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Milestone Report

Biological Water-Gas Shift Conversion of Carbon Monoxide to Hydrogen

Milestone Completion Report

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Wade A. Amos
National Renewable Energy Laboratory

Milestone Report for the U.S. Department of Energy HFCIT Program
Process Analysis Task
September 2003 – Final Version

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1.0 Introduction

The purpose of this report is to summarize the results of research and economic analysis on the biological water-gas shift process being studied at the National Renewable Energy Laboratory. The report describes some of the technical issues regarding the process, addresses some claimed benefits of the process and presents some economic results from economic studies using different process configurations.

While the technical feasibility of the biological water-gas shift process has been demonstrated, there are only limited cases where replacing conventional catalytic reforming with a biological alternative makes economic sense.

2.0 Conventional Catalytic Water-Gas Shift

The water-gas shift (WGS) reaction is used to convert carbon monoxide (CO) to carbon dioxide (CO_2) and hydrogen (H_2) through a reaction with water (H_2O).

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad (1)$$

The reaction is exothermic, which means the reaction equilibrium shifts to the right and favors the formation of the H_2 and CO_2 products at lower temperatures. At higher temperatures, the equilibrium shifts to the left, limiting complete conversion of CO to H_2.

The reaction is the basis for most of the industrial H_2 produced in the world from methane (CH_4) in natural gas through steam-methane reforming. Methane is first reformed to a mixture of CO, CO_2 and H_2 in the presence of steam over a nickel catalyst. A conventional water-gas shift reactor then uses a metallic catalyst in a heterogeneous gas-phase reaction with CO and steam. Although the equilibrium favors formation of products at lower temperatures, the reaction kinetics are faster at elevated temperatures. For this reason, the catalytic water-gas shift reaction is initially carried out in a high-temperature shift (HTS) reactor at 350-370°C. Conversion in the HTS reactor is limited by the equilibrium composition at the high temperature. To achieve higher conversions of CO to H_2, the gas leaving the HTS reactor is cooled to 200-220°C and passed through a low-temperature shift (LTS) reactor (Kirk-Othmer, 1995; Ulllman's, 1989). Approximately 90% of the CO is converted to H_2 in the first HTS reactor and 90% of the *remaining* CO is converted in the LTS reactor.

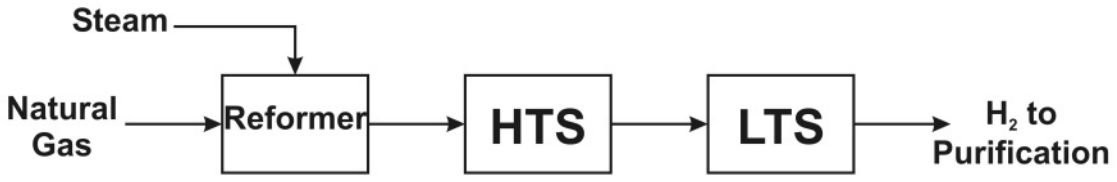

Figure 1 – Catalytic WGS process.

Before pressure-swing adsorption (PSA) purification came into wide use, the preferred hydrogen purification method was HTS, LTS, CO_2 scrubbing/absorption, followed by a methanation reaction to remove any remaining CO:

$$CO + 3\ H_2 \rightarrow CH_4 + H_2O \qquad (2)$$

Because the CO consumes part of the H_2 product during the methanation reaction, H_2 production systems using methanation steps would include a LTS reactor to convert as much CO to H_2 as possible before methanation. Otherwise, large amounts of the product H_2 would be consumed during methanation.

With PSA, both the CO_2 and un-reacted CO are adsorbed, producing hydrogen purities over 99.9%. Because the CO is removed to very low levels (less than 10 ppm), the methanation step is no longer needed. The CO_2 scrubbing step can also be eliminated with PSA purification, which simplifies the system and reduces the overall system cost. Without methanation, there is less need to remove CO before the PSA, so the LTS reactor is sometimes eliminated to reduce capital costs. If desired, the HTS reactor operating temperature can be adjusted to balance higher conversion versus a larger reactor size. Eliminating the LTS reactor results in slightly lower hydrogen yield, but this is balanced against lower capital costs.

3.0 Biological Water-Gas Shift Reaction

The organism *Rubrivivax gelatinosus* CBS is a non-sulfur, purple photosynthetic bacteria that is capable of performing the same water-gas shift reaction under anaerobic conditions, atmospheric pressure and an ambient temperature of 25°C. Wolfrum (2003) has shown the organism can perform the shift reaction at pressures up to 4 atmospheres absolute pressure. It is believed that the organisms can be effective at even higher pressures with increased cell loading to the reactor, but these tests have not been performed.

The organism uses the biological WGS reaction as a means to obtain energy to maintain metabolic processes and grow. In the wild, *Rx. gelatinosus* CBS can obtain energy through photosynthesis, aerobic heterotrophic metabolism (e.g., acetate or malate) and anaerobic fermentation pathways. The biological WGS represents an anaerobic, dark-phase pathway. This pathway produces much less energy for metabolic activities as compared with either the photosynthetic or aerobic pathways. This lower energy production results in a slower cellular growth rate which increases the time needed to reach steady-state, but reduces the amount of waste cell mass produced by the biological WGS process once it is operating. The benefit of the dark-phase reaction is that the biological WGS system can be operated in a conventional closed reactor, similar to trickling filters used for wastewater treatment—no expensive photo-bioreactor is required.

The energy obtained through the biological WGS is obtained by transferring electrons from CO to H_2O in the following coupled reactions:

$CO + H_2O \rightarrow CO_2 + 2e^- + 2H^+$ (3)

$H^+ + 2e^- \rightarrow H_2$ (4)

$CO + H_2O \rightarrow CO_2 + H_2$ (5)

This reaction produces 4.46 kcal/mol CO reacted. For comparison, the aerobic conversion of 1 mol of CO to CO_2 would produce 61.1 kcal/mol CO.

$CO + O_2 \rightarrow CO_2$ (6)

The aerobic reaction would result in more energy to the organism, resulting in more cell growth per mol CO but no H_2 would be produced under aerobic conditions. It is desirable to minimize cell growth so less excess cell waste is produced, but if the growth rate is less than the natural death rate, the reactor operation will not be stable. In any biological system, cells are continually dying. Many of the nutrients in the dead cells are recycled when the cells lyse or split, but a portion of the cell remains as refractory or inert material that cannot be "re-digested" and used for new cells. (This can be thought of as the "teeth and bones" of the cells—insoluble minerals that cannot dissolve.) In many batch systems, not enough refractory material builds up to affect operation of the system, but in continuous systems, the accumulation of this refractory material must be removed.

Cell growth rates are also important for reactor startup and recovering from process upsets. Initial reactors can be "seeded" or inoculated with a sterile culture, but most of the cells used to convert the CO to H_2 come from new cell growth after the inoculation. The higher the growth rate, the faster the reactor will reach full production capacity. Upsets in pH or temperature can also result in a loss of biological activity due to damage to or death of the cells. Higher growth rates would allow quicker recovery in the reactor. One possibility during startup is to provide the *Rx. gelatinosus* CBS with "food" in the form of acetate, malate or a low-cost sugar source (i.e., corn-steep liquor) and provide oxygen to temporarily boost the energy production and growth rate of the cells. Once the oxygen is removed, there will be some delay while the cells produce new enzymes for their anaerobic pathway, but the cells will eventually switch back to using CO for generating energy and H_2.

One concern with using this approach to boosting cell growth is that there are many organisms that could potentially use acetate and oxygen for growth. If there is any contamination, other cells may grow faster than the *Rx. gelatinosus* CBS and take over the reactor. When switched back over to CO, little or no H_2 would be produced. There are believed to be fewer organisms that can grow in the presence of only CO, so startup on CO may be a safer approach, even though it may take more time.

