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THE MATHEMATICAL ANALYSIS OF A NOVEL APPROACH TO MAXIMIZE WASTE RECOVERY IN A LIFE SUPPORT SYSTEM

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ABSTRACT

NASA has been evaluating closed-loop atmosphere revitalization architectures that include carbon dioxide (CO₂) reduction technologies. The CO₂ and steam (H₂O) co-electrolysis process is one of the reduction options that NASA has investigated. Utilizing recent advances in the fuel cell technology sector, the Idaho National Laboratory, INL, has developed a CO₂ and H₂O co-electrolysis process to produce oxygen and syngas (carbon monoxide (CO) and hydrogen (H₂) mixture) for terrestrial (energy production) application. The technology is a combined process that involves steam electrolysis, CO₂ electrolysis, and the reverse water gas shift (RWGS) reaction. Two process models were developed to evaluate novel approaches for energy storage and resource recovery in a life support system. In the first model, products from the INL co-electrolysis process are combined to produce methanol fuel. In the second co-electrolysis, products are separated with a pressure swing adsorption (PSA) process. In both models the fuels are burned with added oxygen to produce H₂O and CO₂, the original reactants. For both processes, the overall power increases as the syngas ratio, H₂/CO, increases because more water is needed to produce more hydrogen at a set CO₂ incoming flow rate. The power for the methanol cases is less than pressure swing adsorption, PSA, because heat is available from the methanol reactor to preheat the water and carbon dioxide entering the co-electrolysis process.

INTRODUCTION

The carbon dioxide, CO₂ and steam, H₂O electrolyzer is an alternative to NASA's currently considered Sabatier reactor and water electrolyzer for CO₂ reduction and oxygen generation, respectively.

In a potential, closed-loop life support architecture, the co-electrolysis unit will receive compressed CO₂ from an adsorption compressor, which is part of its atmosphere revitalization system (ARS), to generate oxygen and fuel. NASA's traditional closed-loop life support system design has separate systems for chemical reduction of CO₂ (CDRe) and water electrolysis to reclaim O₂ from metabolic CO₂. Co-electrolysis combines the CO₂ reduction and oxygen generation processes efficiently into a single hardware, reducing overall system mass. Syngas, the byproduct of co-electrolysis, can be used as a raw material for production of synthetic fuels. If syngas is used to produce liquid products, one needs to consider the increase in system mass due to the addition of the synthetic fuel process.

Syngas is a mixture of carbon monoxide (CO) and hydrogen (H₂). Loop closure can be maximized by converting syngas to storage-efficient liquid fuels, or by separating H₂ from CO for reuse. This investigation will compare these two approaches to syngas utilization with methanol as the target synthetic fuel. Methanol, H₂, and CO have fuel value and their products of combustion, CO₂ and water, can be captured and recycled to complete loop closure.

The Advanced Process and Decision Systems Department at Idaho National Laboratory (INL) has spent several years developing detailed process simulations of chemical and

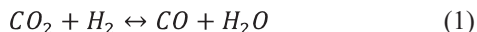
thermodynamic processes. These simulations have been developed using UniSim and ASPEN PLUS—state-of-the-art, steady-state, thermodynamic, and chemical process simulators developed by Honeywell and ASPEN. This study makes extensive use of these models and the modeling capability at INL to evaluate the integration of co-electrolysis process with the methanol and the pressure swing adsorption processes.

PROCESS MODELS

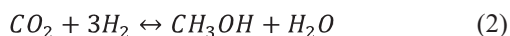
Methanol Process with Co-Electrolysis

A co-electrolysis module was developed at the INL using the UniSim process modeling software. UniSim has a large thermodynamic property database and ensures mass, energy and chemical balances. The module uses an embedded spreadsheet to calculate the Nernst potential based on the compositions, temperatures, and pressures of the inlet and outlet streams. Details of the module may be found in reference 1.

