

High Purity Hydrogen Production with in-situ CO₂ and Sulfur Capture

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ABSTRACT

Enhancement in the production of high purity hydrogen (H₂) from synthesis gas, obtained by coal gasification, is limited by the thermodynamics of the water-gas shift reaction (WGSR). However, this constraint can be overcome by concurrent WGSR and carbonation (of calcium oxide) reaction to enhance H₂ production. The carbonation of calcium oxide forming calcium carbonate incessantly drives the equilibrium-limited WGSR forward by removing the carbon dioxide (CO₂) product from the reaction mixture. Calcium carbonate can be separately calcined to yield a pure CO₂ stream for its subsequent sequestration and the calcium oxide recycled back. This calcium looping scheme not only improves the hydrogen yield and purity but also integrates a CO₂ management scheme in the hydrogen production process while achieving near complete conversion of the carbon monoxide reactant. This process developed at the Ohio State University can effectively and economically produce a pure H₂ stream, at high temperature and pressure, by coal gasification with integrated capture of CO₂ emissions, for its subsequent sequestration. We have identified a high reactivity patented, mesoporous calcium oxide sorbent for the *in-situ* CO₂ capture as well as H₂S removal. The morphological properties of our patented precipitated calcium carbonate sorbent (PCC) can be tailored using surface modifiers to demonstrate a high CO₂ capture capacity of about 70% by weight (~700g of CO₂/kg_{sorbent}), yield a high calcium conversion of above 80% while removing H₂S at high temperatures (700-900 °C). Experimental evidence clearly shows that this proprietary calcium sorbent (PCC) performance dominates over that of commercial limestone sorbents. This integrated “one box” process depicts the potential to achieve higher system efficiencies with lower overall footprint by combining different process units in one stage. This process removes the need for hydrogen separation membranes with integrated CO₂ and sulfur capture.

INTRODUCTION

The foreseeable enhanced use of gasification systems is based upon their higher energy to electricity efficiency, ability to convert fossil fuel energy to hydrogen, and an envisaged ease of carbon management thereby increasing their importance in a carbon constrained world. Numerous agencies are promoting the use of coal, which occurs abundantly, in gasification systems to aid hydrogen production for the envisaged hydrogen economy and to enhance domestic energy security. The major processes for hydrogen production from fossil fuels consist of steam reforming of methane (SMR), coal gasification, catalytic cracking of natural gas, and partial oxidation of heavy oils. Other processes consist of water electrolysis, thermo chemical water decomposition, biological processes, etc. (Rosen and Scott, 1998; Rosen, 1996). However, water electrolysis is not a very energy efficient process. Water gas, a mixture of CO, CO₂, H₂O and H₂, is formed by the gasification of coal by sub-stoichiometric air and/or steam. Irrespective of the initial concentration of these four gases, the reversible water gas shift (WGS) reaction gets initiated until the exact ratio of the

concentration of these gases reaches a particular equilibrium constant K_{WGS} that is a function of temperature and it reduces with increasing temperature. This means that processes aimed at converting coal-derived gas to hydrogen at high temperatures are thermodynamically restricted. While catalysts aid in achieving this equilibrium, they cannot alter the value of K_{WGS} to provide a higher hydrogen yield. An effective technique to shift the reaction to the right for enhanced hydrogen generation has been to remove hydrogen from the reaction mixture. This premise has led to the development of hydrogen separation membranes (Roark, 2005). However, membranes cannot completely remove hydrogen from the mixture. Any remaining hydrogen would dilute CO_2 after its utilization in either a fuel cell or gas turbine.