If reactor upsets can be avoided, it should be possible to run the reactor for months without the need to shutdown and restart the reactor. At the same time, the process must be designed so if there is any contamination, the system can be quickly sterilized and re-inoculated. Ideally, if growth conditions can be determined that favor *Rx. gelatinosus* CBS over most other organisms, contamination would not be a concern because *Rx.*

gelatinosus CBS would dominate and the other organisms would die off. Currently, these growth conditions have not been identified, but laboratory-scale reactors have been run for months with little or no loss in H_2 production capacity. One other possibility would be to transfer the genes responsible for the biological WGS reaction into another organism that is easier to culture and control. This molecular engineering approach would, however, take significant effort.

4.0 Bio-Energetics of the Biological WGS Reaction

Even without knowing the exact metabolic pathways and enzymes involved in the biological WGS reaction, the overall free energy change of the chemical reactions can be used to determine the maximum amount of energy the *Rx. gelatinosus* could obtain from performing the biological WGS. By assuming an average energy efficiency of 60% for biological processes (Gossett, 1995), it is possible to estimate the amount of cells produced per g of CO fed to the bacteria. Under anerobic conditions, *Rx. gelatinosus* should produce 1.4 g of cells per 1 mol of CO. When growing aerobically on O_2 and acetate, the cell yield would be 2.0 g of cell mass per mol of acetate.

What bio-energtic calculations provide is an estimate of the yield for any proposed biological reaction. Bio-energetics also do not provide any information on the kinetic rates of biological reactions. Rates depend upon the efficiencies of the enzymes involved and reactions may not occur at all if the required enzymes are not present in the organism. Bio-energetics can also help determine if reactions are likely to become more favorable or less favorable depending on environmental conditions, such as pH, temperature or feed concentrations. (When a reaction becomes "more favorable" it produces more energy for the organism. Depending on the environmental conditions, some reactions may shut down completely because they become thermodynamically unfavorable.)

Calculations were done to determine the effects of CO concentration, CO_2 concentration, H_2 concentration and pH have on the bio-energetics of the biological WGS reaction. The effects of pH, CO concentration and CO_2 concentration were also confirmed in the laboratory.

5.0 Biological WGS Kinetics

As mentioned in the previous section, the kinetics of a reaction can only be determined experimentally. This is true in catalytic WGS reactions as well. However, the maximum reaction rate for the biological WGS reaction can be estimated using assumptions on the ability of organisms to transfer electrons to external electron acceptors. Measurements show that most organisms transfer electrons to external electron acceptors are a rate of approximately 1 mole of electrons per g cell dry weight (cdw) per day (Gossett, 1995; Perry, 1971, 1972). In the case of H_2, 2 electrons are required per molecule of H_2, so 0.5 mol of H_2 can be produced per day per g of viable cells. With a molecular weight of 2 g/mol, this results in a convenient rule of thumb for biological hydrogen production:

1 g of cells can produce 1 g of H_2 per day (or 1 kg of cells can produce 1 kg of H_2 per day)

This is based upon a temperature of 25°C and the value can range from 0.5 to 2.0 g H_2/g cells/day depending upon the organism (Gossett, 1995; Perry 1971, 1972). Most biological reactions double their reaction rate for every 10°C increase in reaction temperature, but that does not mean increasing the reaction temperature is the answer. While different organisms have different temperature optima depending on the environment to which they have adapted, most organisms can only operate over a small temperature range before its enzymes are denatured and the organism dies. *Rx. gelatinosus* can most likely be used in a reactor operating at up to 37°C, but above this temperature, the organism's water-gas shift activity will drop rapidly and the organism will die. If the enzymes specific to the biological WGS reaction are temperature stable, it might be possible to transfer the enzymes into an organism isolated from a high-temperature environment, but this requires advanced biological techniques. It would also require more expensive, insulated reactors designed to operate above ambient conditions. It also appears that the hydrogenase enzyme responsible for H_2 production in *Rx. gelatinosus* requires auxiliary genes that assist in synthesizing the enzyme within the cell (Wolfrum and Maness, 2003). These genes would need to be present in the new host organism's chromosomal DNA or these auxiliary genes would also need to be transferred to the host organism.

It is important to note that the above kinetic rate is based upon viable cell mass. In biological reactors operated over long time periods, the refractory cell material may build-up. The observed cell concentration may represent 50% or less viable cell mass because of the build-up of dead cells and inert material.

Laboratory estimates of the actual biological shift rates agree with the above estimate.

6.0 CO Inhibition

Another concern with chemical reactions in general is inhibition. For example, the nickel used in conventional SMR catalysts is sensitive to sulfur. In biological process, reactants, products or contaminants can reduce the growth and/or production rate of organisms, if the organisms aren't simply killed. In studying the biological WGS reaction, some potential sources of inhibition are CO and CO_2. The CO_2 also has an effect on pH, especially at higher pressures due to the formation of carbonic acid and its carbonate derivatives.

Studies of the intrinsic rate of the biological WGS reaction show inhibition at high dissolved CO levels. Figure 2 shows the trend of biological shift rate versus the liquid-phase CO concentration. These results were from shake flask experiments conducted with dilute cultures under conditions that approached equilibrium CO concentrations. This data was collected under ambient pressure, so the maximum CO concentration observed by the cells was the equilibrium concentration of CO at one atmosphere of pressure, or approximately 1.0 mmol/L. Increasing the operating pressure increases the

liquid-phase CO concentration. Liquid-phase concentrations greater than 0.15 mmol/L result in decreased reaction rate and eventual shutdown of the biological WGS pathway. High-pressure shake flask experiments were not performed due to the more complex experimental procedures required, however, pressurized experiments were conducted using 1-liter continuous reactors and the effects of inhibition were observed (Wolfrum and Maness, 2003). The reaction rate in Figure 2 is presented per unit cell mass. Higher cell mass in a reactor results in higher potential reaction rates per unit reactor volume.

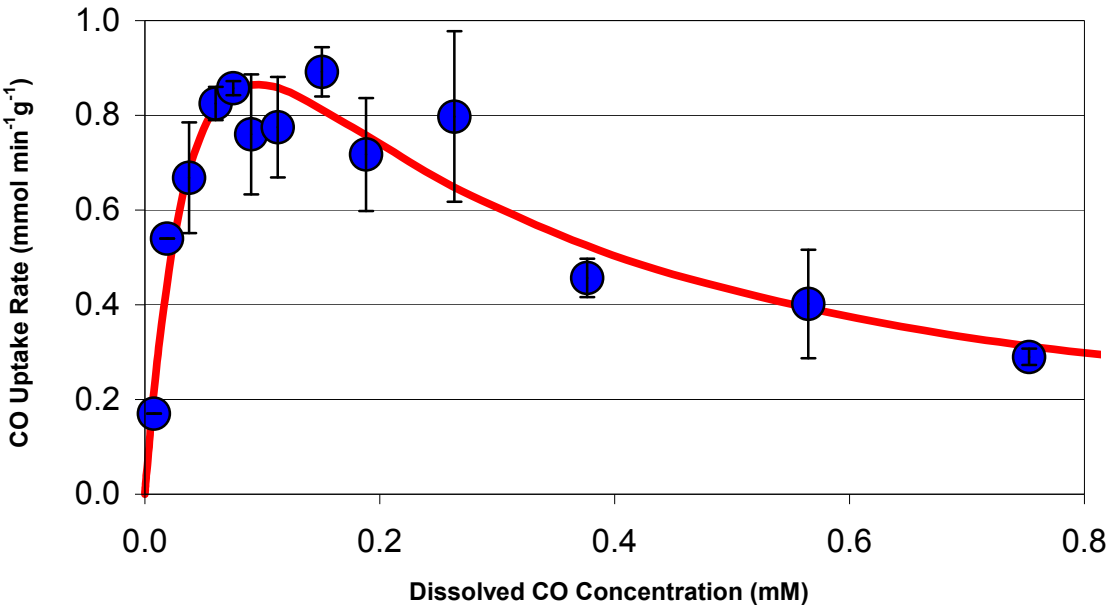

Figure 2 – Carbon Monoxide Inhibition of the Biological WGS Reaction

Because one possible application of the biological water-gas shift reaction is the conditioning of synthesis gas from a gasifier, there was some concern that higher molecular weight contaminants, such as benzene, might adversely affect the cells. To alleviate those concerns, a biological reactor was run using quenched, biomass-derived synthesis gas produced by NREL's Thermo-Chemical User Facility. No significant adverse effects were seen on the organism's health or biological WGS activity due to acetylene, ethylene, benzene concentrations of 5000 ppmv and toluene concentrations of 3000 ppmv (Wolfrum and Watt, 2001).

