

# Thermodynamic Analysis for the Absorption-Enhanced-Water-Gas-Shift Reaction (AEWGS) for the Production of Hydrogen

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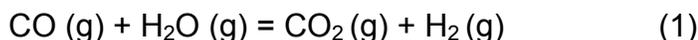
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## Introduction

Hydrogen is an important raw material for the nowadays chemical and petroleum industry. Furthermore, the use of hydrogen, as an energy carrier, has been proposed to be an ideal candidate to substitute fossil fuels as a future option for an environmentally accepted energy economy [1, 2].

An important research field has emerged in recent years, which deals with the production of high purity hydrogen for power generation applications through the use of fuel cells.

Hydrogen production traditionally has been produced from steam reforming, coal gasification and partial oxidation. These mature processes have encountered high operational costs and low efficiencies consequence of extreme operating conditions (i. e. 900°C and 15 atm). Furthermore, the hydrogen produced must be efficiently and economically transported and stored [1, 3, and 4]. In all these processes the fuel is partially oxidized generating synthesis gas (Syngas) as a main product, which is mainly composed of carbon monoxide (CO) and hydrogen (H<sub>2</sub>) in a CO/H<sub>2</sub> = 2 molar ratio [5]. This Syngas is usually sent to another separate reactor to increase its hydrogen concentration through the water gas shift (WGS) reaction, equation (1), where CO and H<sub>2</sub>O are reacted towards formation of carbon dioxide (CO<sub>2</sub>) and hydrogen.



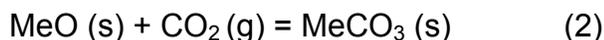
Typically, CO<sub>2</sub> is removed through a CO<sub>2</sub> liquid absorption process based on amines or by pressure swing physical absorption (PSA). Finally, water is removed and the final product consists of high purity hydrogen (99%) [6].

In recent years, new processes that combine the solid CO<sub>2</sub> capture and hydrogen production are being developed. Among all these the sorption enhanced water gas shift (SEWGS) [7] and sorption enhanced steam reforming (SER) are expected to produce important improvements in energy efficiencies of current processes making the hydrogen production through these routes an important technological advance in view of the coming hydrogen economy [8, 9]

From these two processes SEWGS is the one that less attention has received from the technological and scientific community. However, recently an important interest has been awakened in the word arena for the need of hydrogen production in mobile applications. This is due to the poor advance in development of high efficient and economical hydrogen storage technologies to meet US-DOE targets [10]. Therefore, hydrogen production and specifically through SEWGS may play an important role in the so called “onboard” hydrogen generation applications.

One of the big advantages of the SEWGS process resides in the possibility that different CO/H<sub>2</sub>/H<sub>2</sub>O molar ratios can be used as a feed for this process to produce high purity hydrogen. Among these processes that generate different CO/H<sub>2</sub>/H<sub>2</sub>O gas compositions are: coal or biomass gasification, steam reforming, Fischer Tropsch and partial oxidation.

This SEWGS process is a product of the combination of the WGS reaction, equation (1) and the simultaneous solid CO<sub>2</sub> capture, equation (2), in one single step:



where MeO represents a metal oxide subject to be carbonated at appropriate reaction conditions. At high enough temperatures ( $550^\circ\text{C} < T < 800^\circ\text{C}$ ), thermodynamically, the WGS reaction (1), is expected to occur in a homogenous fashion and therefore would not require a catalyst [7]. CO<sub>2</sub> removal during the WGS reaction produces a shift of the thermodynamic equilibrium towards more hydrogen production, thus increasing the overall process yield. Furthermore, since this process simultaneously captures CO<sub>2</sub> a high purity hydrogen stream can be produced. Additionally, a pure CO<sub>2</sub> stream can be produced during the regeneration of the carbonated metal (MeCO<sub>3</sub>) through the reverse equation (2).

Recently, a SEWGS system using Syngas/CaO as a feed was studied by Harrison et al [3], Comas et al [11], Gupta et al., [12], Stevens et al [13] and Wang et al., [14]. However, the CaO-based CO<sub>2</sub> acceptor (calcite, dolomite and huntite, used in those studies) suffered of considerable sintering problems after exposure to high temperatures and several carbonation/regeneration cycles, negatively impacting on the overall process efficiency.

