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Effect of water on performance and sizing of fuel-processing reactors

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Abstract

Many analyses have been completed on the operating characteristics of fuel processors as a function of fuel usage, power density and specific power as related to efficiency. In addition, it is widely recognized that depending on the fuel type, fuel processors will either be net producers or consumers of water. This has led to theoretical simulations to determine the maximum efficiency that can be achieved given a processor's overall water balance. Moreover, the effect of water for steam and autothermal reformers (ATR) has been investigated to gain an understanding of how it will be influenced given the net results of the system water balance. However, little attention has been given to the effect of water on the reactors downstream of the reformer. Furthermore, a simulation that incorporates the actual, not only theoretical, operation of the reactors coupled with the water balance issues has not been investigated until now. This paper will report on the effect of water on the operation of the CO clean-up train, including water–gas-shift (WGS) and preferential oxidation (PROX) reactors, and its influence on the overall efficiency of the processor system as compared to theoretical thermodynamic calculations. The comparison illustrates that a purely thermodynamic simulation can lead to a less efficient system design than could otherwise be possible once actual reactor performance is included.

Keywords: Water balance; Fuel processor

1. Introduction

The quest for clean power generation in conjunction with renewable fuel sources has given rise to significant effort in fuel cell research, development and application. That effort has produced a wide variety of fuel cell types with widely different operating temperatures and fuel requirements. The hydrogen fueled, polymer electrolyte membrane (PEM) fuel cell has been identified as the preferred fuel cell technology choice for transportation applications [1]. That choice is driven by a number of factors, such as moderate temperature operation, high power density, rapid dynamic response and hydrogen as a fuel. Yet issues associated with hydrogen storage and distribution are most problematic, thus, hydrogen is not yet available for PEM fuel cells to be implemented for large scale transportation applications [2]. Therefore, to continue the development of transportation ready PEM fuel cells, hydrogen is currently being extracted from fossil fuels and alcohols. The reactors required to process the fossil fuel to yield hydrogen are coupled together into a fuel processor system. Analysis of fuel processor designs comprising autothermal reformers (ATR), water–gas-shift (WGS) and preferential oxidation (PROX) reactors, either focus on individual reactor performance or on overall system integration and efficiency but usually not both. This has led to a significant level of understanding of the requirements for a fuel processor system. For individual reactors, the analyses have indicated that fast start-up, transient response, size and weight are very important. On the other hand, overall system analyses have highlighted the importance of heat management and the necessity to recycle as much water as possible thereby maintaining water balance. To date, studies have mainly been made on the effect of water on ATR performance and its impact on overall fuel processor design. However, the effect of water on CO clean-up reactors, i.e. the WGS and PROX, and, in turn, the effect on overall system efficiency,

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has been lacking. While it is recognized that water will directly impact the WGS reactor, as water is a reactant in that system, the full extent has not been explored. Kinetic data presented in this paper coupled with a reactor design model provides detailed insight on the impact water has on WGS reactor sizing and performance, such that its impact on the overall system efficiency can be quantified. Moreover, water is generally considered an inert in the PROX reactor, yet our results indicate that water has a significant impact on the multiplicity of steady-state operation and can impact the performance in terms of a synergistic effect with oxygen.

To identify the issues that need to be considered when designing a fuel processor system for optimized efficiency a preliminary process flow diagram (PFD) was generated. The necessary experimental data and kinetic expressions were also programmed in to allow realistic simulations to be done. The PFD was then simulated in ASPEN® to calculate the amount of heat removal or addition that would be needed to ensure efficient operation of the system. The intent of the simulation was to determine the critical issues that need to be investigated when designing a fuel processor system. To that extent, only major components were incorporated and the ancillary components such as blowers, pumps and vaporizers were not included because they are considered secondary in terms of system design for maximum efficiency. It is recognized that those components add some complexity but for a first cut analysis they are considered less important.

