Towards autothermal hydrogen production by sorption-enhanced water gas shift and methanol reforming: A thermodynamic analysis

Diana Iruretagoyena, Klaus Hellgardt, David Chadwick*  
Department of Chemical Engineering, Imperial College London, South Kensington Campus, London SW7 2AZ, U.K.  
*Corresponding author: d.chadwick@imperial.ac.uk

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Abstract

Hydrogen production by the water gas shift reaction (WGS) is equilibrium limited. In the current study, we demonstrate that the overall efficiency of the WGS can be improved by co-feeding methanol and removing CO₂ in situ. The thermodynamics of the water gas shift and methanol reforming/WGS (methanol-to-shift, MtoS) reactions for H₂ production alone and with simultaneous CO₂ adsorption (sorption-enhanced, SEWGS and SEMtoS) were studied using a non-stoichiometric approach based on the minimisation of the Gibbs free energy. A typical composition of the effluent from a steam methane reformer was used for the shift section. The effects of temperature (450-750 K), pressure (5-30 barg), steam and methanol addition, fraction of CO₂ adsorption (0-95%) and energy efficiency of the shift systems have been investigated. Adding methanol to the feed facilitates autothermal operation of the shift unit, with and without CO₂ removal, and enhances significantly the amount of H₂ produced. For a set methanol and CO input, the MtoS and SEMtoS systems show a maximum productivity of H₂ between 523 and 593 K due to the increasing limitation of the exothermic shift reaction while the endothermic methanol steam reforming is no longer limited above 593 K. The heat of adsorption of CO₂ was found to make only a small difference to the H₂ production or the autothermal conditions.

Introduction

During the last decades the continuous increase in the demand of energy and environmental concerns have promoted interest in the use of hydrogen as energy carrier for stationary and mobile applications, since no carbon emissions would be generated by the end users. Hydrogen can be produced from a variety of sources and routes although the cheapest is steam reforming of methane and other hydrocarbons, reaction 1. The process consists of a syngas generator (i.e. reformer or gasifier) followed by a water gas shift (WGS) section, reaction 2. A simplified scheme of a hydrogen manufacturing facility is shown in Figure 1. Typically, the shift stage consists of two consecutive steps: 1) a high temperature shift (HTS) carried out between 573 K and 773 K to benefit from high reaction rates, and 2) a thermodynamically favourable low temperature shift (LTS) that takes place between 483 K and 543 K.

\[
\begin{align*}
\text{CH}_4 + H_2O & \leftrightarrow 3 H_2 + CO \quad \text{(reaction 1)} \\
CO + H_2O & \leftrightarrow H_2 + CO_2 \quad \text{(reaction 2)}
\end{align*}
\]
The energy efficiency of the syngas generators has increased significantly in recent years. However, there has been little progress on improving the efficiency of the shift stage. The temperature of the effluent of the reformer/gasifier is significantly higher (1123 K – 1373 K) than that specified for the WGS catalyst, so cooling is needed before the shift reactor. Many manufacturers cannot export the steam produced in these heat exchangers and therefore it is desirable to reduce this waste. One of the few attempts to enhance the performance of the WGS section is the methanol-to-shift (MtoS) process developed by Haldor Topsøe, which aims to minimise the energy losses while boosting the hydrogen productivity, Figure 2.[1] In the MtoS process, methanol and syngas are co-fed to a reactor where water gas shift occurs alongside methanol decomposition (reaction 3) and steam reforming of methanol (reaction 4). Thus, the heat that needs to be removed downstream of the syngas generator is transferred as sensible and latent heat to the methanol stream. Additionally, the energy released by the exothermic WGS can compensate the heat used in situ by the endothermic steam reforming of methanol, resulting in the autothermal operation of the shift reactor. The reforming of methanol also contributes to the formation of hydrogen and it has been reported that the MtoS process can increase the H2 productivity up to 25%.[1] The Cu/ZnO/Al2O3 based catalyst used in this process is reported to be very selective to both reactions and to tolerate higher temperatures than conventional shift catalysts.[1-2] The Topsøe Methanol-to-Shift Technology was developed to meet the increased demand for extra hydrogen from refineries and other users. In principle, the process is applicable to a hydrogen plant on any scale. An advantage of using methanol as energy carrier in the process is that methanol is produced in very large scale at places where natural gas is cheap, and in the future is expected to serve as a vector for renewable hydrogen.[3,4]

\[ \text{CH}_3\text{OH} \leftrightarrow \text{CO} + 2\text{H}_2 \] \hspace{1cm} (reaction 3)

\[ \text{CH}_3\text{OH} + \text{H}_2\text{O} \leftrightarrow \text{CO}_2 + 3\text{H}_2 \] \hspace{1cm} (reaction 4)

Other significant costs involved in the production of hydrogen are related to the purification of H2 and to the capture of the associated CO2 to meet environmental regulations. The removal of CO2 from the effluent of the WGS reactor is usually conducted at medium pressures in pressure-swing adsorption (PSA) columns. An alternative approach is the in-situ sequestration of CO2 as it is formed in the WGS reactor by means of solid adsorbents. The so-called sorption enhancement process is very appealing as it would also favour the shift reaction thermodynamically, rendering higher yields of H2. Instead of having two shift reactors in series operating at high and low temperatures, sorption-enhanced water gas shift (SEWGS) requires only one reactor at intermediate temperature, where fast kinetics assisted by adsorption potentially result in smaller units.[5] Although the concept of sorption enhancement has been claimed to be useful for various reactions, it has been shown to be more suitable for the WGS.[6] The CO2 adsorption requirements for the WGS reaction are not that demanding and therefore the enhanced process is more feasible than for example sorption-enhanced steam reforming of methane.