Latest studies, have introduced novel CO<sub>2</sub> solid absorbents such as lithium silicates and zirconates [8, 15] and sodium zirconate [16]. These synthetic-based CO<sub>2</sub> acceptors presented as a main feature the ability to withstand several carbonation/regeneration cycles without showing important loss of capacity at high temperatures. Therefore, these novel absorbents became highly attractive to be used under the proposed SEWGS process.

Conventional WGS process is catalytically performed at temperatures lower than 340°C. However, current WGS catalysts are susceptible to suffer deactivation due to the combination of high temperatures ( $T > 400^\circ\text{C}$ ) and repeated steam exposure.

Under the proposed SEWGS process scheme at high temperatures ( $T > 400^\circ\text{C}$ ), at least in theory, it is possible for the homogeneous WGS reaction to proceed without the use of a catalyst. However, that will eventually depend on the right combination of kinetics of both WGS and carbonation reactions to insure high purity hydrogen production. Therefore, if this combination would not provide fast enough kinetics and high selectivities towards hydrogen production the use of a WGS catalyst in the SEWGS process may be needed. It is clear that a conventional WGS catalyst will not be appropriate for the high temperature demanding process conditions ( $T > 400^\circ\text{C}$ ). Therefore, the development of new a WGS catalyst under the SEWGS scheme may be needed.

Even though most of the industrial applications for hydrogen production through water gas shift (WGS) use a Syngas mixture as a feed and this research only considers CO and  $\text{H}_2\text{O}$  as raw materials in the SEWGS process scheme. This was intentionally done in order to study the effects of CO, steam and  $\text{CO}_2$  acceptor on the equilibrium thermodynamics of the SEWGS system towards hydrogen production. Therefore, the objective of the present work is to perform a thermodynamic analysis of the SEWGS process to determine the appropriate  $\text{CO}_2$  acceptor and to establish operating conditions (feed gas molar ratio CO/absorbent/ $\text{H}_2\text{O}$ , temperature, etc) to be used in the proposed process to obtain the maximum high purity hydrogen production.

### **Thermodynamic Analysis Results and Discussion**

Thermodynamic analyses were performed on CO/ $\text{H}_2\text{O}$  and CO/absorbent/ $\text{H}_2\text{O}$  systems using the HSC Chemistry 5.1 software [17]. HSC calculates the equilibrium composition of all possible combination of reactions that are able to take place within the thermodynamic system. These equilibrium calculations make use of the equilibrium composition module of the HSC program that is based on the Gibbs free energy minimization technique. The GIBBS program of this module finds the most stable phase combination and seeks the phase compositions where the Gibbs free energy of the system reaches its minimum at a fixed mass balance (a constraint minimization problem), constant pressure and temperature. This method has been described in detail elsewhere [18].

### **Water Gas Shift Reaction**

In order to verify the feasibility of the water gas shift (WGS) reaction at high temperatures a thermodynamic analysis was performed on the CO/ $\text{H}_2\text{O}$  (WGS) system and results are presented in Figure 1. A restriction of this system consists that only CO and  $\text{H}_2\text{O}$  are being considered as a feed in the reaction. Again, it is important to note that Syngas feed, which may include  $\text{H}_2$ , has not been considered in the present study. Therefore, the feed composition consisted of 2 Kmol of  $\text{H}_2\text{O}$  and 1 Kmol of CO, where all possible compound species from H, C and O elements of the database were included (with the exception of methane gas  $\text{CH}_4$ ) in all calculations. Calculation conditions used a temperature range of 0-1000 $^\circ\text{C}$  and 1 atm.