Enhanced Hydrogen Production by simultaneous WGS and CO_2 capture

Another option for driving the WGS reaction forward is to remove CO_2 from the reaction mixture by reacting it with CaO . The concurrent water-gas shift (WGS) and carbonation reactions is used 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. A simplified schematic of this approach is illustrated in Figure 1 below. This integrated “one box” process depicts the potential to achieve higher system efficiencies with lower overall footprint by combining different process units in one stage. The envisioned system has the flexibility and the potential to produce H_2 of different purity levels by reducing the amount of WGS catalyst and reducing the excess steam requirement. This process removes the need for hydrogen separation membranes with integrated CO_2 and sulfur capture. Besides, the high temperature operation increases the overall conversion and process efficiency produce a high purity hydrogen stream at high temperatures and pressures. This specific mode of operation, which precludes the use of excess steam, facilitates H_2S removal to ppm levels using the calcium oxide sorbent.

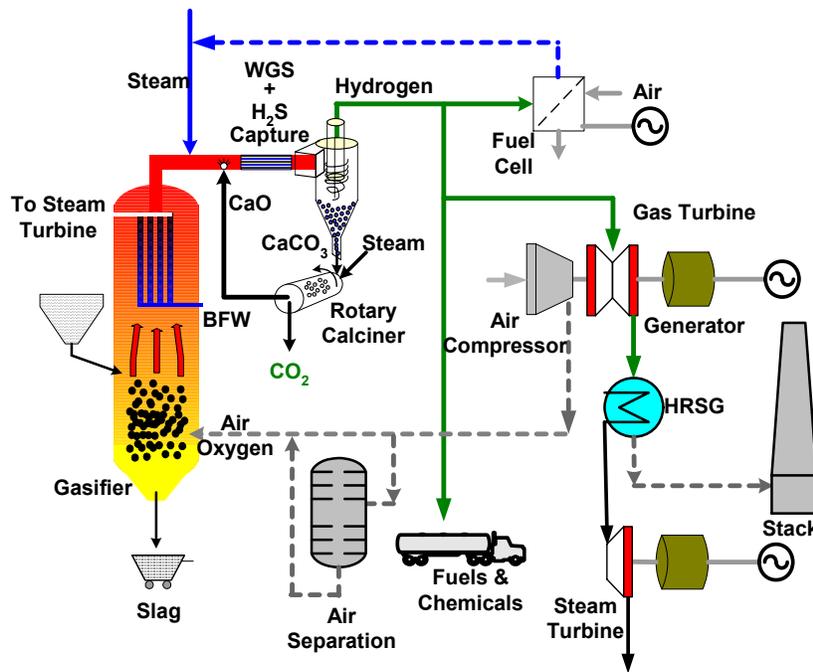
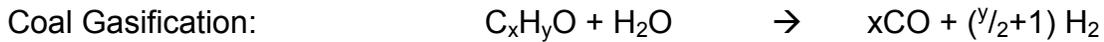


Figure 1: Simplified Flowsheet depicting integration of the current H_2 generation process in typical coal-gasifier facility (Iyer et al. 2006).

Reaction Schemes

From detailed thermodynamic analyses performed for fuel gas streams from typical gasifiers the optimal operating temperature range to prevent CaO hydration and to effect its carbonation is between 575-830 °C (Iyer et al., 2006). The various reaction schemes for coal gasification followed by the simultaneous WGS, carbonation and sulfidation reactions is described below. Also the regeneration scheme includes the calcination of CaCO₃ can be written as.

Reaction phase



Regeneration phase



While various calcium oxide precursors were tested for CO₂ capture, naturally occurring limestones were unable to react completely due to pore pluggage and pore-mouth closure. 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. In contrast, naturally occurring limestone (LC) shows poor performance with a capture capacity of 20% after 50 cycles (Iyer et al., 2004).

The enhanced water gas shift reaction for H₂ production with *in-situ* carbonation was studied using High Temperature Iron Oxide Shift (HTS) catalyst and calcium sorbents. The reactions are investigated over reaction temperatures ranging from 500-750 °C and total pressures varying from 1-20 atm. Experimental evidence clearly shows that the PCC sorbent demonstrates superior performance over that of naturally occurring limestone sorbents (Gupta et al., 2004). 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.