The implications of incorporating a realistic analysis when modeling operational space or designing for optimal performance are applicable to all reactors in general. Issues such as multiple steady states and influence of reactants and flow rates can be accounted for when designing any type of reactor, provided the required information in known. The results achieved and reported in this paper are specific to short contact time reactor (SCT) substrates. To that extent, it is possible that some phenomena are manifested in particular ways that are more evident as compared to other reactor configurations. Even so, the fundamental aspects that yielded the current results would be present, to more or less of a degree, on other reactor substrates. A main attribute of the SCT reactors is the ability to operate with high catalyst effectiveness factors and in a regime where transport limitations are minimized. Previous publications highlight the different aspects of some of those attributes and the reader is referred there for more information [3–8].

2. Model generation

The model to calculate the various scenarios to explore the effect of water on the performance and efficiency of the fuel processor was assembled in ASPEN® with input from experimental data. The ATR was modeled using the RGIBBS reactor module, which minimizes the free energy based on atom balance constraints [9] and extensively validated with reactor performance data with varying amounts of water, air and fuel flow rates. In all instances examined in this study, the ATR achieved equilibrium product distributions for the temperatures achieved. Although the reactor was not completely adiabatic, the results of GC analysis and temperature readings from the experiments were normally within a few percent of the ASPEN calculations. To ensure the integrity of the calculations, the steam to carbon ratio (S/C) and oxygen to carbon ratio (O/C) ranges that were simulated were within the experimental range that provided equilibrium effluent. The data for the ATR reactors has been presented elsewhere [10] and the reader is referred to that publication for further information.

The WGS reactor was more extensively and fundamentally explored resulting in the ability to arrive at a tractable rate expression that captured the CO conversion kinetics with the proper equilibrium constraints. The experiments done on the WGS reactor allowed determination of an overall rate expression where the kinetics were obtained following the method of Kahlich [11]. The WGS reactor was initially investigated using a rigorous first principles approach that led to a specific code which very accurately describes the performance of short contact time reactor substrates with particular catalyst coatings and formulations. In this case, the substrate was coated with an alumina based support and a promoted, platinum-based catalyst formulation. The model iteratively calculates the composition and fluid changes across individual elements, such as the mass transfer and kinetic rates, and the pressure drop based on local properties. The code's only inputs are the initial conditions and the kinetic rate constants. The result also yields pressure-drop predictions, where the pressure-drop correlations developed by Armour and Cannon [12] were closely followed. Modifications were made to account for the unique properties of the short contact time substrate employed in the fuel processor reactors. The model takes into account both the viscous and inertial losses and the total pressure loss is calculated as a function of friction factor.

The experiments were conducted in a differential reactor mode assuming that the WGS reaction proceeds through the following one step reaction model:

$$CO + H_2O \rightleftarrows CO_2 + H_2$$

The methanation reaction was determined to be a very minor contributor in the range of interest. It has been shown that methanation on the short contact time reactors is actually suppressed and does not impact the overall reaction chemistry to the same extent as other types of WGS reactor configurations [13]. The stationary kinetics of this one-step shift reaction was determined using the power-law rate equation. According to the literature [14,15], the power-law rate equation can describe the steady-state kinetics of the

WGS reaction, thus the following one-step power law model was used [16].

$$r_{CO} = k_0 \exp\left(\frac{-E}{RT}\right) C_{CO}^{m} C_{H_2O}^{n} (1-\beta)$$

where E, m and n were empirically determined from the differential reactor experiments. β is the reversibility factor defined as:

$$\beta = \frac{[C_{CO_2}][C_{H_2}]}{[C_{H_2O}][C_{CO}]K_T}$$

where K_T is the equilibrium constant for the WGS reaction.