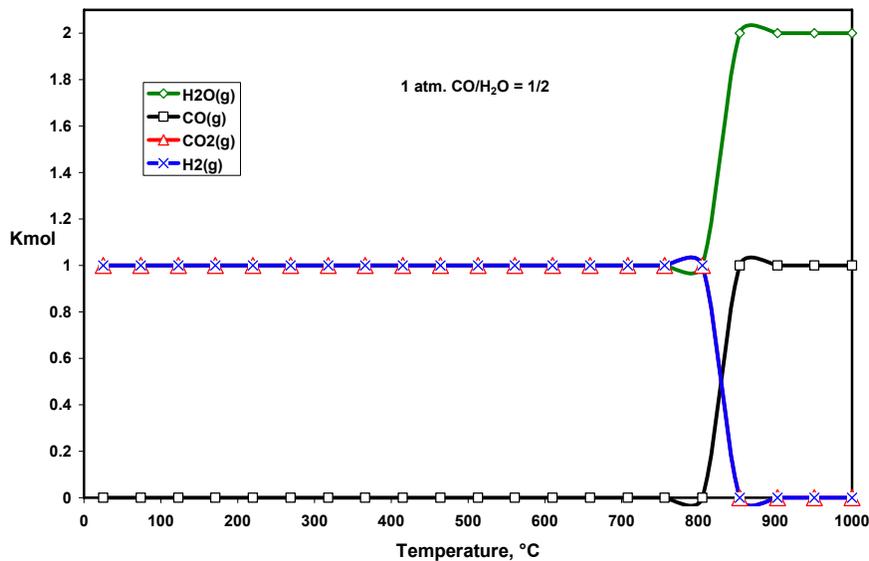


Figure 1. Thermodynamic Analysis of the CO/H<sub>2</sub>O System

According to Figure 1 it can be observed that the WGS reaction is possible to proceed from ambient temperature to 800°C. Greater temperature values result in the reverse reaction (1) to produce CO and H<sub>2</sub>O.

However, in this system the WGS has a consecutive reaction called methanation, equation (3):



The hydrogen produced by the WGS reaction (1) may react with the CO present in the system towards methane formation according to reaction (3). Therefore, contaminants of the hydrogen product may consist of CH<sub>4</sub>, CO<sub>2</sub>, and unreacted CO.

Results of the thermodynamic analysis allowing methane formation is presented in Figure 2. In this Figure the feed to the reaction system consisted of 2 Kmol of H<sub>2</sub>O and 1 Kmol of CO.

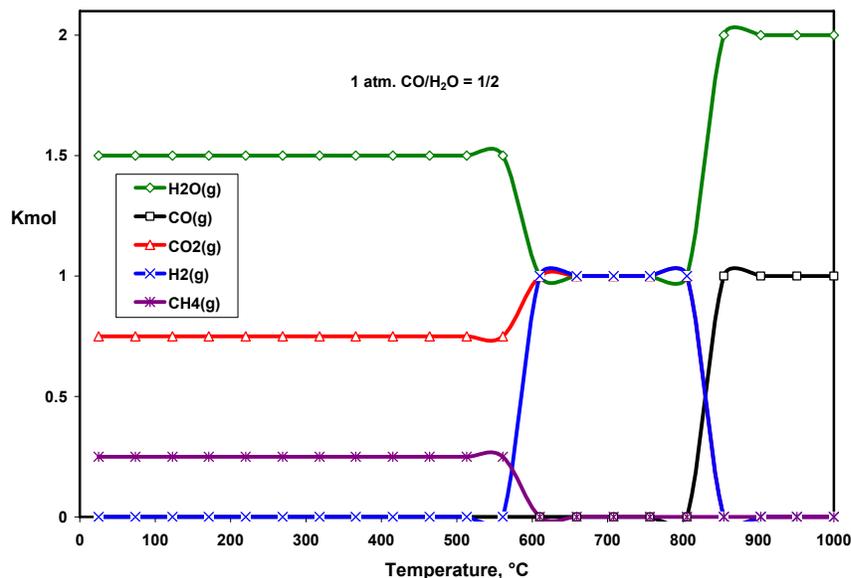


Figure 2. CO/H<sub>2</sub>O System Thermodynamic Analysis Allowing CH<sub>4</sub> Formation.

Calculations in Figure 2 were performed in a temperature range from 0 to 1000°C at 1 atm. In this plot it is evident that in the temperature range between 0-550°C the predominant reaction is methanation (3), while in the range between 550-800°C the WGS reaction (1) governs the thermodynamic equilibrium. Even though, results from Figure 2 indicate that no hydrogen is produced in the temperature range 0-500°C, it is well known that the WGS is industrially operated at temperatures between 200-450°C. This is due to the presence of a WGS catalyst (Cr-Fe/Al<sub>2</sub>O<sub>3</sub>, Cu-ZnO), which enhances the WGS rate thus inhibiting methanation. This effect is also produced when restriction of methane formation was applied during the equilibrium calculations leading to results observed in Figure 1. Finally, higher temperatures than 800°C, inhibit both reactions, since only the feed composition is present at equilibrium.

