

## High Purity Hydrogen From Coal in a Single Step

Kanchan Mondal<sup>1</sup>, Lubor Stonawski<sup>1</sup>, Krzysztof Piotrowski<sup>2</sup>, Tomasz Szymanski<sup>1</sup>, Tomasz Wiltowski<sup>1,2</sup>

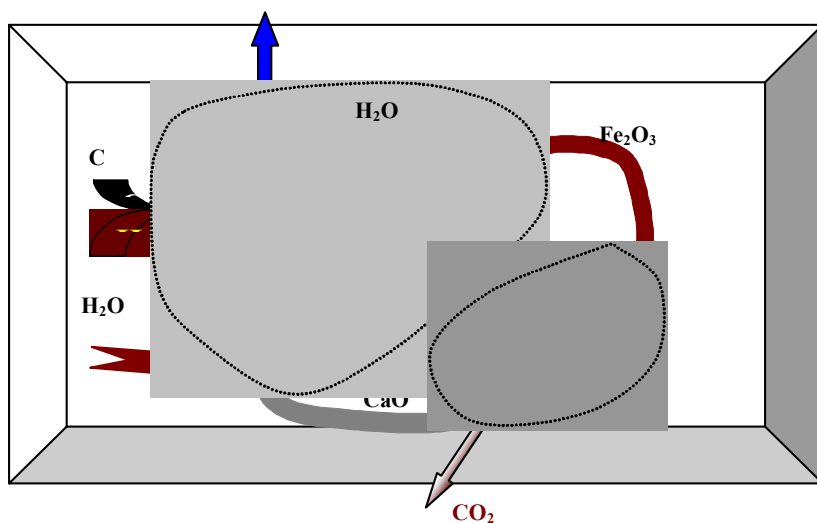
<sup>1</sup>Department of Mechanical Engineering and Energy Resources

<sup>2</sup>Coal Research Center,

Southern Illinois University, Carbondale, IL 62901

### ABSTRACT

The production of high purity hydrogen from steam gasification of coal has been investigated. The separation of carbon monoxide from hydrogen in the gasification products is achieved by carbon monoxide oxidation to carbon dioxide followed by uptake of the carbon dioxide by a suitable removal agent (Figure 1). This uptake of carbon dioxide increases the water gas shift reaction and enhances the yield and purity of hydrogen. In addition to water gas shift reaction, the oxidation is enhanced by the use of a solid oxygen transfer agent (hematite) in the hydrogen enrichment pass. Subsequently, the reduced oxygen transfer agent is reoxidized (and thus regenerated) in the presence of air and the heat liberated via the exothermic reaction is utilized to regenerate carbon dioxide removal agent.