In additional, a specific refinery gas stream was also tested using *Rx. Gelatinosus* CBS through a Work-for-Others agreement with an industrial partner. No significant effects were seen on growth rates of H_2 production rates for the gas compositions tested. (The specific gas compositions and source of the gas stream are proprietary information.) Whatever slight inhibition that was observed was attributed to pH effects in samples containing high CO_2 levels.

With regard to pH, biological WGS activity remained high over a range of pH 6.8 to 8. Below 6.5 pH, the cells lyse and die. In the trickling filter reactors (described in Section

8), biological WGS activity was lost at pH above 8. This may have been due to an inability of the organisms to remain attached to the trickling filter packing at high pH. The pH was expected to drop with increased pressure due to higher concentrations of dissolved CO_2, but bubble column reactors (see Section 8) were operated at pressures up to 3 atmospheres absolute pressure without any obvious losses of activity.

No tests were conducted to determine if H_2 was inhibitory, but it is known that *Rx. gelatinosus* CBS can uptake H_2 to support cell growth, so the main effect may be reduced hydrogen yield and not reduced production rates.

7.0 Mass Transfer Limitations

In a chemical reactor, there are two limitations on overall reaction rate: the intrinsic reaction rate and the mass transfer rate. The intrinsic reaction rate is the maximum reaction rate for the chemical reaction for given the concentration of reactants and temperature. If mass transfer is not a limiting factor, the overall reaction rate observed will very closely equal the intrinsic reaction rate. However, when mass transfer limitations is a limiting factor, the reaction can't proceed faster than the reactants can be transported to the reaction site. Even though the reaction may be inherently fast, if the reactants can't be supplied fast enough, the overall reaction will be slow. In the case of the biological WGS reaction, the transfer of CO from the bulk gas phase into the liquid is a limiting factor for most reactor configurations. The organisms are waiting to consume CO once it makes it into solution, but the mass transfer rate into solution is slow.

The following equation governs mass transfer from the gas phase to the liquid phase:

$$N = k_L a * (C^*_{CO,l} - C_{CO,l}) \qquad (7)$$

where N = the mass transfer rate
k_L = the mass transfer rate coefficient
a = the interface area
$C^*_{CO,l}$ = the equilibrium CO concentration at the interface of the gas and liquid
$C_{CO,l}$ = the CO concentration in the liquid.

For sparingly soluble gases like CO, $C^*_{CO,l}$ is small. The limited solubility of CO is one of the factors affecting the slow mass transfer rate. In a catalytic WGS reactor, all the reactants are in gaseous state (i.e, the water is steam). The mass transfer from the bulk gas into the pores of the catalyst are diffusion limited, but the rate of mass transfer is much higher than the rate of mass transfer from a gas into a liquid.

Looking at Equation 7, we can see that there are several ways to increase the mass transfer. First, an increase in k_L will improve mass transfer. This is generally accomplished by increasing the turbulence, often by increasing the flow rate of the liquid and/or gas. The second method of increasing mass transfer is by increasing the surface area for mass transfer. In a bubble column, more bubbles and smaller bubble sizes result in higher surface area and increased mass transfer. Third, increasing the bulk gas

concentration of the CO in the gas will increase the concentration gradient (the term in parenthesis) increasing mass transfer. Lastly, if the CO is consumed almost immediately, the concentration of CO in the liquid will be low, improving mass transfer.

If mass transfer rate is higher than the reaction rate, the CO concentration in solution will increase until it reaches the equilibrium concentration at the gas-liquid interface. At that point, the concentration gradient will be zero and no gas transfer will take place. Note that in Figure 2, if the CO concentration exceeds 0.15 mmol/L, the reaction rate starts dropping, causing even higher CO concentrations and more inhibition.

In the shake flask experiments used to obtain the intrinsic reaction rates, very high shaker speeds are used to provide high turbulence and increased gas-liquid interface area to improve mass transfer. Cell concentrations in the shake flasks were also kept low so that the biological reaction rate was much less than the mass transfer rate when shaking. It is, however, very difficult to duplicate these conditions in a commercial-scale reactor.

8.0 Pressurized Operation

One method of increasing mass transfer is to pressurize the reactor. Pressurizing the reactor increases the equilibrium concentration of CO at the gas-liquid interface, increasing mass transfer into the liquid. At ambient pressures, an increase in CO concentration in the gas-phase increases the equilibrium concentration of CO and increases the mass transfer rate.

If the reactor shift rate is limited by the mass transfer, operating at increased pressure will improve mass transfer and increase the overall reaction rate. However, increasing the reactor pressure can increase the mass transfer rate above the intrinsic biological reaction rate. When this happens, the liquid-phase CO concentration builds up and eventually inhibits the biological reaction, reducing hydrogen production.

A simple graphical model can be used to compare the intrinsic bioreactor rate with the mass transfer limitation for a give reactor. Under steady-state conditions, there will be a liquid-phase CO concentration where the rate of biological uptake of CO exactly matches the bulk mass transfer rate of CO into the liquid. Figure 3 shows the gas transfer operating line superimposed on the bioreactor rate curve for an arbitrary reactor design. The point where these two lines cross is the steady-state bioreactor rate and the steady-state liquid-phase CO concentration. In Figure 3, this represents a stable operating point because if the liquid-phase CO concentration increases slightly, the mass transfer rate will drop slightly (moving right along the sloped line) and the bioreactor reaction rate will increase slightly, pulling the CO concentration back down to the steady-state point. If the CO concentration drops slightly, the mass transfer rate will increase while the bioreactor rate drops slightly. This will force the reactor back to the steady-state CO concentration.

In Figure 4, the pressure has increased to 2 atm. The bioreactor rate curve remains the same, but the y-axis intercept (representing the maximum mass transfer rate) has

increased and the x-axis intercept (representing the equilibrium liquid-phase CO concentration) has increased. Compared to Figure 3, the steady-state point has moved to a higher CO concentration and a higher bioreactor rate.