In addition the effects of varying the steam to carbon monoxide ratios are also investigated. Finally the effects of sulfur (H₂S) in the feed stream on the CO₂ removal and subsequent hydrogen production were explored. The incessant removal of CO₂ 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 H₂S removal by CaO.

EXPERIMENTAL

The high and low temperature water gas shift (WGS) reaction catalysts were procured from Süd-Chemie Inc., Louisville, KY. The high temperature shift (HTS) catalyst comprises of iron (III) oxide supported on chromium oxide. The details of the precipitated calcium sorbent synthesis, procurement of various natural limestone sorbents and their characterization are detailed elsewhere (Iyer et al., 2004, Gupta et al, 2004). The sorbents and catalyst were analyzed to determine their morphologies using a BET analyzer. The BET surface areas, pore volumes, and pore size distributions of the catalysts and sorbents were measured at $-196\text{ }^{\circ}\text{C}$ using nitrogen as the adsorbent in a Nova 2200 Quantachrome BET analyzer. Special care was taken to ensure that all samples were vacuum degassed at $250\text{ }^{\circ}\text{C}$ for 5 hours prior to BET analysis. An integral fixed bed reactor setup was designed, and assembled to carry out the water gas shift reactions in the presence of CaO and catalyst. The reactor design assembly used to carry out these experiments is shown in Figure 2. This setup enables us to carry out both the water gas shift reaction in the presence of CaO as well as the regeneration of the sorbent in flowing gas such as nitrogen and/or steam. 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. The setup consists of a tube furnace, a steel tube reactor, a steam generating unit, a set of gas analyzers for the online monitoring of CO , H_2 and CO_2 concentrations, a condenser to remove water from the exit gas stream and a high pressure water syringe pump. All the reactant gases are metered using Brooks Instrument Model 5850E Mass Flow Controllers. The mass flow controllers meter the gases up to an outlet pressure of 310 psig within an accuracy of 1%. The modified WGS reactor system includes a single-pass countercurrent shell-tube heat removal system as part of the steam condenser system. The coolant fluid is pure ethylene glycol entering the heat exchanger at $-3\text{ }^{\circ}\text{C}$. The coolant fluid is regulated at $-3\text{ }^{\circ}\text{C}$ through a Julabo F25 Refrigerated and Heating Circulator. The syringe pump is used to supply very accurate flow-rates of water into the heated zone of the steam-generating unit in the 0.01-0.5 ml/min range. Once the steam is generated, it is picked up by the CO/N_2 gas mixture and enters the main reactor where the sorbent/ catalyst mixture is loaded. All the lines connecting the steam-generating unit to the main reactor are heated using heating tapes. The steam generator is also packed with quartz chips in order to distribute the water drops as they enter into the heating zone. The packing is utilized in order to provide greater surface for water evaporation and to dampen out fluctuations in steam formation. The packing ultimately ensures a more continuous and constant overall gas flow rate into the main reactor and into the analyzers. A steel tube reactor is used to hold the Ca-based sorbent and catalyst, and is kept heated using a tube furnace. The sorbent loading unit of the reactor is detachable which enables easy removal and loading of the sorbent and therefore minimizes the sorbent loading time between runs. Also, the sorbent can be changed without having to cool down the entire reactor. The gas mixture entering the reactor is preheated to the reaction temperature before contacting the sorbent/ catalyst particles. The gases exiting the reactor first flow through a condenser in order to remove the moisture from the gases before flowing through a set of gas analyzers which monitor the CO , CO_2 and H_2 concentrations.