## SEWGS Reaction System

### CO<sub>2</sub> Acceptor Screening

Figure 3 shows comparative results of H<sub>2</sub> equilibrium compositions (dry basis) as a function of temperature for the SEWGS system using three different CO<sub>2</sub> solid acceptors for screening purposes: calcined dolomite (CaO\*MgO), lithium orthosilicate (Li<sub>4</sub>SiO<sub>4</sub>) and sodium zirconate (Na<sub>2</sub>ZrO<sub>3</sub>). In this analysis the molar feed composition consisted in 2 mols of water (H<sub>2</sub>O), 1 mol of carbon monoxide (CO) and 1 mol of absorbent.

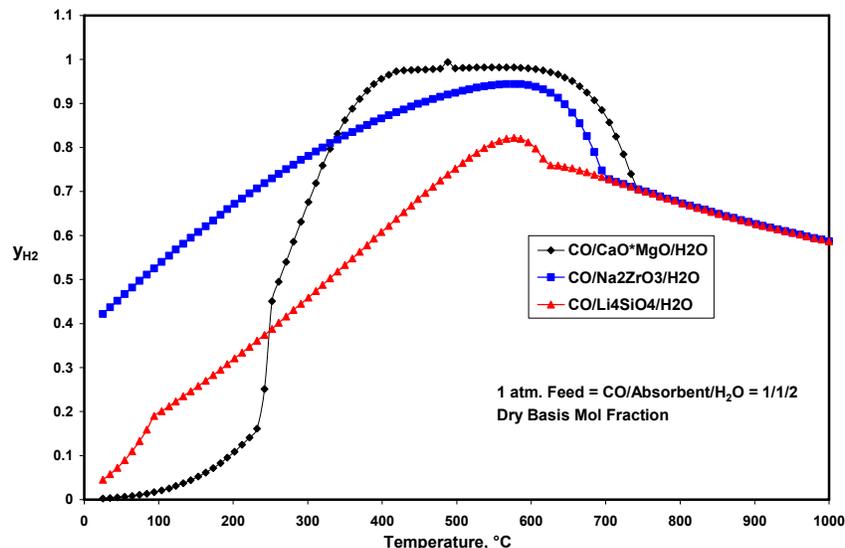


Figure 3. Equilibrium Results of the SEWGS Process using CaO\*MgO, Li<sub>4</sub>SiO<sub>4</sub> and Na<sub>2</sub>ZrO<sub>3</sub>.

In the case of dolomite the H<sub>2</sub> concentration presents a maximum value of 98% mol in the temperature range of 450-600°C. However, the high temperature needed to regenerate this CO<sub>2</sub> acceptor (850°C, 1 atm) produce sintering of the material and consequently loss of activity as the number of carbonation/regeneration cycles is increased. This ultimately is traduced in a gradual decrease of hydrogen production during experimental operation [7]. Even though, the use of Li<sub>4</sub>SiO<sub>4</sub> is reported to experimentally present high thermal stability [8], a maximum H<sub>2</sub> concentration of only 81% at 550°C is possible to be produced.

These results also show that the use of  $\text{Na}_2\text{ZrO}_3$  presents a maximum  $\text{H}_2$  concentration value of 95% at  $550^\circ\text{C}$ . Lopez-Ortiz et al. reported that this acceptor presents fast  $\text{CO}_2$  capture kinetics at this temperature ( $550^\circ\text{C}$ ) and can be regenerated at a temperature as low as  $790^\circ\text{C}$  (1 atm). They also experimentally found that  $\text{Na}_2\text{ZrO}_3$  presented high thermal stability during repeated carbonation/regeneration cycles [19].

Based on the previous screening analysis it is possible to conclude that the most suitable  $\text{CO}_2$  acceptor to be used for the SEWGS process is  $\text{Na}_2\text{ZrO}_3$ . This is due to  $\text{Na}_2\text{ZrO}_3$  combination of high purity hydrogen production (95%), relatively low regeneration temperature, high thermal stability and convenient fast  $\text{CO}_2$  sorption and regeneration kinetics.