The co-electrolysis process was used to create syngas which then was used as feedstock into a methanol production process. The process flow diagram of the combined processes is shown in Figure 1. Water and carbon dioxide are mixed with recycled syngas and heated to 800°C through heat recuperation and direct heating. The direct heating in this analysis is assumed to be from electric heaters. At co-electrolysis temperatures $\sim 800^\circ\text{C}$, the stream composition will shift according to the reverse water gas shift reaction:

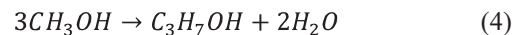
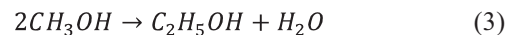


The water and carbon dioxide are electrolyzed to produce hydrogen and carbon monoxide on the cathode side of the electrodes and oxygen on the anode side. Both hot product streams are cooled using the recuperating heat exchangers. A portion of the syngas produced is mixed with the incoming water and carbon dioxide to create reducing conditions at the electrolysis electrodes. Most of the water in the syngas is removed and recycled using a water knock out tank. The co-electrolysis process is running at near atmospheric conditions, ~ 20 psia. The syngas must be compressed to methanol process pressures of ~ 1000 psia by way of a multistage compressor with intercooling. Recycle gas from the methanol process, primarily hydrogen, combines with the incoming syngas and is further compressed. The syngas is heated using another recuperating heat exchanger within the methanol process. The methanol process is modeled using two different types of chemical reactors. The first reactor is a chemical equilibrium reactor where the reverse water gas shift reaction, Eq. (1), and the methanol reaction occur, Eq. (2).



The reactions occur at 227°C and 1024 psia. The reactions are exothermic and some heat is released. This heat may be used in preheating the incoming water and carbon

dioxide just before the co-electrolysis process. The process also produces some dimethyl ether and propanol as byproducts simulated with a stoichiometric conversion reactor using equations 3 and 4.



With each reaction only 5% of the methanol is converted resulting in low concentrations in the exiting stream. The stream passes through a condenser to separate the water and methanol from the hydrogen, carbon monoxide and carbon dioxide. Two distillation columns are used to purify the methanol to 99%. Combustion processes close the loop in which both the methanol and the light gases are combusted. The methanol combustion process is a rough simulation of the fuel cell process.

For methanol production, stoichiometric ratios are used to gauge the suitability of the feed gas for methanol production. A few different metrics can be used. The first metric is the molar ratio:

$$\frac{(\text{H}_2 - \text{CO}_2)}{(\text{CO} + \text{CO}_2)} \quad (5)$$

Literature indicates that the optimal value for this metric for methanol synthesis is around 2, [2]. Many technology providers prefer to run slightly higher than 2. A target value for this analysis of 2.1 was selected, [3].

The second metric is the molar ratio:

$$\frac{\text{H}_2}{(2\text{CO} + 3\text{CO}_2)} \quad (19)$$

Literature indicates that the optimal value for this metric for methanol synthesis is 1.05, [4]. It is also useful to know the molar syngas ratio, H_2/CO , of the inlet gas. All of these metrics are for the feed gas to the methanol synthesis loop, not the methanol reactor itself. Studies have shown that conversion in the reactor is enhanced by having some CO_2 present at the reactor inlet. However, if too much CO_2 is present, conversion will be hindered. An upper limit of 4 mol.% is presented in the literature to maintain good conversion, [4].