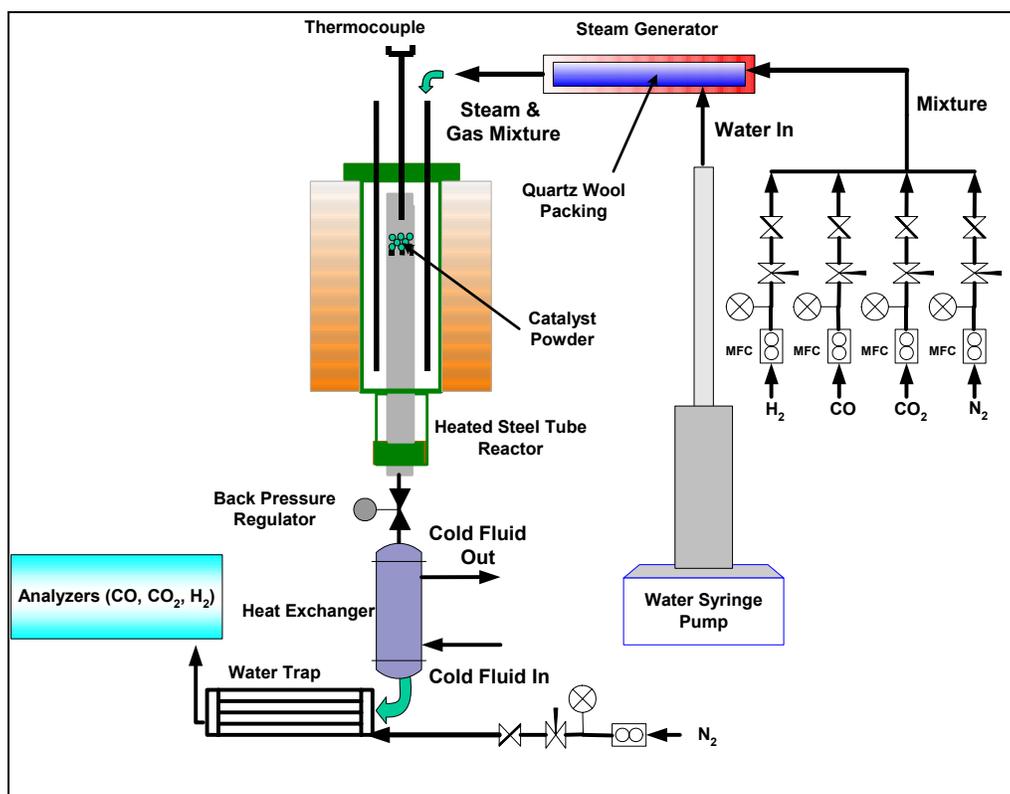


Figure 2: Integral fixed-bed reactor setup for conducting high pressure WGS and carbonation reactions

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. 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, CO₂ and H₂ gas analyzer system. 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

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. The PCC is calcined in-situ at 700°C in a stream of nitrogen until the carbon dioxide analyzer confirms the absence of CO₂ 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.

RESULTS AND DISCUSSION

High Pressure Water Gas Shift Reaction Testing

Figure 3 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 °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 °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 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.

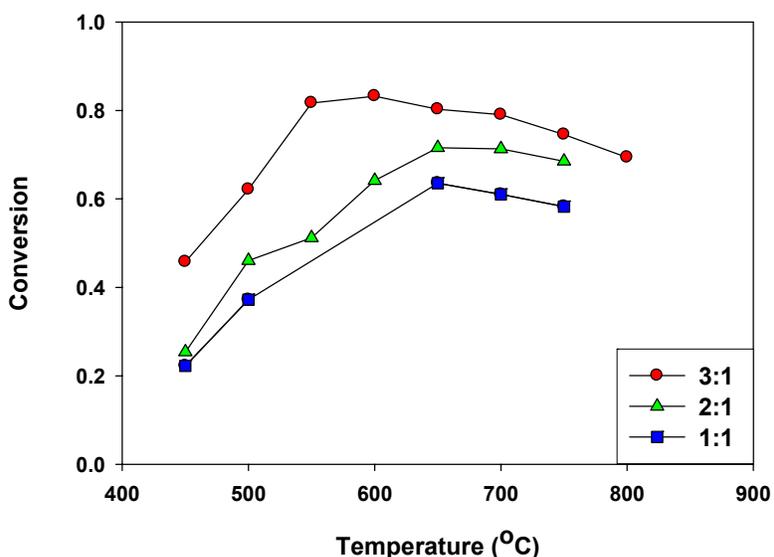


Figure 3: Effect of reaction temperature on CO conversions for various steam: CO ratios at 0 psig (0.25g HTS, Total flow = 0.725 slpm)

From Figure 3 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.