These expressions, with the appropriate constants, were extensively tested using an in-house code to ensure accurate representation of reactor performance. A custom reactor module was then programmed, using a FORTRAN based subroutine, in ASPEN® using these expression and constants. Running the simulation then included the RGIBBS and the RPLUG, which is a programmable module where user-defined kinetics of specific reactions can be input, modules and satisfactory comparisons were obtained between ASPEN® and the in-house model. It should be noted that the sub-routine programmed into ASPEN® was adapted from a detailed model that was built from first principles in terms of transport and reaction kinetics and later validated through experiments. This model is capable of predicting the kinetic and transport controlled regimes of the reactor both spatially and temporally without any adjustable parameters.

These reactor modules provided the basis for the fuel processor simulation. The process streams from each reactor were integrated to provide a measure of the overall efficiency of the fuel processor. The resulting PFD consisted of the ATR, as represented by the equilibrium reactor RGIBBS, the WGS, represented by the actual kinetics in the RPLUG module and integrated heat exchangers with temperature approach values of ~30 °C. Fig. 1 shows a representation of the model used to determine the effect of water on actual reactor operation and the impact on overall fuel processor efficiency.

The PROX reactor was more complicated because of the number of simultaneous reactions occurring, as well as multiple steady-state behavior. The combination of those complexities rendered the determination of accurate kinetics a more involved task and as such was not included in the ASPEN model. However, to complete the effect of water on the CO cleanup train reactors, investigation via experimentation into PROX performance was done for various water concentrations. The PROX reactors were tested in the integral mode to allow rudimentary correlations to be developed and provide a basis for prediction of the PROX reactor performance and its impact on overall efficiency. A more detailed discussion in the following section elaborates on the unusual performance of the PROX reactor with varying water concentrations.

It is interesting to note that a similar effort to the one just described was done for reforming studies of *iso*-octane, used as a surrogate to naphtha, to predict trends of hydrogen yields and product distribution of a liquid fueled processor [17]. A very extensive and thorough analysis was done on the reformer, which consisted of the ATR and WGS reactors. It included regressed kinetic expressions for the ATR and compared performance with effectiveness factors through a Theile analysis and transport effects for the ATR and WGS reactors. Results of the simulation were compared to experimental data with good agreements. That study also identified the catalyst effectiveness factor as a critical issue for good reformer design.

3. Results and discussion

The results of the integrated ATR and WGS PFD simulation identified issues that should be a focus for proper design and layout of the component reactors of the fuel processor. One key issue that was revealed during the simulation was the complexity of fully integrating the various streams to achieve maximum efficiency. Not only is the heat balance issue very important for efficient operation, the optimal use of water is equally or more important. Because the processor design strives to maximize the power density (kW/kg) and the specific power (kW/l), the amount of water that needs to be fed to the processor has a large impact. That is because the weight burden of carrying liquid water and the energy requirement to vaporize the necessary amount of water. These few issues alone require a multivariable optimization. If one tries to include startup, shutdown and transient operation the optimization problem almost becomes intractable. Therefore, most analyses usually optimize a subset of variables with the hope that different subsets can then be integrated and overlapping solutions identified. To date, no analysis has taken into account the actual performance of the reactor components during optimization calculations. Usually only thermody-

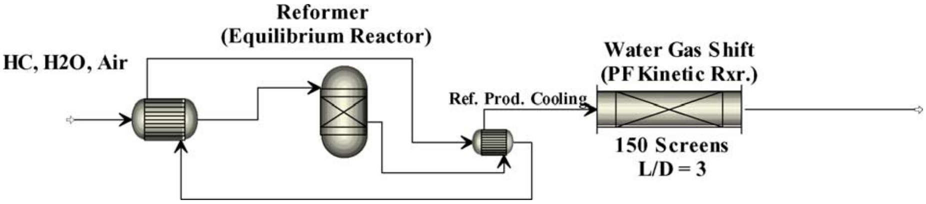

Fig. 1. ASPEN® schematic of fuel processor. Output of shift reactor (CO ~ 1%) enters PROX.

namic calculations are used to find a pseudo operating space for the reactor components within the optimization scheme or parametric studies are done on a limited number of designs.