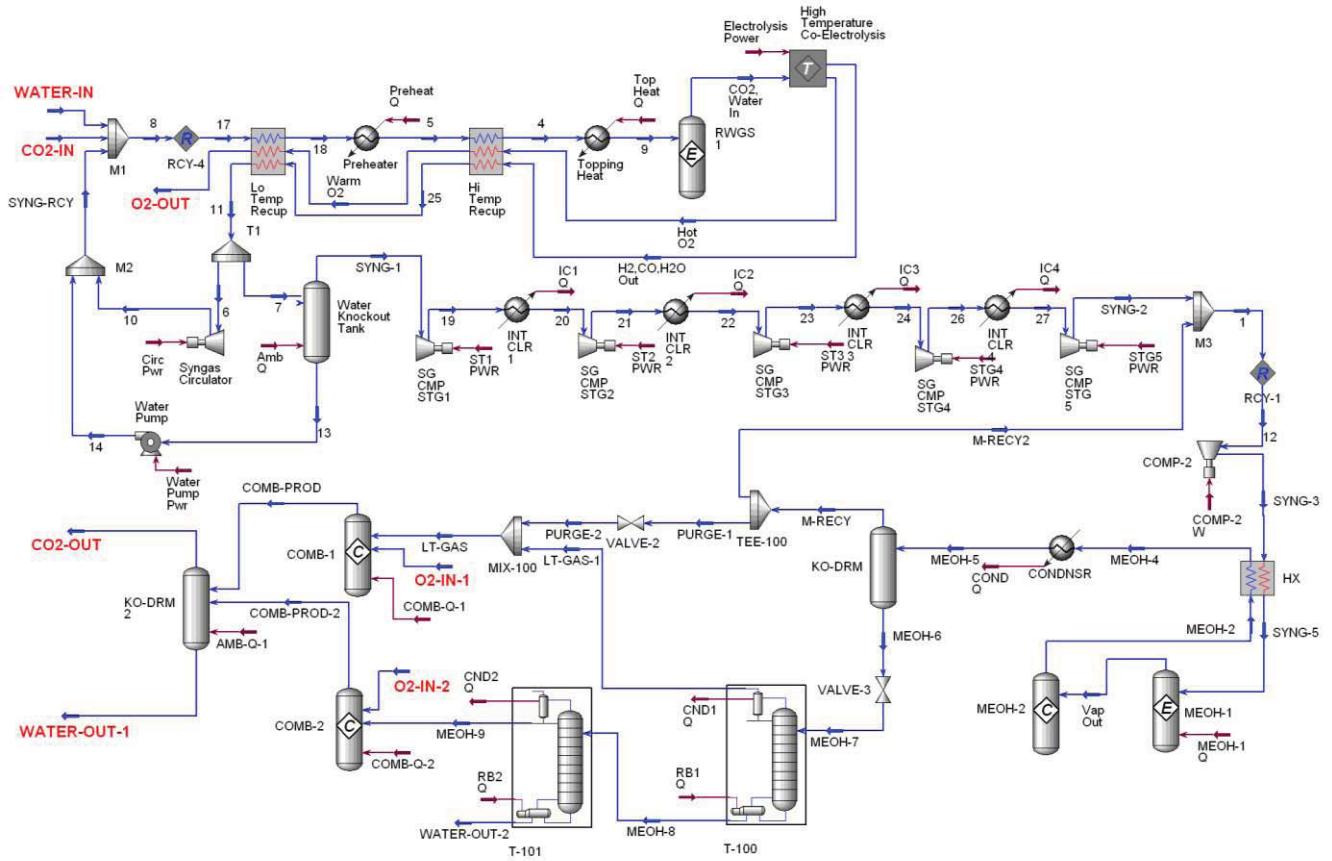


Figure 1. Unisim model of methanol process with co-electrolysis.

Co-electrolysis with pressure swing adsorption

The process model of the co-electrolysis process with pressure swing adsorption (PSA) is very similar to the previous process except a PSA unit replaces the methanol production process. The model for the PSA unit is a very simplified model which uses a splitter block to separate the gases in the PSA unit. PSA is a transient process which relies on the kinetics of the adsorption process. The process model is a steady state model therefore some simplifying assumptions were used to develop a black box type of model.

Based on literature about PSA units, the pressure ratio of the inlet stream to the purge gas is typically 4 or greater, [5, 6, 7]. Therefore, the pressure into the PSA unit was set to 100 psia. Based on this pressure ratio, 85% of the incoming hydrogen exits as part of the hydrogen stream with 0.03% of the incoming carbon monoxide, and 0.003% of the incoming carbon dioxide. The remaining gas exits the splitter block in the purge gas stream. Based on the literature, the power needed to run the PSA process is given by the following function [7]:

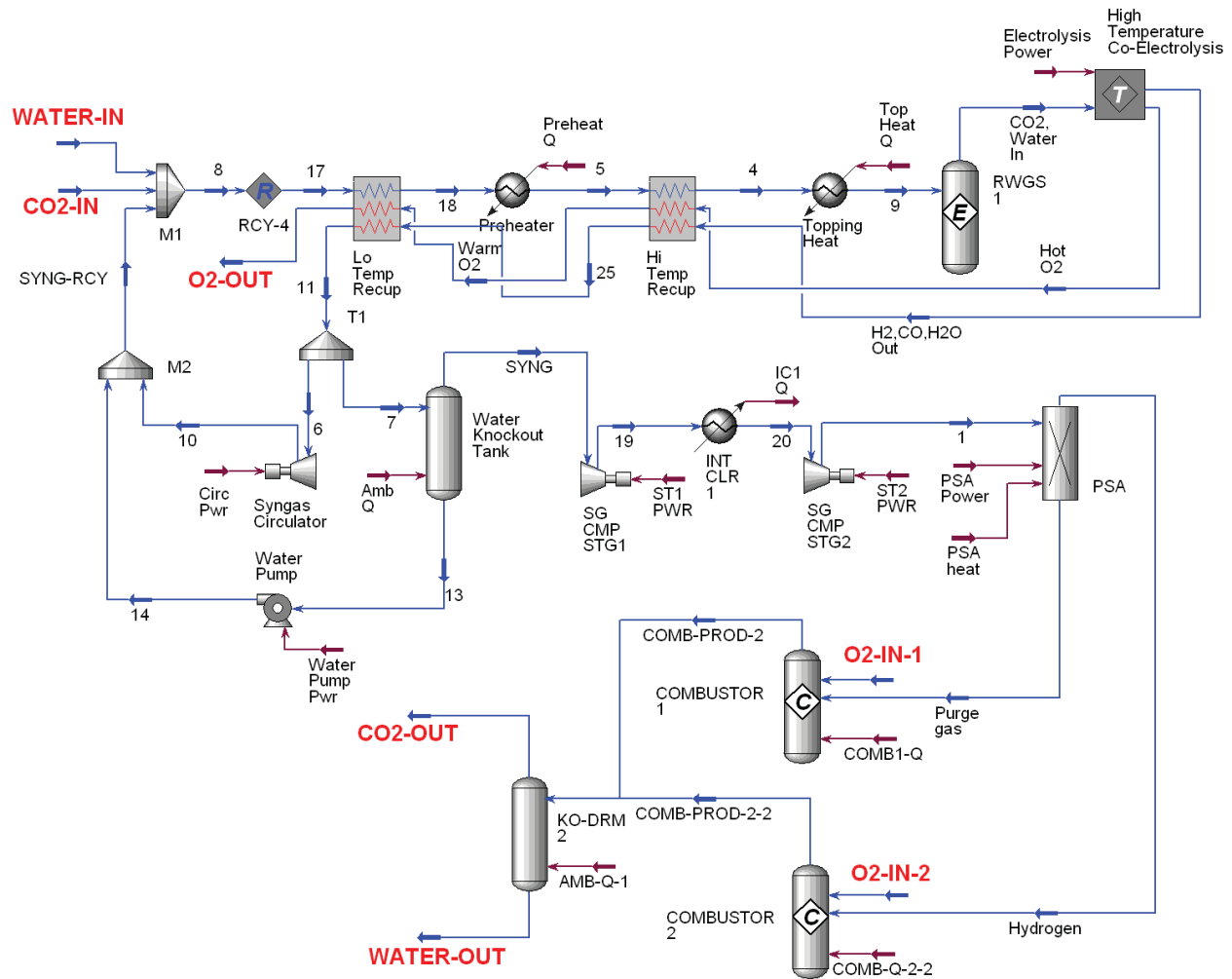


Figure 2. Unisim model of co-electrolysis with pressure swing adsorption.

$$\text{Power (kW)} = 0.0009858 * \text{Inlet Molar Flow Rate (lbmole/hr)}$$

The outlet temperature of the hydrogen stream is adjusted until the PSA process is adiabatic, ("PSA heat" stream equals zero). As with the previous model, the purge gas and hydrogen stream are combusted.