The gas-solid reaction that takes place when  $\text{Na}_2\text{ZrO}_3$  is exposed to  $\text{CO}_2$  is represented by the following equation (4):



This reversible reaction highly depends on the temperature and  $\text{CO}_2$  concentration present in the system. Results of thermodynamic calculations of the carbonation reaction (4) performed as a function of temperature and  $\text{CO}_2$  partial pressure indicate the feasibility of the carbonation reaction in the temperature range of  $0$ - $785^\circ\text{C}$  (1 atm). Higher temperatures than  $785^\circ\text{C}$  insure  $\text{Na}_2\text{ZrO}_3$  regeneration for a  $\text{CO}_2$  partial pressure of 1 atm. Therefore, atmospheric pure  $\text{CO}_2$  would need temperatures higher than  $785^\circ\text{C}$  for reaction (4) to proceed reversibly.

### **CO/ $\text{Na}_2\text{ZrO}_3$ / $\text{H}_2\text{O}$ Reaction System**

The use of  $\text{Na}_2\text{ZrO}_3$  combined with the WGS reaction (1) causes, in principle, greater hydrogen concentrations through the *in situ*  $\text{CO}_2$  removal. The Gibbs free energy and enthalpy for the simultaneous reactions (1) and (3) result in negative Gibbs free energies from ambient temperature up to  $780^\circ\text{C}$ , which indicate that hydrogen production is favored in that temperature range. Therefore, in the proposed SEWGS system, using  $\text{Na}_2\text{ZrO}_3$  as a  $\text{CO}_2$  acceptor results in a wide temperature range where this process can be operated. However, this may ultimately depend on the overall kinetics of the combined reactions. Since, in the case that faster WGS than carbonation rates occur, this may cause lower hydrogen concentrations in the product gas due to  $\text{CO}_2$  not being fast enough removed by the acceptor. Therefore, for the SEWGS process to be (from the kinetics point of view) feasible, it is required that the carbonation reaction kinetics to be at least equal or superior to that of the WGS reaction in order to increase the hydrogen product concentration as long as the solid acceptor ( $\text{Na}_2\text{ZrO}_3$ ) is able to retain  $\text{CO}_2$  in its solid structure. This is why a suitable  $\text{CO}_2$  acceptor must present fast carbonation kinetics as it's the case of the proposed  $\text{Na}_2\text{ZrO}_3$  [16, 19]. Also the exothermic nature of the combined reactions (3) and (4) ( $\Delta H_{@700^\circ\text{C}} = -41.5$  Kcal/mol) make possible some energy integration options such as taking advantage of the sensible heat released during the carbonation step for steam generation as byproduct credit.

Regeneration of  $\text{ZrO}_2$  and  $\text{Na}_2\text{CO}_3$  back to  $\text{Na}_2\text{ZrO}_3$ , reverse reaction (4), has a drawback of highly endothermic reaction ( $\Delta H_{@790^\circ\text{C}} = +32.4$  Kcal/mol) with the

consequent need of supplemental heat to regenerate this solid acceptor. However, this regeneration process step opens the opportunity to generate a pure CO<sub>2</sub> product stream if CO<sub>2</sub> is used as a carrier gas. Also it is important to notice that temperatures greater than 800°C (specifically 790°C) are needed in order to regenerate the acceptor.

Figure 4 shows the thermodynamic analysis of the CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O system for a feed of 1Kmol of CO, 1Kmol of Na<sub>2</sub>ZrO<sub>3</sub> and 2 Kmol of H<sub>2</sub>O where all the possible species of H, Na, Zr, C and O of the 135 possible combination of compounds in the database were included for the calculations at a temperature range of 0-1000°C and 1 atm.