Examples of those types of approaches are often seen in the literature. A very good classic type of analysis is shown by Zalc and Loffler [18] where basic chemical engineering principles are used to elucidate the boundaries in which the fuel processor reactors operate. This type of study sets the stage for incorporation of actual performance characteristics and helps identify the more important steps associated with efficient fuel processing. Wheeldon et al. [19] combines a membrane permeation model with thermodynamics to investigate the variation of temperature and pressure for steam–methanol fuel cells. A collaboration between NREL, Vulcanworks and Nuvera Fuel Cells, Inc. has resulted in an Advanced Engineering Environment (AEE) package that allows extremely rapid iterations of system design and enables identification of optimized systems. While it is a very powerful tool, which allows many scenarios to be tested, it relies on a database of design and manufacturing rules and mathematical models for fuel cells and fuel processors [20]. A very good analysis on a gasoline fuel FPS for automotive applications has been conducted by Argonne National Laboratory. It was a parametric study on a limited set of reactors and attempts to generalize findings were subject to assumptions used in the thermodynamic equilibrium analyses [21]. One study that does incorporate more realistic reactor operation, by including kinetic expressions for the ATR, is from Lattner and Harold [22]. Their study, however, uses a palladium based membrane to eliminate the need for the WGS and PROX reactors and thus does not contain the information that this study provides should one design a system using the CO cleanup train. Lastly, a review study which helps to identify the areas that are well understood and other areas that either need more work or where work should be initiated is presented by Song [23].

While those examples are valuable for the systems they pertain to and provide a set of boundaries to be used as guidelines during initial design stages, they can miss the intricacies that exist during actual operation. For instance, the use of a condensing heat exchanger is often suggested as a way to recover and recycle water to improve the efficiency of the FPS. The water recovered is fed into the ATR and lessens the demand of fresh water feed and, in turn, the amount of water needed to be stored. However, when realistic performance parameters are used for the heat exchanger design, such as temperature approach, heat transfer coefficients and materials of construction, it is soon realized that the heat exchanger becomes so large that power density and specific power are inordinately reduced compared to any gains achieved from carrying less fresh feed water. Overlaying on that the energy considerations for carrying such a large and heavy exchanger and the gains disappear. Since the ATR and WGS performance primarily determines the energy demands of the processor, it is imperative to accurately represent the performance of the units against the optimization variable considered.

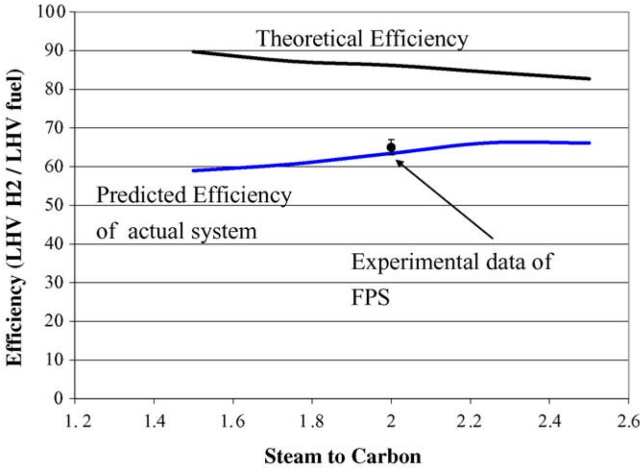

Fig. 2. Theoretical FPS efficiency compared to actual FPS efficiency for various S/C ratios.