RESULTS

The scale of the process models was set to 1 kg/day of carbon dioxide processed to allow for comparison. Figure 3 compares the power output needed to process the carbon dioxide for both the methanol and pressure swing adsorption (PSA) separation processes as a function of the syngas ratio. The power needed for both cases is close. Both cases require more power as the ratio of the hydrogen increases because more input water is needed to supply the hydrogen while the flow rate of the incoming carbon dioxide is constant. The power requirement for the methanol case is slightly less because heat from the methanol reactor is used to raise the

temperature of the water and carbon dioxide streams entering the co-electrolysis process where no process heat is available for the PSA cases. The methanol production case is slightly non-linear due to the amount of process heat available for the incoming streams. For the cases where the syngas ratios are 2 and 2.5, there is sufficient heat supplied to the preheater. At higher syngas ratios, some additional electric heat is needed at the preheater.

The specific power can be defined as the power needed to process 1 kg/day of CO₂ divided by the feed water flow rate. The specific power is a measure of the power needed per inlet water flow and can be a measure of the effective use of water to process the CO₂. As the syngas ratio increases, the specific power for both processes decreases, see Figure 4. At higher syngas ratios, the curves approach each other and level out indicating that although the power usage per feed water flow may decrease, the addition of feed water does not significantly change the specific power.

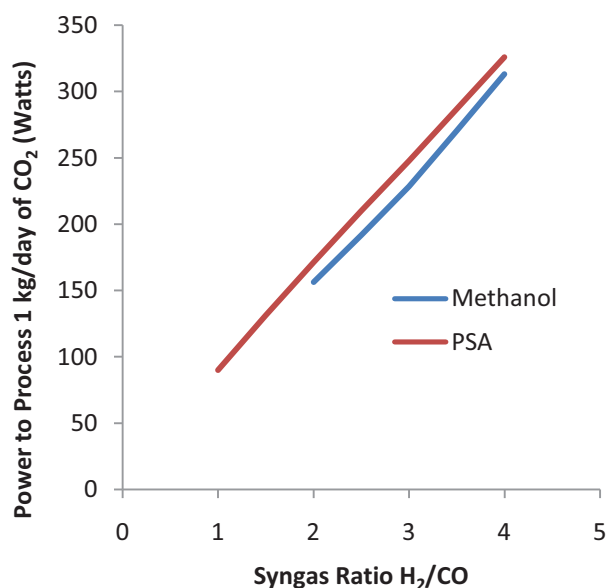


Figure 3. Comparing power required to process 1 kg/day of CO_2 between methanol synthesis and PSA separation.

Figure 5 shows the inlet mass flow rates of water and carbon dioxide, compared to the methanol production, water from the distillation columns, light gas, and oxygen production flow rates. The methanol production and water from the distillation columns flow rates level out at a syngas ratio of 3. The light gas flow rate decreases. The methanol purity varies between 99 to 100% mole with water as the other component. The distilled water varies between 95 to 97%

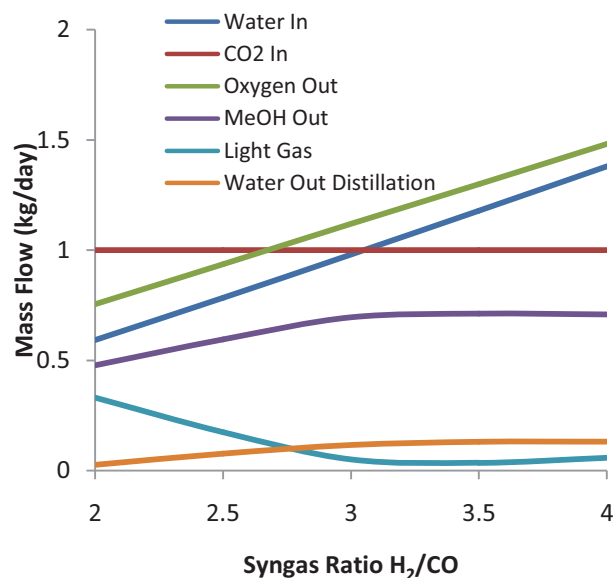


Figure 5. Comparison of methanol, light gas, distilled water, and oxygen flow with inlet flows.