From Figure 4 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.

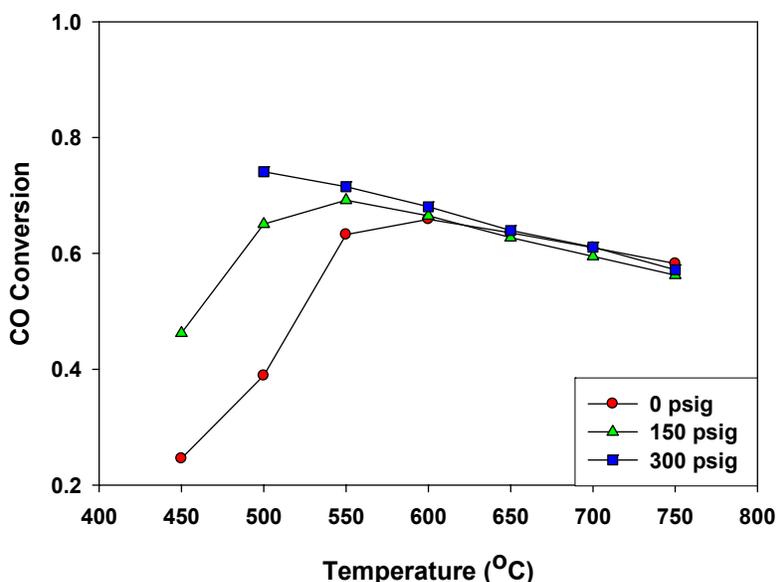


Figure 4: Effect of reaction temperature on CO conversions for various pressures (S/C ratio = 1:1; Total flow = 0.725 slpm)

Simultaneous WGS and Carbonation at High Pressures

Figures 5-7 illustrate the breakthrough curves for CO conversions with varying total pressure (0-300 psig) and a S/C ratio of 3:1. From Figure 5 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 6 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 breakthrough 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 breakthrough 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%.