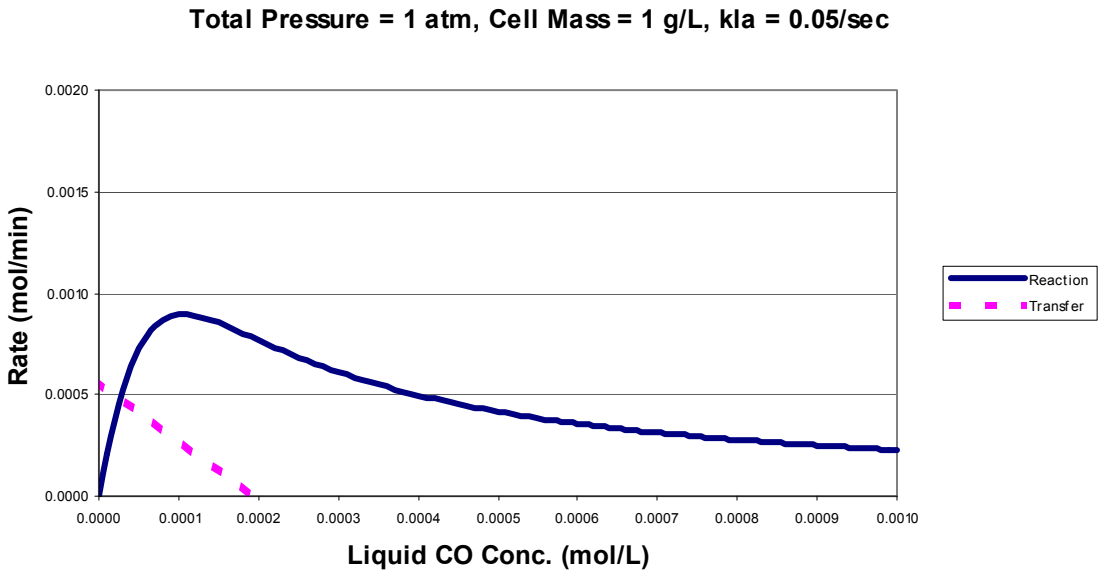

Figure 3 – Steady-State Mass Transfer

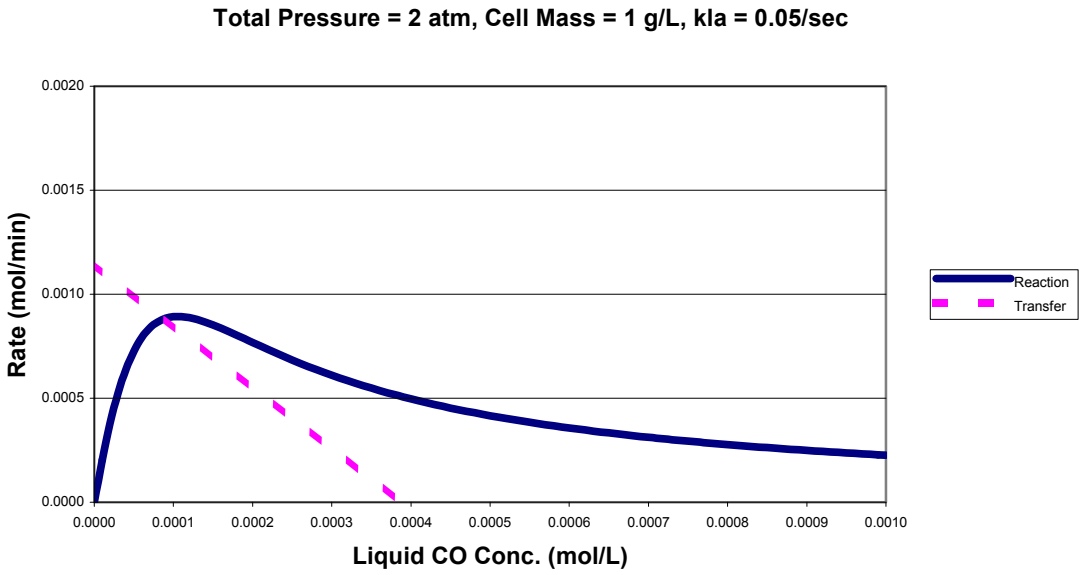

Figure 4 – Increased Operating Pressure Increases Mass Transfer

In Figure 5, the pressure has been increased to 3 atm. The mass transfer line now crosses the bioreactor rate curve to the right of the peak bioreactor reaction rate. This is an unstable operating point because if the CO concentration increases slightly, the reaction

rate drops, which will push the CO concentration even higher and cause the bioreactor reaction rate to drop even further, until the biological WGS reaction effectively shuts down.

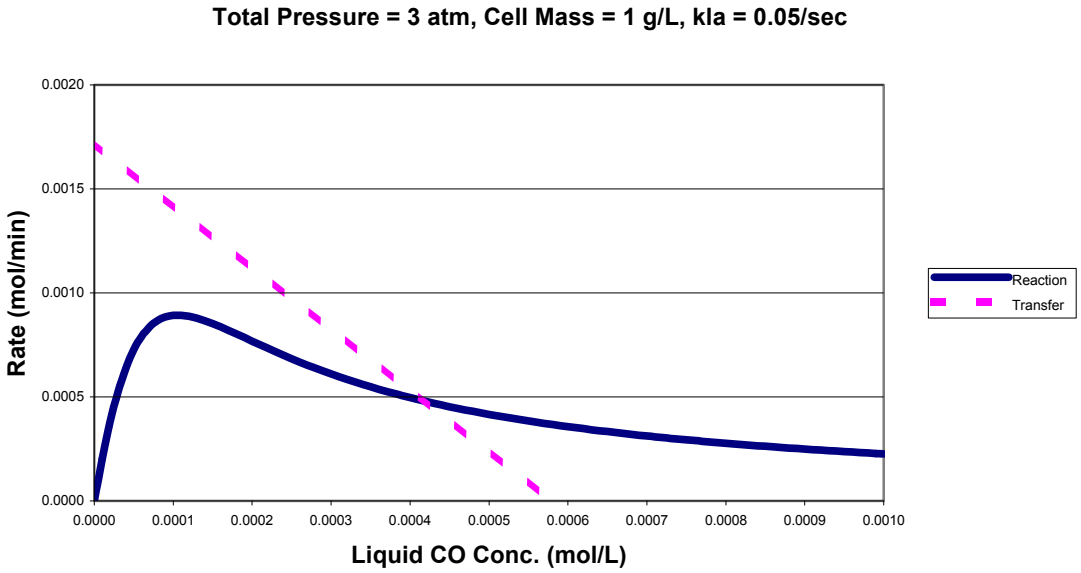

Figure 5 – Further Increases in Pressure Result in Unstable Operation

Keeping in mind that the bioreactor reaction rate is based upon the mass of viable cells, increasing the cell mass would allow operation at higher pressures and higher mass transfer rates. Figure 6 shows the effect of doubling the cell mass. The mass transfer operating line is in the same position as in Figure 5, but the bioreactor rate for the given reactor has increased and the steady-state solution is again a stable point on the left side of the peak reaction rate.

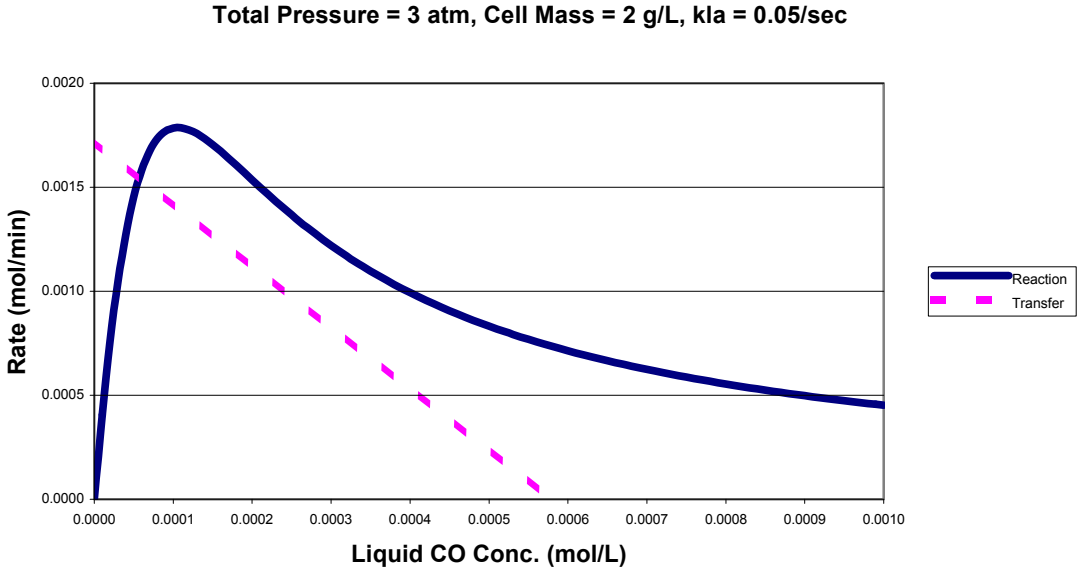

Figure 6 – Stable Operation at 3 atm Due to Increased Cell Mass

A second option that would allow operation at higher pressures would be to decrease the k_La value of the reactor, reducing mass transfer. This could be accomplished by decreasing the area for mass transfer or reducing turbulence in the reactor. The net effect is shown in Figure 7. Comparing Figure 7 with Figure 5, the maximum mass transfer (the y-intercept) has decreased, but the equilibrium CO concentration (the x-intercept) remains the same. However, increasing the mass of cells in the reactor is a more desirable solution because the steady-state bioreactor rate in Figure 6 is almost twice that of Figure 7 for the same reactor volume.