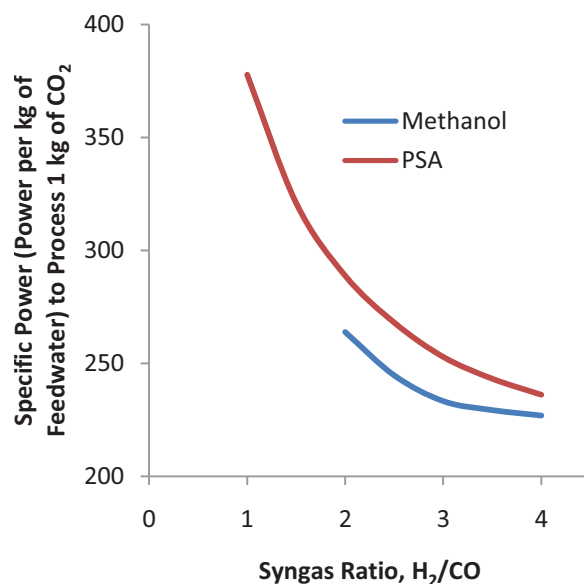


Figure 4. Specific power to process 1 kg of CO_2 as a function of the syngas ratio

mole with methanol as the other component. The purity of both is more dependent on column conditions than methanol reactor chemistry and syngas ratio.

However the light gas composition is a function of syngas ratio as shown in Figure 6. As the syngas ratio increase, the composition of the light gas shifts from carbon dioxide to hydrogen due to the increased amount of hydrogen produced. More of the carbon is made into liquid methanol as opposed to carbon dioxide as the syngas ratio is increased.

Figure 7 shows the performance ratios and % carbon

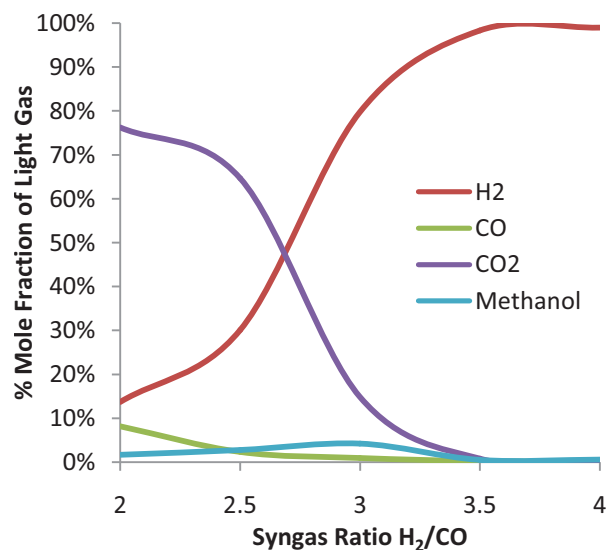


Figure 6. Comparison of methanol, light gas, distilled water, and oxygen flow with inlet flows.

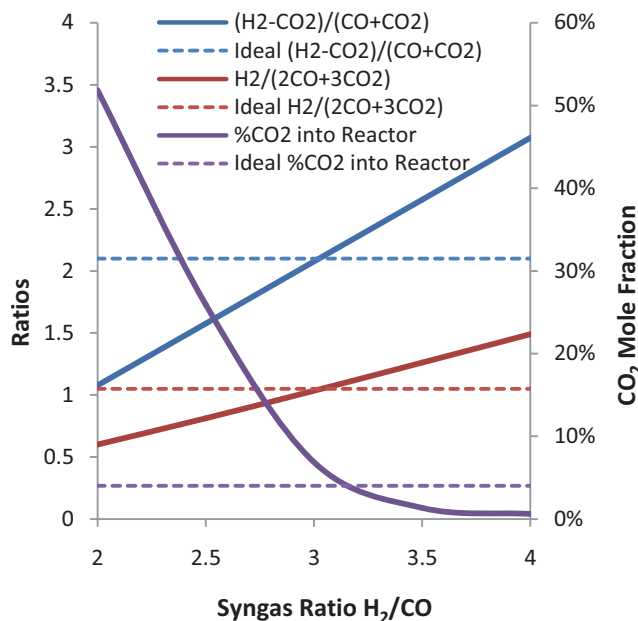


Figure 7. Performance ratios and carbon dioxide fraction for methanol production as a function of the syngas ratio.

dioxide content for the various syngas ratios and compares them to the optimal performance conditions. At a syngas ratio of around 3, the metrics are met and the ideal carbon dioxide condition is closely met.

