 (2004).

Keiski R. L. and Salmi T. " Deactivation of the High Temperature water-gas shift catalyst in nonisothermal conditions" Applied Catal A: General, **87** 185-203 (1992).

Lin S.; Harada M. Suzuki Y.; Hatano H. "Process Analysis for Hydrogen Production by Reaction Integrated Novel Gasification (HyPr-RING)". *Energy Conv. Mgmt.* 2005, 46, 869–880.

Lin, Shi-Ying; Suzuki, Yoshizo; Hatano, Hiroyuki; Harada, Michiaki. "Developing an Innovative Method, HyPr-RING, to Produce Hydrogen from Hydrocarbons." *Energy Conversion and Management*. 2002, 43, 1283-1290.

Lopez-Ortiz, A. and Harrison D. P., "Hydrogen Production Using Sorption Enhanced Reaction", *Ind. Eng. Chem. Res.,* **40**, 5102-5109 (2001).

Newsome D. S., "The water-gas shift reaction", *Catal. Rev. Sci. Eng.,* 21(2), 275-318 (1980).

Reithwisch D.G., Phillips J., Chen Y., Hayden T.F. and Dumesic J.A. "Water Gas Shift over Magnetite Particles Supported on Graphite: Effects of Treatments in CO/CO_2 and H_2/H_2O Gas mixtures" J. Catal., **91,** 167-180 (1985).

Roark, S. E.; Mackay, R.; Sammells, A. F. "Hydrogen Separation Membranes for Vision 21 Energy Plants". *Proceedings of the International Technical Conference on Coal Utilization & Fuel Systems*. 2002, 27 (Vol. 1), 101-112.

Rosen, M. A. "Thermodynamic Comparison of Hydrogen Production Processes", *Int. J. Hydrogen Energy*, **21 (5)** 349-365 (1996).

Rosen, M. A. and Scott, D. S., "Comparative Efficiency Assessments for a Range of Hydrogen Production Processes", *Int. J. Hydrogen Energy*, **23 (8),** 653-659 (1998).

Ross H.U. "Physical Chemistry Part I- Thermodynamics" in "Direct Reduced Iron - technology and economics of production and use" Stephenson R.L. and Smailer R. M. (eds) The Iron & Steel Society of AIME (1980).

Stiegel, Gary J.; Ramezan, Massood. "Hydrogen from Coal Gasification: An Economical Pathway to a Sustainable Energy Future". *International Journal of Coal Geology*. 2006, 65, 173-190.

Ziock, H.-J; Lackner, K.S.; Harrison, D.P. "Zero Emission Coal Power, a New Concept."
http://www.netl.doe.gov/publications/proceedings/01/carbon_seq/2b2.pdf.