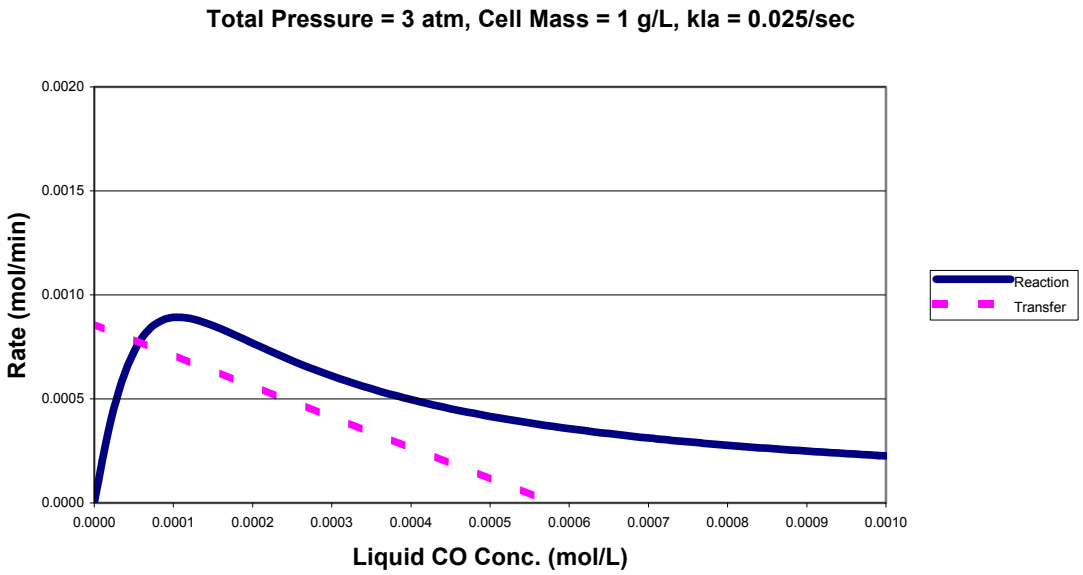

Figure 7 – Reduction in Mass Transfer Coefficient

Increasing the cell mass in the reactors has not been demonstrated in the laboratory for the biological WGS reaction, but there would be a number of ways of increasing cell mass in the reactor, if desired. The net effect is that there are so many cells in the reactor that any CO transferred is consumed before it can build up to levels that cause inhibition of the biological WGS reaction. If for some reason the operating line moves to the right of the peak biological reaction rate, the mass transfer must then be reduced until stable operation is re-established to the left of the peak biological reaction rate. This can be accomplished by reducing the mass transfer coefficient k_la or by decreasing the reactor operating pressure.

To summarize the results of comparing the bioreactor rate with the mass transfer rate, increasing the pressure of the reactor will increase the mass transfer rate, while increasing the cell loading increases the bioreactor rate. For stable operation, the two operating lines must cross to the left of the peak reaction rate.

9.0 Reactor Designs

Three different reactor designs were tested for biological WGS of CO to H_2: a trickling filter, a bubble column and a bubble column with gas recycle. Batch shake flasks experiments were also conducted for determining intrinsic reaction rates.

The trickling filter consists of a tubular reactor containing a solid packing support that cells can attach to (see Figure 10a). Various packings were tested, including wood, activated carbon, lava rock, plastic industrial packing and porous ceramic supports. The configuration tested in the lab was a counter-current design with the gas flowing upwards through the bed and water flowing down through the packed bed. The water flow rate is kept low to prevent flooding in the column. The main purpose of the water was to keep the cells moist with the secondary purpose of supplying nutrients for cell growth. While increased liquid flow rates might increase the mass transfer slightly, the main advantage of the design was increased gas-transfer area with a minimal pressure drop. Another possible configuration to increase mass transfer while still avoiding flooding would be a co-current down-flow reactor, but this configuration was not tested.

Two reactor sizes of trickling filter reactors were tested: 1-liter and 5-liter. Figure 8 shows typical conversions for different reactor packings in the 1-liter reactor (Wolfrum and Watt, 2001). Figure 9 compares the conversion of the 1-liter and 5-liter reactors under similar operating conditions. This data shows that a 5-fold increase in reactor volume with the same residence time yielded the same conversion, confirming that the 1-liter data could be used to predict the performance of larger reactors.