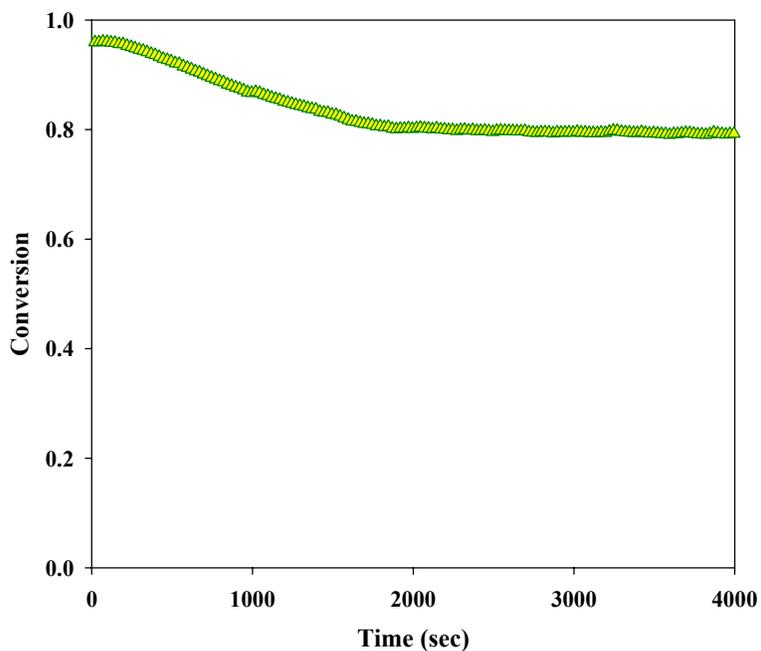


Figure 5: Break through curve for CO conversion at 650C, 0psig and S/C ratio=3:1

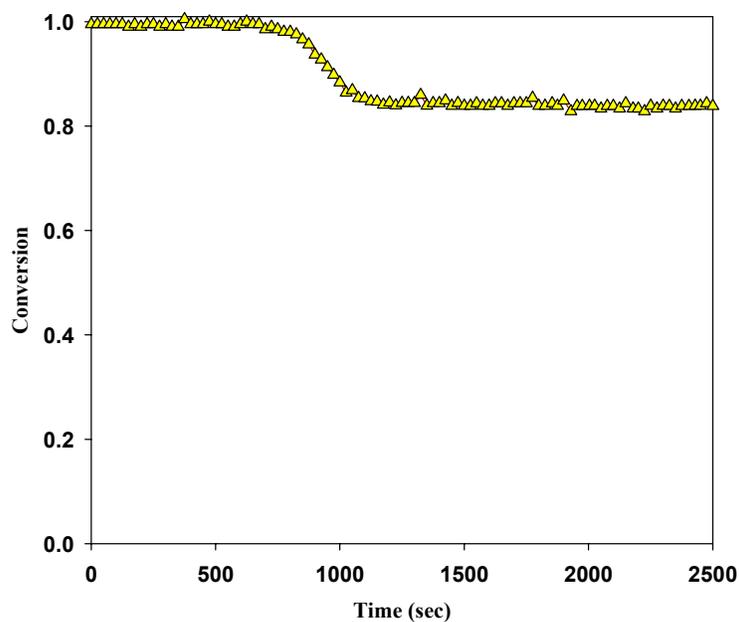


Figure 6: Break through curve for CO conversion at 650C, 150 psig and S/C ratio=3:1

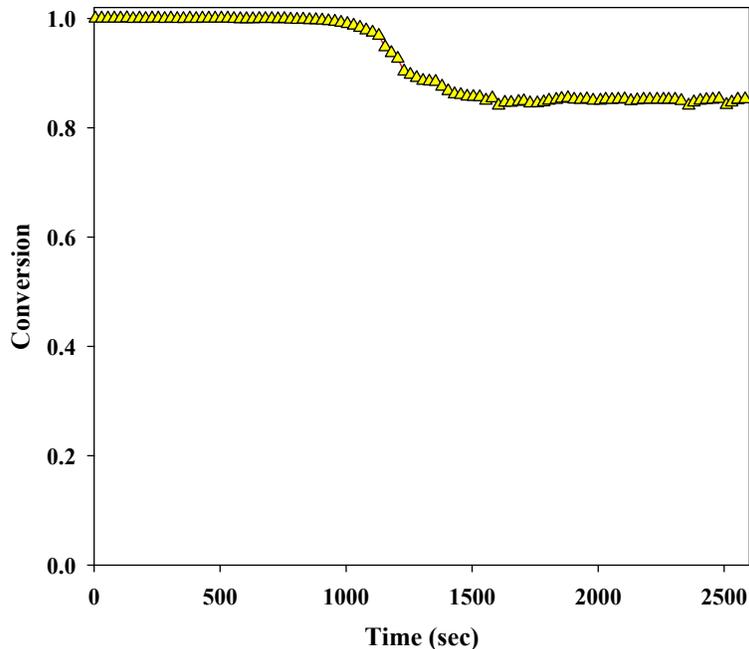


Figure 7: Break through curve for CO conversion at 650C, 300 psig and S/C ratio=3:1

CONCLUSIONS

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 3:1 and 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.

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