As stated previously, this study analyzed the effect of water, either fresh feed or recycle, on the actual performance of the ATR, WGS and PROX reactors and yielded some unexpected results. Fig. 2 shows the results of a set of calculations done on a fuel processor for theoretical and actual system efficiencies. The theoretical efficiencies were calculated using ideal reaction stiochiometries and enthalpy balances similar to those done elsewhere [24]. The predicted efficiency of the actual system was achieved using the method described in the above section. Each subsection of the model was validated using test data from each individual component. To validate the composite FPS model, an integrated fuel processor was tested in a configuration similar to that shown in Fig. 1. The main objective for the system design and testing was to ensure that the reactors could be coupled together in a simple manner and deliver the reformate needed to drive a fuel cell. To that extent, balance of plant (BOP) components, such as heat exchangers and controllers, were implemented in an elementary manner so as not to complicate the testing and elucidation of the interaction between reactors. For example, a simple heat exchanger was installed between the ATR and WGS reactors to ensure that the desired temperature change could be achieved to determine the optimal inlet temperature for the WGS operation with the ATR effluent. The parameters controlling reactor-train performance and interaction as well as the feedback between the reactors will have to be refined and quantified for the system to be considered field ready. The effluent from the ATR was passed through an integrated, open-loop, controllable heat exchanger to drop the temperature to 370 °C and directly fed to a WGS reactor. The CO conversion across the WGS reactor was about 95% of the equilibrium CO conversion possible for the temperatures tested. The ATR volume for this performance was about 1.5 cm^3 (0.1 in^3) and the WGS reactor was about

3.0 cm^3 (0.2 in^3) for a 100 watt thermal fuel reformate. The steam to carbon and oxygen to carbon ratios chosen during operation impacts the reactor sizes.

As seen in Fig. 2, the composite model accurately predicts the operation of the entire FPS. Fig. 2 illustrates one of the unexpected results obtained during the study. That is the S/C ratio that yield the highest efficiency is not at 1.5, as theory predicts, instead it is near 2.3. Investigation of this result led to the conclusion that higher steam ratios allow the ATR to produce more H_2 in the same volume as compared to lower S/C. In addition, the ATR operated at a lower temperature, which translates into extended reactor life. Extended testing at those temperatures also indicated no carbon deposition on the catalyst surface as observed by SEM investigation. Impacts on the WGS and PROX reactors are discussed separately in the following section because of the compounded effect water had on their overall performance. All gas compositions are taken on a wet basis unless specifically stated otherwise.

4. Water–gas- shift reactor analysis

The WGS reactor was investigated in order to determine the required space velocities to achieve 90% or higher of equilibrium CO conversion. The results were used to generate input data for the ASPEN$^{®}$ sub-routine and to explore the impact of water on reactor performance. The experimental matrix consisted of variations of steam to carbon ratio entering the autothermal reactor (ATR) from 1.5 to 2.0, while keeping O/C ratio constant at 0.9. The test results show that a higher water concentration in the ATR stage allows smaller WGS reactors. In general, a slight increase in water addition to the ATR inlet results in a significant decrease in WGS reactor size and consequently pressure drop. In fact, if the water supplied to the ATR results in a steam to carbon ratio of 2.0, the shift reactor can reduce the CO, in a single stage, to below 1%, which is where a PROX reactor could be used. Experiments and calculations indicate that for every 1% increase in H_2O to the ATR, there is almost a 10% decrease in water–gas-shift reactor size when using conditions approximately similar to those tested.

Fig. 3 shows the results from the experiments and modeling of the WGS reactor with variations in water concentrations to the ATR reactor. From the data, it is clear that ATR S/C ratio greater than 1.5 would allow an efficient WGS reactor design. The ability of the WGS reactor to convert 72% more CO at 50% higher space velocity at a S/C ratio of 1.8 versus 1.5 illustrates the importance of actual reactor performance on optimization calculations. This type of result would not have been borne out of a theoretical calculation that does not take into account the actual WGS kinetics. Theory would focus on the weight and energy requirements needed to maintain a S/C of 1.8 and lead to the erroneous conclusion that less water is desirable. Because water is a reactant for the WGS reaction, and has a power law dependence slightly greater than one, there is a net benefit. Additional water increases the reaction rate to allow for a smaller WGS reactor, thus the decrease in reactor weight, more than offsets the increase in additional water weight. Not included in the ASPEN$^{®}$ sub-routine are the effects of pressure drop throughout the FPS and the impact on power output. Those correlations are however included in the detailed, first principles model and have been calculated for all the reactors. The impact that pressure drop will have on the system efficiency is not totally clear since it will vary with the type of pumps or blowers chosen for the particular design. Thus, it was not incorporated into the current analysis. As noted previously, the model used for the system efficiency calculations does not have any adjustable parameters, since they were all determined from relevant experimental data and thus fixed for the range of analysis.