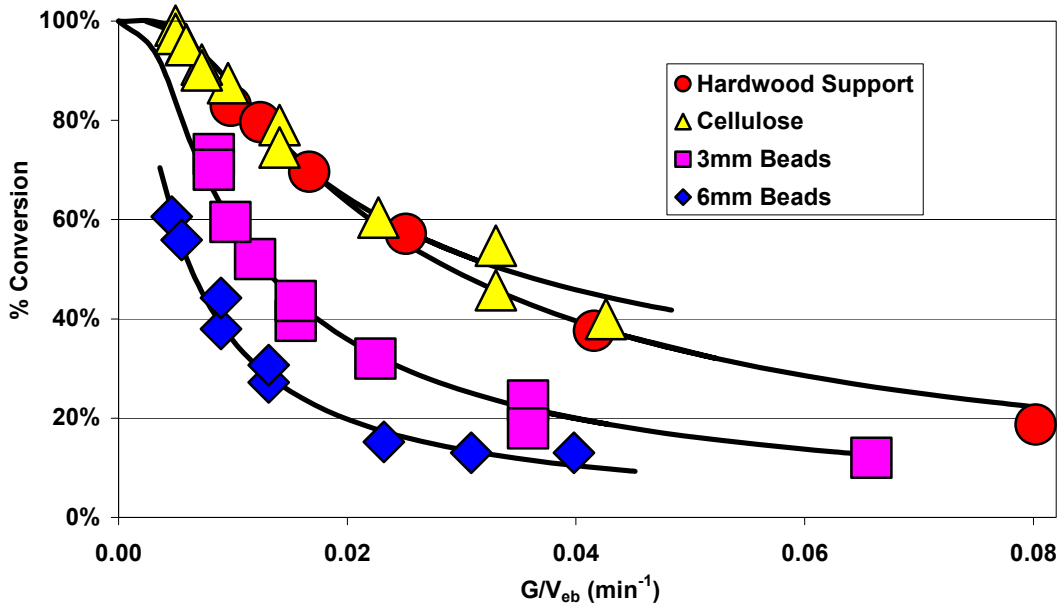

Figure 8 – Typical Biological WGS Conversion Data

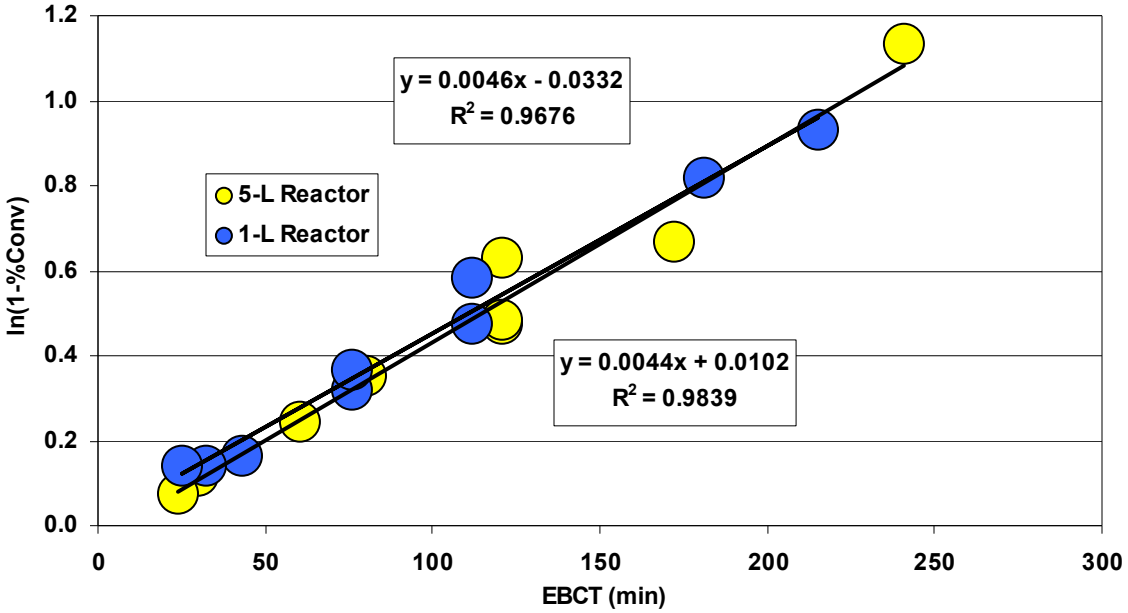

Figure 9 – Trickling Filter Scale-Up

Trickling filter reactors were operated under pressurized conditions. The higher pressures increased the effective the bulk gas CO concentration, increasing the driving force for mass transfer. However, at times the increased pressure would increase the CO liquid-phase concentration enough to inhibit the biological WGS reaction and shut down the reactor until the mass transfer rate was reduced. This result is expected based upon the shape of the rate curve in Figure 2.

The other two reactor configurations tested were bubble column designs (Figures 10b and 10c). Good mass transfer in a bubble column is achieved through high surface area for mass transfer and increased turbulence as the bubbles rise through the column of liquid. Ideally, a bubble column should be designed to produce small bubbles, which have high surface-to-volume ratios and low rise-velocities though the liquid, resulting in long residence times in the reactor. Large bubbles have less area for mass transfer and rise very quickly up through the reactor liquid. Producing small bubbles, however, requires pushing the gaseous feed through small opening, such as those in a porous frit. This means there is a high pressure drop across the reactor. The liquid head in the reactor adds an additional pressure drop, which is not present in a trickling filter.

The short residence time and high pressure drop in the bubble reactor make it impractical for commercial-scale biological WGS, but there is a advantage in obtaining reactor design information: it is easy to estimate the amount of cell biomass in the reactor. Since the reactor is well-mixed, a small amount of liquid can be tested to determine the total reactor cell density. In the trickling filters, it was more difficult to determine the amount of cellular material attached to the packing without disassembling the reactor.

Stand-alone bubble columns produce very small single-pass conversions of just a few percent for a 1-meter column, making it difficult to accurately calculate conversion rates for the reactors. To increase the accuracy of the calculations, but still use the bubble column, a gas recycle loop was added. This allowed the simulation of a longer residence time in the reactor, resulting in overall conversions of over 50% in reactors with 10:1 recycle-to-feed ratios. The bubble columns ran more stable than the trickling filters, presumably due to the higher cell mass, more liquid available to buffer upsets and lower inlet CO concentrations to the reactor.

Figures 10a, 10b, 10c show the three reactor designs.

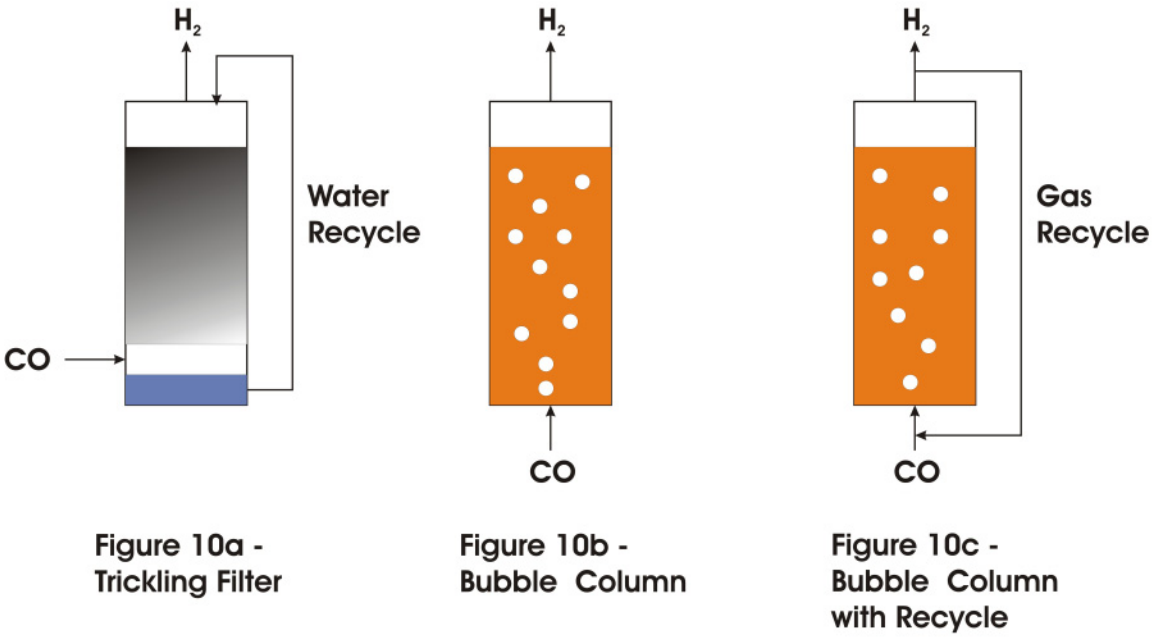

Figure 10 – Three Biological WGS Reactor Designs

Some factors affecting operation of the reactors are operating pressure, inlet CO concentration, recycle-to-feed ratio and cell concentration. Both the trickling filter and recycle bubble column reactors were operated under pressure. The recycling bubble column reactor was also operated with variable recycle ratios. Gradual increases in the recycle-to-feed ratio initially resulted in higher mass transfer rates as the volume/number of bubbles increased, but at very high recycle rates, the bubbles combine and the surface-to-volume ratio drops, hurting mass transfer.

10.0 Process Economics

In the course of studying the biological WGS process, several alternative process configurations were studied. Several of the processes concentrated on biomass-derived synthesis gas, but any stream containing CO would be a possible feed to the biological WGS process.

10.1 Biomass-Derived Synthesis Gas with a Trickle-Bed Reactor

In 2001, a study was done to look at the economics of the biological WGS process using a quenched gas leaving a FERCO/BCL indirectly-heated gasifier (Amos, 2001). The assumed gas composition was an equal mixture of CO, H_2, and CO_2. The process layout consisted of compression of the cool gas, followed by a water quench before the gas entered a counter-current packed-bed trickling-filter biological WGS reactor. The shifted gas would then go through a MEA CO_2 scrubber before passing through drying beds to remove any residual water. A 2.5 MM scfd plant had a capital cost of $17 million and resulted in an incremental processing cost $3.40/kg. Adding in the cost of the syngas at $5/MM Btu gave a minimum hydrogen selling price of $4.25/kg. This is compared to $1.00-1.50/kg for hydrogen via catalytic steam-methane reforming.