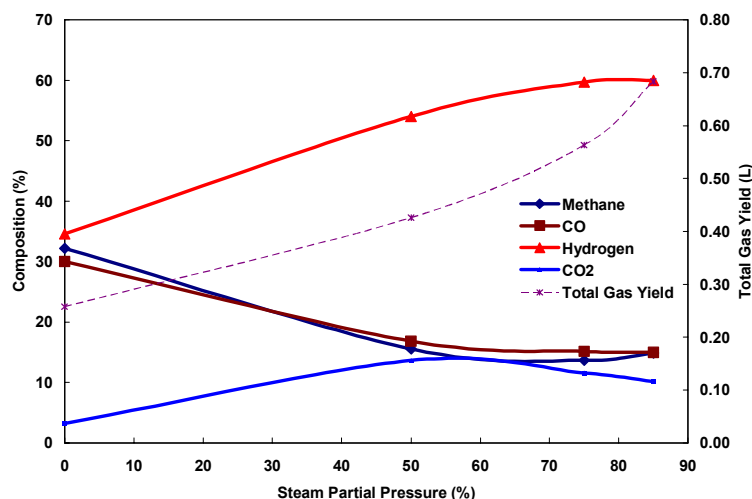


**Figure 1** Schematic of the Overall Process

In this study, the effect of process variables on coal gasification and hydrogen enrichment have been evaluated. Thermogravimetric analysis (TGA) were conducted to understand the mechanism of iron oxide reduction in syngas atmosphere and the uptake of CO<sub>2</sub> by lime. TGA experiments were also conducted to evaluate the long term effects of cycling of CaO and Fe<sub>2</sub>O<sub>3</sub>. A bench scale fluidized bed reactor was employed to study the efficacy of the simultaneous gasification-hydrogen enrichment process. The reactions were conducted in the temperature range of 670°C -900°C at atmospheric pressures. The results from the fundamental studies, the fixed bed reactor studies and the fluidized bed reactor studies are presented. Preliminary experiments were conducted in a fluidized bed reactor. 2 g of coal was added to 60 gms of solids. The solids were fluidized at 15 times the minimum fluidization

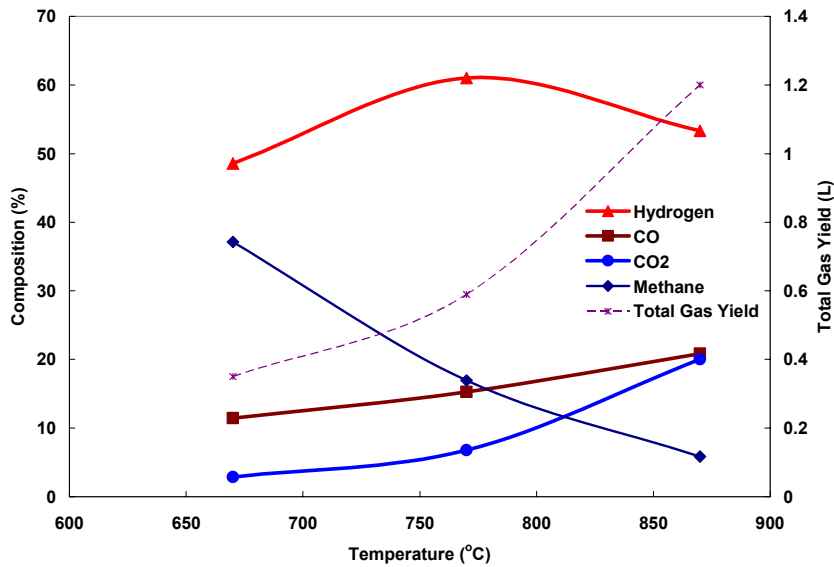
velocity (based on previous studies). Silica sand was added as the filler material to make up the solids mass. Figure 2 shows the product profile and the total gas output under different steam partial pressures at 670 °C. Only sand was used as the fluidized solids. A gradual rise in the total gas output is observed with an increase in steam partial pressure upto to 75 % steam. A sudden increase is observed when the steam pressure is increased to 85 %. The hydrogen content, however, does not change (61 %) when the steam partial pressure is increased from 75 % to 85 %. Both methane and CO decreases with the increase in the amount of steam present in the reactor. Steam reformation of the produced methane is primarily responsible for the decrease in the CH<sub>4</sub> content in the product gases while an increase in the water gas shift reaction causes the decrease in the CO content with steam pressure. This is accompanied by an increase in the CO<sub>2</sub> content which decreases at higher steam contents. The results show that 85 % steam is ideal for these studies. Higher steam partial pressures caused operational problems.

The effect of temperature on the product gas profile and the total gas output at steam partial pressure of 75 % is shown in Figure 3. The total gas produced at the end of 15 minutes increases drastically at temperatures above 770 °C. A maximum hydrogen content (61 %) was obtained at 770 °C, which decreased to 54 % at 870°C. It is known that at 900 °C, the calcinations of CaCO<sub>3</sub> is favored over the carbonation of CaO. This results in the reduction of CO<sub>2</sub> removal capacity of the CaO and is reflected in the sudden increase in the CO<sub>2</sub> content at 870 °C. Rates of methane reformation reactions, on the other hand, was observed to increase. Nonetheless, the high gas output (due to coal conversion) at 870 °C meant a higher yield of hydrogen and has been considered suitable for further studies.