For the PSA cases, the mass flow rates of hydrogen production, purge gas, and oxygen production are compared to the inlet carbon dioxide and water flow rates, see Figure 8. As

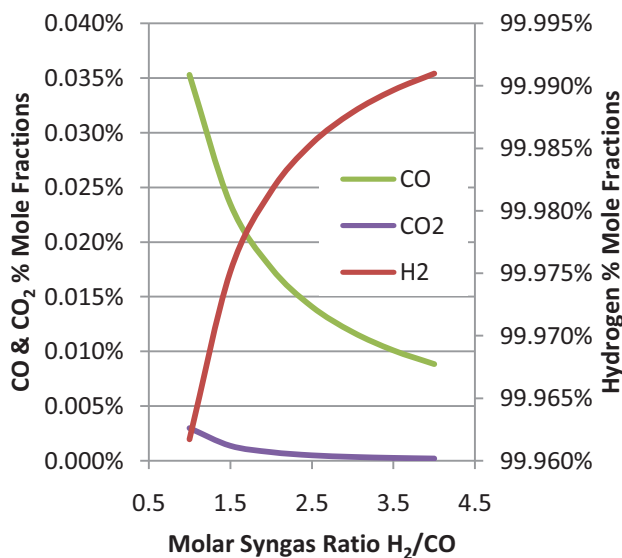


Figure 9. Performance ratios and carbon dioxide fraction for methanol production as a function of the syngas ratio.

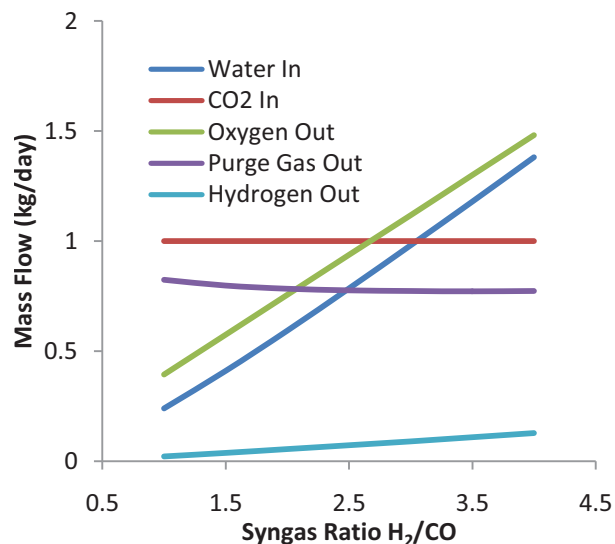


Figure 8. Mass flows of purge gas, hydrogen and oxygen flow rates compared to inlet water and carbon dioxide flow rates.

the syngas ratio increases, the hydrogen production rate increases and the purge gas flow rate decreases.

Figures 9 and 10 show the compositions of the hydrogen and purge gas streams. The hydrogen stream increases from a purity of 99.9 to 99.99% as the syngas ratio increases. Both the carbon dioxide and carbon monoxide content decrease as this ratio increases because there is increased hydrogen (as water) entering the co-electrolysis process.