Sensitivity studies conducted included looking at the effects of reaction rate, outlet CO concentration, packing cost, labor required and non-pressurized operation. One important conclusion of this work was that the trickling filter needed to operate under pressure. If the system operated at ambient pressures, the large reactor size would result in a minimum hydrogen selling price of over $30/kg.

10.2 Industrial Collaboration

NREL conducted a series of laboratory studies and economic analysis through a Work-For-Others agreement with an industrial partner interested in refinery applications of the biological WGS process. One aspect of these studies was the removal and/or recovery of CO_2 from the process outline in Section 9.1.

Reducing reactor size is important to the economics of the biological WGS process. One way to reduce the size of the biological WGS reactor is to remove the CO_2 from the inlet gas before it enters the reactor. Because the inlet gas from a FERCO/BCL gasifier can contain 33% CO_2, this could result in a 33% reduction in reactor volume. The CO_2 resulting from the shift reaction can also be removed from the gas steam after the reactor, improving downstream hydrogen purification steps.

A significant amount of time was spent studying the options for CO_2 recovery. The process design for biomass-derived gas included MEA scrubbing. One issue with this method of CO_2 removal is the high natural gas consumption associated with the subsequent CO_2 stripping column used to regenerate the MEA. The natural gas costs significantly added to the operating expenses. To help reduce this cost, an alternative stripper design used air stripping to regenerate the MEA and not recover the CO_2. Even with the lost CO_2 revenues, this was a cheaper alternative to consuming natural gas and recovering the CO_2.

The next CO_2 recovery option examined was to compress and freeze-out the CO_2 in the inlet stream. The gas was compressed and cooled using a refrigeration system. Solid CO_2 would deposit on the inside of a set of heat exchangers. The CO_2 would then be periodically vaporized by passing hot water through the heat exchanger. This would allow capture of gaseous CO_2, but liquid CO_2 brings in considerably higher revenues.

An alternative process consisting of more compression and cryogenic condensers was examined. While a stripping column is required for purifying the liquid CO_2 before sale, low-quality waste heat from the compression intercoolers is sufficient for providing heat to the stripping column reboiler. Condensing the CO_2 also required operation at higher pressures, which increased compression costs.

The results from the economic studies indicated that the overall process economics strongly depended upon how much the CO_2 could be sold for. Liquid, food-grade CO_2 can be sold for up to $50/ton in some areas, but the sales are limited by region and are seasonal in nature. The CO_2 removal did, however, improve the economics of the process and reduce the reactor size for the biological WGS.

10.3 Drop-in replacement in SMR

One early argument in support of the biological WGS process was as a drop-in replacement for conventional high- and low-temperature WGS reactors. However, the biological WGS reactor would be significantly larger than a comparable catalytic reactor. The larger reactor volume for the biological WGS doesn't reduce capital or operating costs for SMR.

One argument for biological WGS was that the lower operating temperature (25°C) would result in high conversions of CO to H_2, possibly eliminating the need for PSA purification. While it is true that the chemical equilibrium is shifted to producing almost all H_2 with little CO at 25°C, the production rate of a full-scale biological WGS reactor will be limited by mass transfer, not equilibrium. Mass transfer from the gas phase to the liquid phase—where the biological WGS reaction takes place—is a first-order reaction. That means for every order of magnitude increase in conversion, the reactor volume doubles. To increase the conversion of a reactor achieving 90% conversion to 99% conversion, the reactor volume would need to be doubled. To achieve 99.9% conversion, the reactor volume would need to be doubled yet again to 4 times the original volume. While it is theoretically possible to achieve CO concentrations in the ppm range, the large reactor size wouldn't justify going to such high conversions. A far better method is to get a conversion of 90% in the biological WGS, then use a PSA to remove the additional CO. Since the CO_2 and other possible trace contaminants must be removed to produce pure H_2, a PSA would be required anyway.

There were also questions concerning whether there were any heat transfer benefits to using a biological WGS reactor operating at 25°C. In the conventional reforming, HTS, LTS, PSA design, heat from the reformer is used to preheat the inlet gas to the reformer, then steam is generated from the outlet to the HTS. A relatively large amount of low-quality heat can be recovered from the outlet of the LTS reactor—mostly from condensing the steam in the gas stream—but since the LTS is operating at 200°C, this is not high-quality steam. Some cooling water is also needed to condense as much water as possible before entering drying beds prior to the PSA purification. The net effect is recovering heat from 350°C down to 25°C before the PSA in multiple steps. With the biological WGS process, the gas is still cooled down from 350°C to 25°C before entering the biological WGS reactor, but it is done in one step. Because the conventional catalytic

WGS reaction is exothermic, some extra heat is produced and recovered leaving the shift reactors. The biological WGS uses some of the exothermic energy of the shift reaction for metabolic processes and the remaining heat is lost at ambient temperatures and can't be recovered. The biological WGS reactor actually has worse heat recovery because the exothermic heat of reaction of the water-gas shift reaction is given off at 25°C.

One cost analysis looked at exactly how much of the commercial H_2 price is due to the capital and catalyst costs associated with the shift reactors. The result was that completely eliminating the capital and catalyst replacement costs of the conventional catalytic WGS only reduced the hydrogen selling price from a modern SMR plant by $0.10/kg of hydrogen. The biological WGS alternative would cost considerably more.

10.4 Non-reforming applications

While the costs associated with the conventional catalytic WGS reactor are small, larger savings are possible if the reforming and steam production associated with hydrogen production can be eliminated. As was mentioned earlier, one difference between catalytic and biological water-gas shift is that the water used in the reaction is in liquid form for the biological process; for catalytic WGS, high-pressure steam is used. There are both capital and operating costs associated with producing this steam. The reformer in SMR hydrogen production also represents a significant capital investment for high-pressure, high-temperature reactor tubes. If the reformer and the steam production can be eliminated, this might make a low-temperature biological WGS reactor attractive.

Amos *et al* (2003) conducted a series of process simulations using different feed compositions and four different combinations of reforming, HTS, LTS and biological WGS. The four process configurations were:

1. Conventional SMR with natural gas
2. Reforming, catalytic HTS, PSA
3. No reforming, catalytic HTS, PSA
4. No reforming, biological WGS, PSA

Figure 11 shows these four process configurations. No CO_2 recovery was attempted in these designs. For conventional SMR, natural gas at $3.50/MM Btu was assumed. For the remaining cases, equal concentrations of CO, CO_2 and H_2 were assumed with 0-25% methane. The assumed cost of the synthesis gas was $5.00 MM/Btu.

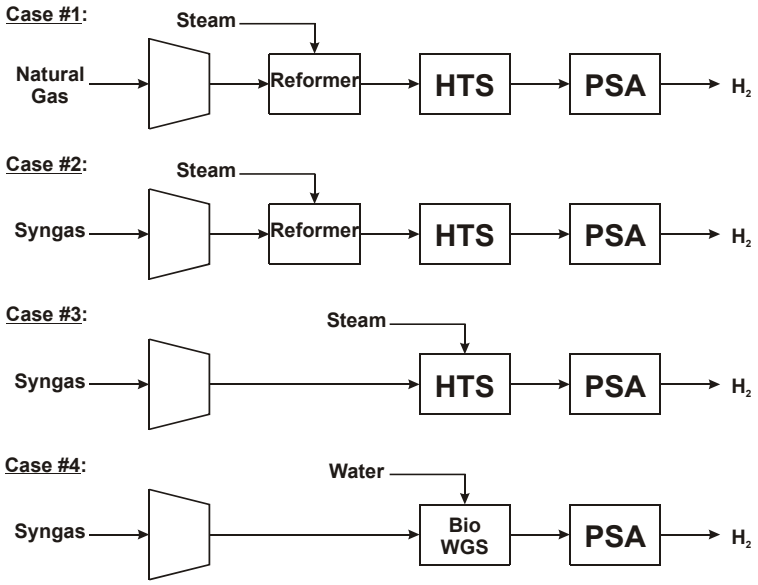

Figure 11 – Alternative Reformer/Shift Processes

Figure 12 compares the alternative reforming and shift strategies with conventional SMR (Case 1). As suspected, at low methane/hydrocarbon concentrations, eliminating the reforming and steam production resulted in lower hydrogen costs with a pressurized biological WGS process. However, if the methane concentration was over 5%, installing the equipment for steam production and reforming resulted in enough of an increase in hydrogen yield from the reformed methane to justify the higher capital and operating expenses with the reformer and steam production.