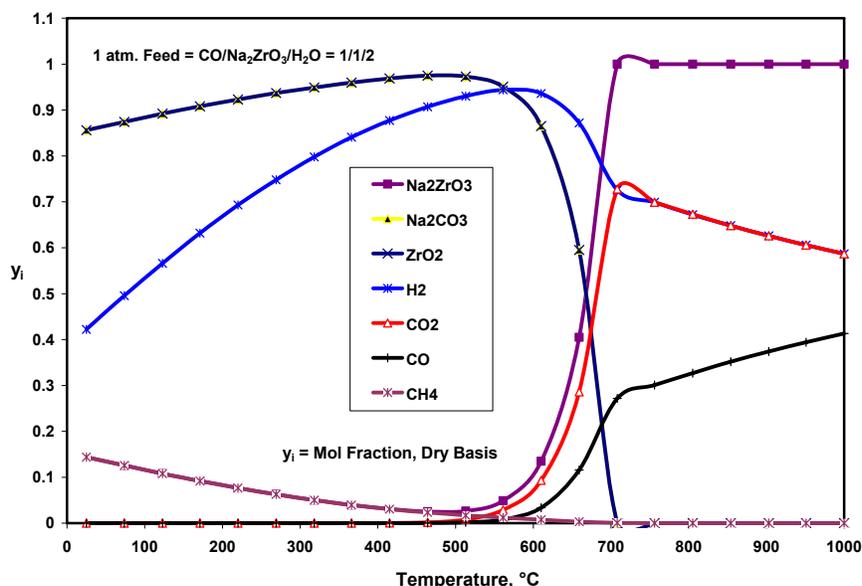


Figure 4. Equilibrium Mol Fraction as a Function of Temperature for the CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O

In this Figure, gaseous dry basis mol fractions of product species are plotted against temperature. Results indicate that for temperatures lower than 450°C, CH<sub>4</sub> and H<sub>2</sub> are the main product species with only minimal amounts of carbon oxides (0.1% CO and 0.5% CO<sub>2</sub>). The most interesting result is that for a temperature range between 500 and 600°C the hydrogen curve presents a maximum hydrogen concentration of about 97%. In this region again, carbon oxide concentrations (0.5% CO and 2% CO<sub>2</sub>) are very small. Temperature values greater than 600°C produced a gradual reduction in hydrogen concentrations combined with an increase of carbon oxides. After this point, Na<sub>2</sub>ZrO<sub>3</sub> regeneration, reverse reaction (4) starts at the corresponding CO<sub>2</sub> partial pressure of the system.

These results indicate that, in principle, it is feasible to generate high purity hydrogen as high as 97%, accompanied with carbon oxide concentrations lower than 0.6%. In particular, it is important to note that CO concentration can be as low as 90 ppmv, which makes this product-gas highly suitable to be used in a PEM fuel cell as a feed. With the only need of a polishing step needed to reduce the CO content to values below 50 ppmv, that is the actual limit for CO concentration to avoid poisoning of the Pt-base electrocatalyst [20]. Furthermore, methane and carbon oxide concentrations gradually increase with the consequent reduction of hydrogen production at temperature values greater than 550°C.

## CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O Molar Feed Ratio

In order to determine the maximum hydrogen production in the SEWGS process, a thermodynamic analysis was performed as a function of the steam concentration, while fixing the CO/Na<sub>2</sub>ZrO<sub>3</sub> ratio equal to 1.

Figure 5 shows results of dry basis hydrogen concentration (mol fraction) as a function of reaction temperature and CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O feed ratio. In this Figure, CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O feed ratio was varied in from 1/1/1 to 1/1/4.

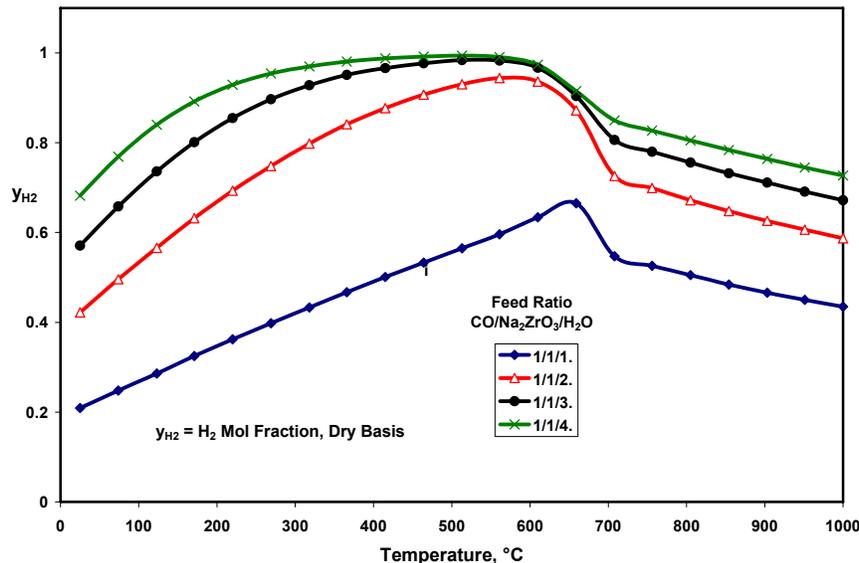


Figure 5. Water Content Effect as a Function of Temperature for the CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O System.