The carbon dioxide composition of the purge gas

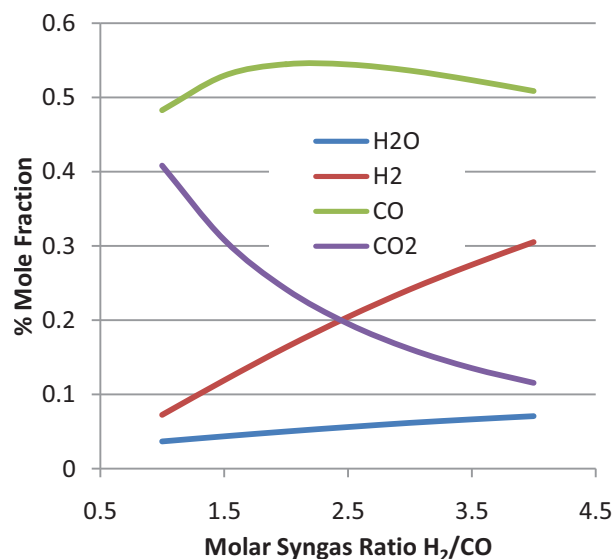


Figure 10. Performance ratios and carbon dioxide fraction for methanol production as a function of the syngas ratio.

decreases rapidly and then begins to level out, as the syngas ratio increases. The carbon monoxide composition increases until the ratio is 2 and then decreases as the ratio increases. The water content of the purge gas increases linearly, as the ratio increases. The hydrogen composition also increases linearly but at a higher rate. As the hydrogen increases, more of the carbon dioxide is shifted to carbon monoxide due to the water gas shift reaction. However, the hydrogen increases at a faster rate than the carbon dioxide resulting in a higher composition of hydrogen and a decrease in carbon monoxide as the ratio increases.

CONCLUSIONS

A comparison was made between two processes for fuel production and combustion which used the syngas product from the co-electrolysis of water and carbon dioxide. In the first process liquid methanol is produced for storage and/or combustion; in the second process hydrogen is separated from syngas and the components are then combusted separately. Power and products were plotted vs. the molar ratio of H_2/CO in the syngas. The following conclusions are drawn:

- The power required to make methanol is less than the power required to separate the syngas, over all syngas H_2/CO ratios evaluated, because process heat from methanol production may be used to reduce the power required to heat up the gases feeding the co-electrolysis process.
- If fuels were to be stored for any length of time prior to combustion, pressurization of the separated gases would be necessary, accentuating the advantage of liquid fuel production/storage. Hydrogen gas from the PSA separation process would need to be further compressed to much higher pressures for storage, where no compression is necessary for the liquid methanol fuel.
- Methanol production is optimal at a syngas ratio of 3. This corresponds to an input H_2O/CO_2 ratio of 0.98:1 or a molar ratio of 2.4:1. Humans respire/release H_2O and CO_2 in a molar ratio from about 5:1 - 6:1, providing ample water for the syngas ratios evaluated here (up to 4:1). The oxygen output from co-electrolysis can be extracted for human use (but would need to be separated from the purge) or used for combustion.
- At higher syngas ratios (higher water input), the hydrogen product from pressure swing adsorption increases and becomes purer, and the purge gas flow and carbon dioxide content decrease. Specific power (power per kg water feed, with constant 1 kg CO_2 feed) for the two models decreases as syngas ratio increases.
- The methanol production process introduces a small amount of light hydrocarbons, propanol and Di-methyl-Ether, in the combustion product CO_2 stream. The effect of these contaminants on the co-electrolysis system is

unknown. If returned to the space cabin, the trace contaminant control system would have to remove them.

The following recommendations should be considered:

- With co-electrolysis, it is theoretically possible to revitalize the atmosphere of a space cabin and recover oxygen for human metabolic use, simultaneously providing fuel/energy for transportation or other crew needs. Additional oxygen is needed to burn the fuel. If the combustion products can be captured and used for fuel production again, power/fuel needs can be nearly self-sustaining.
- From a power perspective, methanol production is preferable to separation of syngas. Optimal production of methanol should be at a syngas ratio of 3.
- The co-electrolysis process produces the desired syngas ratio if fed the appropriate ratio of H_2O/CO_2 . The desired syngas ratio can be easily obtained using co-electrolysis by adjusting the inlet flows of CO_2 and H_2O .

From a purity perspective, separation of gases is preferable to methanol production. In the separation scenario, feed with higher water content produces higher purity hydrogen.

ACKNOWLEDGMENTS

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