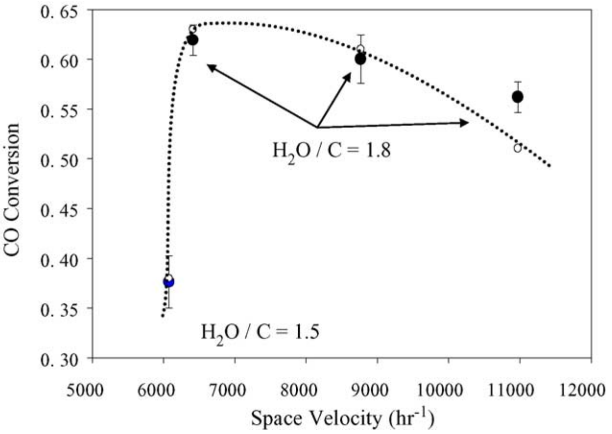

Fig. 3. Effect of water on water–gas-shift reactor size and performance. Experimental conversions are greater than or equal to 90% of the calculated equilibrium constrained conversions.

5. Preferential oxidation reactor analysis

To complete the effect of water on the CO cleanup train reactors, investigation into PROX performance for the various water concentration changes was explored. Due to the complex nature of the PROX reactions, complete elucidation of the kinetic expressions has not yet been done. To get insight into the operation of the PROX reactors, parametric tests were done which allowed correlations to be made. Those tests resulted in two significant findings that impact the design of PROX reactors and consequently system design. Multiple steady-state behavior of the reactor was the first finding from those tests. The second significant result from the PROX testing with various water concentrations was evidence of a water–oxygen synergy within the reactor. These are other instances where theoretical calculations alone of the type described above would not capture experimental behavioral differences and their impact on system level efficiency. The theoretical calculations would lead to a design that minimizes the amount of water used, yet it is precisely the low water conditions that push the PROX reactor into an undesired steady state that consumes significant amounts of hydrogen and reduces the synergistic effect of water and oxygen. While investigation into these effects is ongoing, a rudimentary explanation is given below.

Table 1
Results of dual steady-state behavior of the PROX reactor

Inlet concentrations					Reactor temperature		Conversion	
O_2	H_2	CO	CO_2	H_2O	Inlet	Surface	O_2	CO
1.69	43.46	1.41	18.08	7.30	91.8	160.1	30.12	22.15
1.68	44.40	1.41	18.10	7.30	90.0	253.5	101.34	23.01

6. Dual steady-state nature of the PROX reactor

Selective oxidation of CO in hydrogen over different catalysts has been extensively examined with different precious metal catalysts having been found to be highly selective for the PROX reaction [25–28]. A general understanding of these systems is that at temperatures before the onset of the CO light-off the surface is covered with adsorbed CO. As the temperature is increased the fraction of the surface covered with CO decreases, and this opens up sites for oxygen adsorption and subsequent reaction. Above a certain temperature the fraction of CO occupying the surface decreases even further and hydrogen chemisorbs and reacts on the surface in competition with CO, reducing the selectivity towards CO oxidation. Therefore, a common feature of all these systems is that there exists a window of operation in temperature between the light-off curves for CO and H_2, the object being to operate at a catalyst temperature sufficient for high activity of CO oxidation (for reduced size of catalytic reactor), but below that for significant consumption of the hydrogen. This results in different temperature windows and optimum catalyst temperatures, which need to be identified for different catalyst formulations.