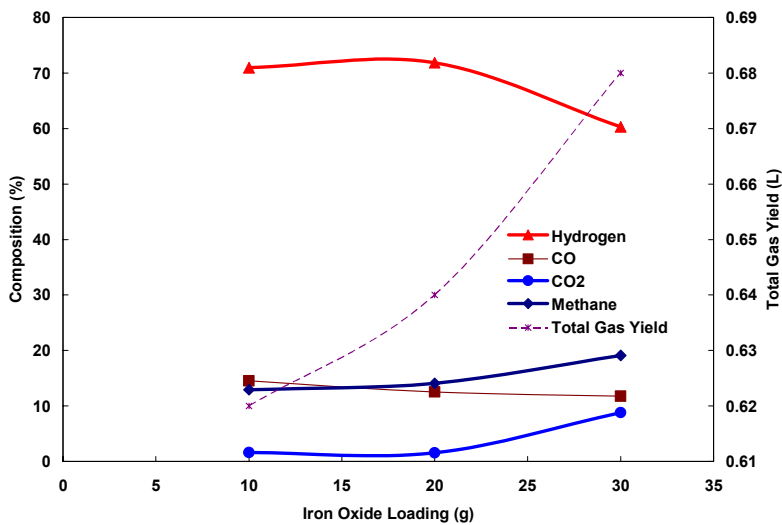


**Figure 2 Product characteristics as a function of steam partial pressure in a fluidized bed reactor**

Figure 4 contains the data on the product profile and the total gas output as a function of iron oxide loading at 770°C and 85 % steam. 40 g of CaO was used for these studies. It is observed that the hydrogen content decreased by 14 % on increasing the iron oxide content in the reactive mixture from 20 g to 30 g. A maximum of 70 % hydrogen was observed when 20 g of iron oxide was employed. On the other hand, the total gas output increased by only by 6 %. In addition the CO<sub>2</sub> and CH<sub>4</sub> contents were also observed to increase at the highest iron oxide loadings of 30 g. Thus 20 gms of iron oxide was found to be suitable for enhancing the conversion of CO to CO<sub>2</sub>.