Results indicate that a CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O ratio equal to 1/1/2 generates the highest hydrogen concentration. Water feed lower than 2 Kmols results in a reduction of hydrogen content and the use of CO/Na<sub>2</sub>ZrO<sub>3</sub>/H<sub>2</sub>O ratio = 1/1/3 and 1/1/4 only produce marginal increases of hydrogen concentrations. Furthermore, water contents greater than 2 Kmols may produce a reduction of the system efficiency, since additional energy supply will be needed to generate the excess steam required for that purpose.

## SEWGS Reaction Process

In the proposed SEWGS process it is envisioned with the use of two fluidized bed reactors interconnected allowing the circulation and transportation of the absorbent material (Na<sub>2</sub>ZrO<sub>3</sub>) from the primary reactor, where the hydrogen production occurs, to the regenerator, where the calcination of the acceptor takes place and back to the primary reactor, closing a cyclic loop. This reaction system also allows the correct temperature control in each separate reactor. Similar designs have been used in the past for the oxidation [21] and reforming of hydrocarbons [22].

In the primary reactor (550°C, 1 atm), carbon monoxide and water vapor are fed in a molar ratio of H<sub>2</sub>O/CO = 2 and are converted to hydrogen and carbon dioxide through the WGS reaction, equation (1). Also in this reactor the CO<sub>2</sub> solid acceptor, Na<sub>2</sub>ZrO<sub>3</sub>, reacts with the CO<sub>2</sub> produced within the reactor transforming this into Na<sub>2</sub>CO<sub>3</sub> and ZrO<sub>2</sub> as solid products. According to results from Figure 3, 96% hydrogen can be produced at a temperature range from 500-600°C and 1 atm. Therefore, these

conditions are expected to govern the operation of the SEWGS primary reactor. The heat liberated by the exothermic carbonation reaction (2) ( $\Delta H_R @ 550^\circ\text{C} = -33.85$  Kcal/mol) and the WGS ( $\Delta H_R @ 550^\circ\text{C} = -8.77$  Kcal/mol) can be used to generate the needed steam feed in the primary reactor. The saturated  $\text{CO}_2$  absorbent ( $\text{Na}_2\text{CO}_3 + \text{ZrO}_2$ ) is then transferred to the fluidized bed regenerator ( $790^\circ\text{C}$ ). In order to obtain a pure  $\text{CO}_2$  product and the regenerated solid absorbent ( $\text{Na}_2\text{ZrO}_3$ ), the saturated absorbent is exposed to a pure  $\text{CO}_2$  stream.

## Conclusions

A new high purity hydrogen production and  $\text{CO}_2$  emission-free system (SEWGS) has been presented. Thermodynamic analysis of the reaction system and literature results were used for selection of the most suitable  $\text{CO}_2$  absorbent from dolomite,  $\text{Li}_4\text{SiO}_4$  and  $\text{Na}_2\text{ZrO}_3$  to insure highest hydrogen production in the SEWGS system. This analysis resulted in the selection of  $\text{Na}_2\text{ZrO}_3$  based on its highest hydrogen production, thermal stability and fast carbonation/regeneration kinetics.

Equilibrium calculations allowed to investigate the temperature and feed ratio effects on the hydrogen production through the WGS reaction and the proposed SEWGS system composed by  $\text{CO}/\text{Na}_2\text{ZrO}_3/\text{H}_2\text{O}$ .  $\text{CO}_2$  partial pressure analysis of the  $\text{Na}_2\text{ZrO}_3$  carbonation reaction indicated that this reaction is feasible in a temperature range of  $0$ - $790^\circ\text{C}$  and  $\text{CO}_2$  partial pressures of  $0$ - $1$  atm.

Thermodynamic analysis of the  $\text{CO}/\text{Na}_2\text{ZrO}_3/\text{H}_2\text{O}$  system resulted in a hydrogen gas product with 97% purity at  $500^\circ\text{C}$  and 1atm. The feed  $\text{CO}/\text{Na}_2\text{ZrO}_3/\text{H}_2\text{O}$  ratio that generates the highest hydrogen concentration was  $\text{CO}/\text{Na}_2\text{ZrO}_3/\text{H}_2\text{O} = 1/1/2$ . Even though theoretical (thermodynamic) optimal conditions were determined in the present study for the production of high purity hydrogen through the SEWGS system, it is possible that these conditions could change experimentally. This mainly due to reaction kinetic effects not accounted in the present study.

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