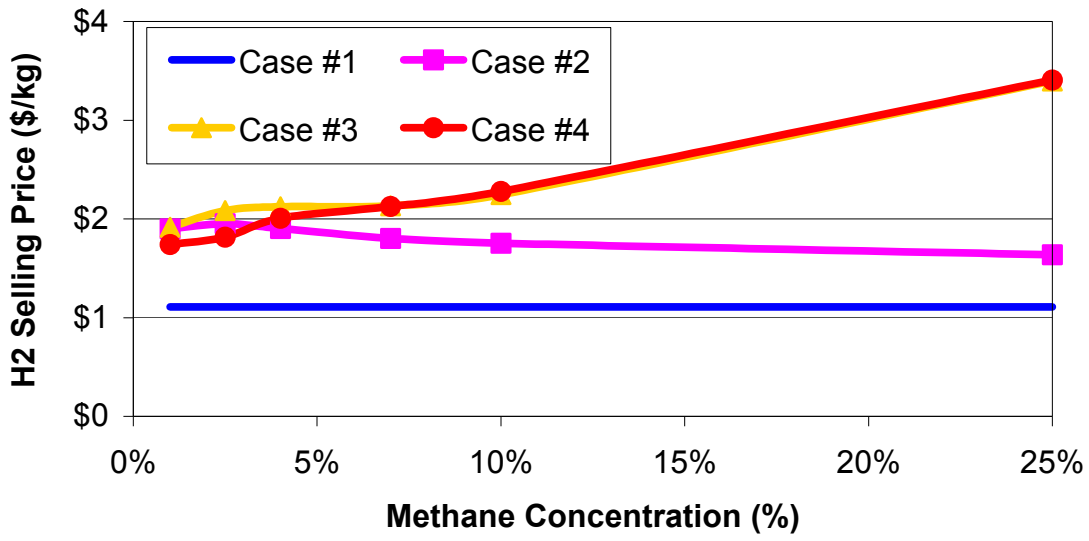

Figure 12 – Minimum Hydrogen Selling Price for Various Syngas Compositions

It is important to note that if one decides to steam reform the inlet stream to boost hydrogen yields, the stream leaving the reformer already contains sufficient steam for the WGS reaction and is already hot enough for the HTS reactor, so no additional steam and no additional heat must be supplied. Because of this, it makes sense to go directly into a conventional catalytic reactor, rather than cooling the gas to go into a significantly larger and slower biological WGS reactor. The ideal stream for biological WGS would be a pressurized CO-containing stream with little or no hydrocarbons that could be reformed into CO_2 and hydrogen.

10.5 Interface to a Gasifier

With respect to coupling a WGS process to a gasifier, for any low-pressure gasifier, in order to minimize the size of the reformer and/or shift reactors, the gas would need to be pressurized. In order to pressurize the gas in a cost-effective manner, the gas must be cooled and any steam condensed, before compressing the gas. That means the gas from any low-pressure gasifier will pass through a low-temperature compression step—what the gasifier and heat integration looks like before that step is irrelevant. Whether a catalytic or biological WGS is used, the gasifier, quench/heat recovery and compression sections will most likely be designed the same.

For a high-pressure gasifier, no compression would be needed—just some variation of hot-gas cleanup and possibly pre-reforming or tar cracking at the gasifier outlet temperature. In any case, if the gas leaves the gasifier at a high pressure, at a high temperature and with steam present, it is the perfect stream to pass into a catalytic reformer and/or catalytic shift reactor. Like in the SMR case, it makes no sense to cool the gas stream to go through a larger, slower biological WGS reactor if the stream is already hot and contains steam.

10.6 HyCO Plants

In July 2003, the author toured an Air Liquide HyCO plant. This plant was designed to supply CO to a chemical manufacturing site. The CO was the primary product, but some of the H_2 produced by methane reforming was purified using a PSA and sold into a hydrogen pipeline onsite. Because CO was the primary product, there was no need for a WGS reactor. In fact, CO_2 was recycled back to the reformer to boost CO production.

However, there was one operational concern with the plant. At times, the CO demand would drop, but not completely disappear. The reformer could not operate stably under 60% capacity. If the CO demand was less than 60% of the plant capacity, the reformer must still operate at 60% of capacity and the plant would flare the extra CO. It would not make sense to install a catalytic shift reactor for occasional use because it would require a lengthy heat up time to reach the proper operating temperature.

A biological WGS reactor would fit into the process because the pure CO stream is pressurized to 120 psig and the shifted H_2-containing stream could be fed into the system ahead of the existing CO_2 scrubber. The CO_2 produced could be removed and then the hydrogen would be sent through the existing PSA and sold to the pipeline merchant.

When CO demand was over 60%, only a small slipstream would be required to maintain the health of the biological WGS reactor. Because the biological WGS reactor operates at ambient temperatures, no warm-up would be required. In this HyCO plant design, the biological WGS reactor would be the only piece of equipment that would need to be installed; all compression, scrubbing and purification equipment is already in place.

The applicability of this technology to other HyCO plants is unknown.

11.0 Conclusions

Based upon the laboratory research completed and the various economic analyses mentioned in Section 9, several conclusions can be made about the suitability of the biological WGS reaction for hydrogen production.

1). A biological WGS will always be larger than catalytic WGS due to the lower mass transfer and slower kinetics as compared to a catalytic WGS reactor. For this reason, using a biological WGS reactor as a drop-in replacement for a WGS reactor won't improve the process economics.

2). There are not significant heat integration advantages with using a biological WGS reactor in place of a conventional catalytic WGS reactor. It would be possible to recover approximately the same amount of heat from both systems—the conventional system uses multiple steps to recover the heat, while the heat recovery for the biological WGS could be done in one step.

3). If steam reforming is already included as a process step, it makes sense to pass the outlet from the reforming to a catalytic WGS reactor because the gas is already hot and already contains enough steam for the WGS reaction.

4). If no steam reforming is required, the capital cost reduction associated with eliminating steam production might justify the larger biological WGS reactor. However, if significant amounts of reformable hydrocarbons are present (i.e., greater than 5% by volume), adding a reforming step to increase hydrogen yields improves the economics.

5). Pressurized operation of the biological WGS reactor would be a requirement to improve mass transfer and reduce reactor size. However, due to CO inhibition, operating at higher pressures requires higher cell mass in the biological WGS reactor. Successful operation at pressures above 3 atm with elevated cell mass in a biological WGS reactor has not been demonstrated.

6). Recovery of carbon dioxide as a co-product can have a major effect on the process economics, depending upon the CO_2 recovery process used and the market value of the CO_2. This is true of both catalytic and biological WGS processes and depends upon the inlet gas composition.

7). The best application for the biological WGS process is conversion of a pressurized CO-containing stream low in hydrocarbons to hydrogen with CO_2 recovery. At least one such commercial site has been identified where biological WGS might be applicable, but no economic analysis has been performed.

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13. ABSTRACT *(Maximum 200 words)*

This report summarizes the results of research and economic analysis on a biological water-gas shift process for the production of hydrogen. The organism Rubrivivax gelatinosus CBS is a photosynthetic bacteria which can perform the water-gas shift reaction under anaerobic conditions. The report describes some of the technical issues regarding the process, addresses some claimed benefits of the process and presents some results from economic studies of different process configurations.

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