We observed the dual steady-state behavior of the reactor only at very dry feed conditions. However, when the water content is above 15% in the feed to the PROX, the reactor consistently gives high CO conversion with nearly 45% selectivity, defined as rate of CO conversion over rate of H_2 conversion. In addition, oxygen is detected in the product stream at varying levels, depending on the conditions tested. In comparison to monolith or pellet beds, we suspect that short contact time substrates should allow PROX reactors to operate at significantly lower water concentrations before the onset of the hydrogen oxidation reaction, i.e. the high temperature steady state. Initial analysis indicates that heat removal at the catalyst surface is a very important parameter in avoiding dual steady-state operation because heat generated from the CO oxidation reaction is quickly transferred into the gas phase, thus moderating the surface temperature.

Table 1 displays representative results from experiments that show the dual steady-state nature of the selective CO oxidation reactor. The first row provides the results of the reactor operating in the preferred steady state. The CO conversion was 22% with oxygen conversion at 30%, which results in a selectivity of slightly above 40% with a commensurate temperature rise. The second row shows for the exact same inlet compositions and temperature, the reactor was operated in another, high temperature and undesired steady state. The data indicates that this state was one in which high hydrogen consumption occurred. The evidence for that was seen in the complete conversion of oxygen, without a change in CO conversion and the higher surface temperature as compared to the previous state. Since hydrogen is the fuel in this case, this state must be avoided to ensure that the efficiency of the reactor system remains high.

Additional experiments have been conducted that varied O_2/CO (lambda) from 0.7 to 3.0 holding all other feed conditions constant. Dual steady-state operation was observed for the entire range tested providing more evidence that the water amount in the feed composition is probably the dominant factor. This type of experiment was repeated for a different CO feed concentration and nearly the same behavior was recorded. This dual steady-state nature persists for a wide range of lambda, which points to the fact that dual steady state is more influenced by feed composition and more specifically by water amount. Since, water has high-heat capacity this may temper the heat rise and delay the onset of H_2 oxidation reaction.

7. Water–oxygen synergy of the PROX reactor

The second significant result from the PROX testing with various water concentrations was evidence of a water–oxygen synergy within the reactor. Table 2 comprises representative conditions and results from repeat experiments, that indicated a water–oxygen synergistic reaction occurring. The objective of the three experiments whose results are shown in Table 2, were to determine the contribution of oxygen and water separately toward oxidation of CO and consumption of hydrogen. The first row of the table provides the conditions and results of a baseline experiment, where the system was operating at its targeted steady-state position. Here the conversion is as expected, greater than 90% with 50% selectivity. The temperature rise from the inlet to the outlet is consistent with the amount of reaction. The surface temperature rise also tracks with the gas phase temperature rise; this is one of the attributes of the SCT reactors and has been extensively described elsewhere [29]. The second row has the results of the condition where the water is not included in the feed. The third row shows the results of an experiment where the water

Table 2
Evidence for a water–oxygen synergy within the PROX reactor

Inlet concentrations					Reactor temperature			Conversion		
O_2	H_2	CO	CO_2	H_2O	Inlet	Surface	Outlet	O_2	CO	lamba
0.65	31.79	0.55	13.90	32.88	101.2	194.3	192.2	73.33	92.36	2.36
0.65	31.74	0.55	13.91	–	109.6	136.0	135.5	6.15	26.23	2.36
–	31.86	0.55	13.91	32.88	110.4	112.4	109.9	–	−0.50	–

was resumed and the oxygen was turned off. Each time a reactant was turned off, nitrogen was adjusted to compensate for that loss to maintain a constant GHSV. Inspection of the CO conversion shows that the sum of the CO conversions from the individual reactants does not add up to the conversion when they are both present. In fact, the water alone shows nearly zero reaction which is expected because that condition represents a water–gas-shift reaction of which the kinetics are very slow at that temperature. It is clear, however, that it is not only the oxygen that is converting the CO since its conversion is only 26% as compared to a 92% conversion when water is present. It is evident that water somehow initiates or promotes the CO oxidation reaction.