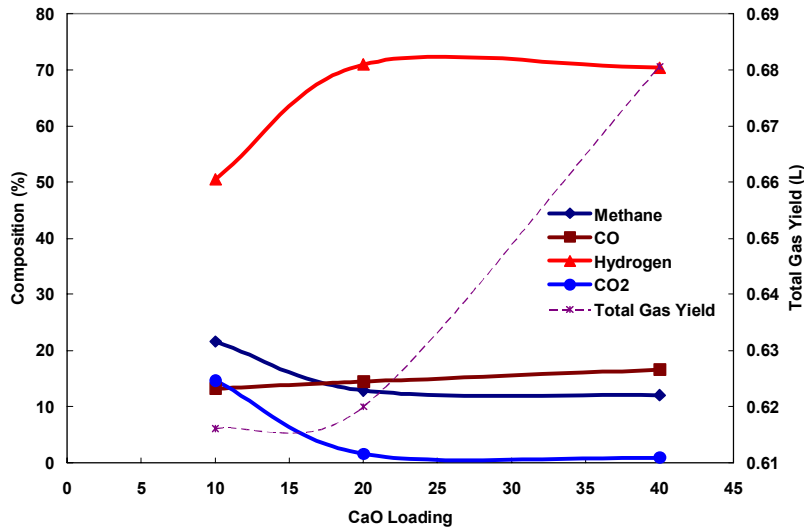


**Figure 3 Product characteristics as a function of temperature in a fluidized bed reactor**

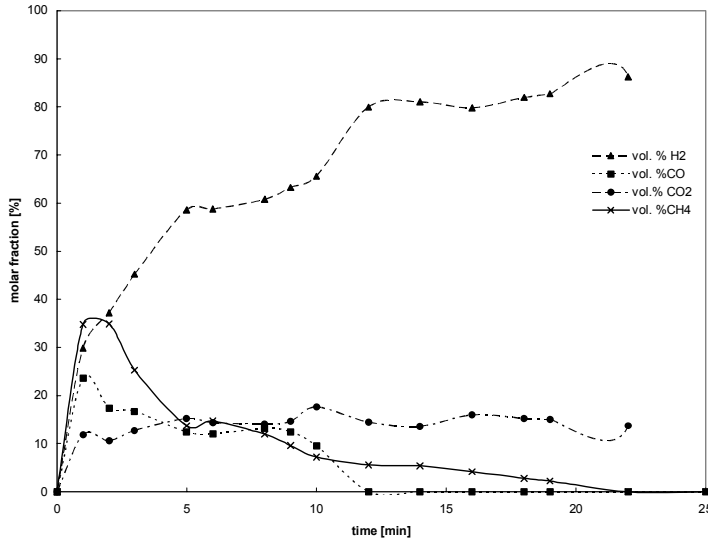


**Figure 4 Product characteristics as a function of iron oxide loading in a fluidized bed reactor**

The results from experiments conducted with 20 g of iron oxide and varying loads of CaO are shown in Figure 5. The temperature in the reactor was maintained at 770° C and 85 % steam was introduced for these experiments. Increasing the CaO loading was observed to have a positive effect on the hydrogen purity. As observed in the Figure, increasing the CaO loading from 10 to 20 gms resulted in 40 % enhancement in purity (from 50 % to 70 %). Simultaneously the CH<sub>4</sub> and CO<sub>2</sub> in the product gases is observed to decrease. Further increase in the CaO content did not significantly enhance the hydrogen purity. However, it improved the coal gasification characteristics by increasing the gas output by an additional 10 %.



**Figure 5** Product characteristics as a function of CaO loading in a fluidized bed reactor



**Figure 6** Typical product distribution as a function of time in a fluidized bed reactor

The following results were obtained from this investigation

- 1) Thermodynamic analysis shows that this process can achieve more than 98 % pure hydrogen.
- 2) Both iron oxide and calcium oxide can be used and then generated without a significant loss of activity
- 3) Iron oxide oxidizes hydrogen at a much faster rate than CO (10 – 20 times).
- 4) Lower temperatures (> 700 °C) result in higher CO<sub>2</sub> removal.
- 5) The ratio of CaO in the bed to the coal charge should be maintained around 50.
- 6) The ratio of iron oxide to coal charge should be maintained around 2 – 5.
- 7) The temperature in the reaction zone should be between 800 – 850 °C. Coal conversion increases with temperature.
- 8) The steam partial pressure should be as high as operationally possible.

- 9) Boudouard reaction takes place even with inert solids.
- 10) The CO and H<sub>2</sub> purity is decreased when syn gas is passed through an inert bed of sand. This is primarily due to the CO disintegration to C and CO<sub>2</sub>. The C then reacts with H<sub>2</sub> to form CH<sub>4</sub>.
- 11) The presence of CO<sub>2</sub> initiates dry reforming of methane.
- 12) Iron oxide also aids in demethanation
- 13) The presence of CaO aids methanation only to a certain loading. If the loading is too high then the CH<sub>4</sub> molecules are not in the proximity of the CO<sub>2</sub> released temporarily on the CaO surface.
- 14) Low residence times and high CaO:Fe<sub>2</sub>O<sub>3</sub> ratios or large residence times and low CaO:Fe<sub>2</sub>O<sub>3</sub> ratios are desirable to maximize H<sub>2</sub> purity and yield.
- 15) The optimal conditions in the fluidized bed reactor (within the range of the experiments) are **40 g of CaO, 20 g Fe<sub>2</sub>O<sub>3</sub>, 850 °C, and 85 % steam (Figure 6)**.