While there has not been any literature found specifically on water–oxygen synergy, other researchers have observed similar water enhanced reactions. For example, there was a study that showed a hydrogen water synergy [30] and a carbon dioxide water synergy [31]. Both studies indicated that water addition increased the amount of CO oxidation more than expected or predicted. The current experiments, shown in Table 2, provide additional evidence to the water assisted or water enhanced CO oxidation observations. These results point toward water acting as a catalyst or promoter for the selective CO oxidation on alumina supported platinum-based catalysts. It is known that water has a high-heat capacity, thus its temperature controlling, or heat absorbing, capability is recognized as one way to control reactions that liberate heat. In the case of the selective oxidation of CO this is very important, as discussed above, so as not to activate or light-off the hydrogen oxidation reaction. Yet water plays a significant role as a promoter in this reaction sequence. Fig. 4 attempts to conceptually show the water–oxygen synergy effect where formate-like species are identified to help explain the promoter effect water has on CO oxidation.

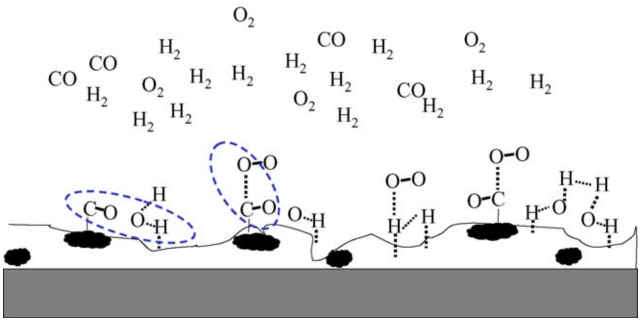

Fig. 4. Conceptual depiction of the water–oxygen synergy effect.

Incorporating some of the other researchers' reasoning provides one possible explanation for why water promotes this type of reaction. Water is conjectured to absorb and become activated by the stabilized alumina support while the CO is preferentially absorbed and activated by the catalyst metal. The CO can now be oxidized by the activated water or incoming oxygen. That leaves behind a hydrogen molecule from the water and an oxygen radical. The oxygen radical probably reacts with gas phase hydrogen more readily than gas phase CO purely because of the abundance of hydrogen. However, the hydrogen molecule left behind from the water may desorb or become displaced by another incoming CO molecule and enter the gas phase. The CO oxidation activity on the catalysts described above is reported to be enhanced by moisture in some cases with surface formate species postulated as intermediates in this reaction. For example, Kahlich et al. [32] observed that the CO oxidation rate is enhanced in the presence of water and attributes this enhancement to the interaction of the hydroxylated Al_2O_3-support and CO adsorbed on Pt. The researchers describe the formation of formate species on the support if the CO oxidation reaction is carried out in the presence of either H_2 or H_2O. Shubert et al. [30] reports that if a mixture of 1% CO in H_2 is passed over Pt/α-Al_2O_3, conditioned at 400 °C, the formate band barely reaches the detection limit. However, if 0.6% H_2O is added to the same mixture, the formate growth rate increases by a factor of nearly 300 times. This may help explain why we see a water–oxygen synergy and a high selectivity toward CO oxidation when the hydrogen concentration is nearly 60 times greater.

8. Conclusion

This paper reports on the effect of water on the overall fuel processor efficiency based on actual, as opposed to theoretical, component performance. The resulting implication is that when realistic performance parameters are incorporated into system efficiency analyses, it is possible to obtain unexpected results in terms of where to optimally operate the system. For example, the major finding here indicates that a theoretical calculation would lead to a design goal of minimization of water concentration into the ATR yielding a S/C ratio of 1.5. Yet, under realistic operating conditions, a S/C ratio of 2.3 yields a higher efficiency for the FPS. In addition, other findings that theoretical calculations would not capture are highlighted in the multiple steady-state behavior and water–oxygen synergy of the PROX reactors. There still is the need to ensure that each component performance equation incorporates parameters that affect the overall system and is coupled to other parameters such as volume and weight impacts.

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