Accurate description of the chemical equilibrium is crucial for the design of sorption-reaction units. While previous studies have addressed the thermodynamics of sorption-enhanced hydrogen production for reactions such as steam reforming of methane,[7,8,9] water gas shift reaction,[10,6,11] steam reforming of biomass,[12,13] and more recently for glycerol steam reforming,[14,15] bio-oil,[16] and ethanol reforming,[17,18,19] to our
knowledge it is the first time that the thermodynamic analysis of the methanol-to-shift and sorption-enhanced methanol-to-shift reactions is reported. The analysis of the shift section has been based on a typical composition of the effluent from a steam methane reformer.[2] The range of temperatures covers typical low-temperature shift conditions, i.e. from 473 K, and up to 723 K where thermal cracking of methanol occurs. The effects of pressure and steam addition are evaluated for sorption-enhanced WGS and MtoS. For methanol-to-shift, the effect of feed molar ratio of CO to methanol is assessed. In addition, the amount of methanol required for autothermal operation is investigated. Sorption-enhanced methanol-to-shift appears as a promising technology to enhance the productivity of hydrogen and the energy efficiency of the shift section while a CO₂ rich stream for sequestration is produced.

2. Methods

2.1 Equilibrium Calculations

An algorithm to calculate the chemical equilibrium of the water gas shift and the methanol-to-shift reactions with simultaneous CO₂ adsorption was developed following a non-stoichiometric approach based on the minimisation of the Gibbs free energy. The total Gibbs free energy of a chemical system at constant temperature and pressure is expressed as:

\[ G(n_i) = \sum_{i=1}^{N} \mu_i n_i \quad i = 1 \ldots N \]  

\( G \) is the total Gibbs free energy and \( \mu_i \) and \( n_i \) are the chemical potential and the number of moles of species \( i \), respectively. The thermodynamic function needs to be minimised constrained to the element balance

\[ \sum_{i=1}^{N} n_i a_{ij} = A_j \quad j = 1 \ldots M \]  

where \( a_{ij} \) is the number of atoms \( j \) in the molecule \( i \) and \( A_j \) is the total number of atoms \( j \) in the system. By introducing the Lagrange multipliers, \( \lambda_j \), the Gibbs free energy can be expressed as a new function which includes the element balance constraints

\[ L(n_i, \lambda_j) = \sum_{i=1}^{N} \mu_i n_i + \sum_{j=1}^{M} \lambda_j \left( \sum_{i=1}^{N} n_i a_{ij} - A_j \right) \]  

The second term in the right hand side of equation 3 is zero, in agreement with equation 2, and therefore \( G(n_i) \) and \( L(n_i, \lambda_j) \) are equivalent. The critical point of the function \( L(n_i, \lambda_j) \) is obtained by making the partial derivatives with respect to \( n_i \) and \( \lambda_j \) equal to zero. It is obvious by simple inspection that this corresponds to a local minimum since the second derivatives of \( L(n_i, \lambda_j) \) are all positive.

For a gaseous chemical system a set of \( N + M \) non-linear algebraic equations can be written as follows:

\[ \frac{\partial L(n_i, \lambda_j)}{\partial n_i} = \Delta G_i^f + RT \ln \left( P \frac{n_i}{\sum_{i=1}^{N} n_i} \right) + RT \ln \phi_i + \sum_{j=1}^{M} \lambda_j a_{ij} = 0 \]  

\[ \frac{\partial L(n_i, \lambda_j)}{\partial \lambda_j} = \left( \sum_{i=1}^{N} n_i a_{ij} \right) - A_j \]  

\( \Delta G_i^f \) is the standard Gibbs free energy of formation of component \( i \), \( P \) is the pressure, \( n_i \) is the number of moles of species \( i \), and \( \phi_i \) is the fugacity coefficient. The critical point of the function is obtained by making the partial derivatives with respect to \( n_i \) and \( \lambda_j \) equal to zero. It is obvious by simple inspection that this corresponds to a local minimum since the second derivatives of \( L(n_i, \lambda_j) \) are all positive.
where $\Delta G_i^f$ is the standard Gibbs free energy of formation of species $i$ at the temperature, $T$, and $\phi_i$ is the fugacity coefficient of species $i$. Additionally, a particular version of equation 4 has to be written for carbon dioxide to account for the fraction, $f$, of CO$_2$ removed by adsorption.

$$\Delta G_{CO_2}^f + RT \ln \left( \frac{P \cdot \sum_{i=1}^{N} n_i}{n_{CO_2} \cdot (1-f)} \right) + RT \ln \phi_{CO_2} + \lambda_c + 2 \lambda_o = 0$$  \hspace{1cm} \text{(equation 6)}$$

There are $N + M$ equations and $N + M$ unknown variables, i.e. the number of moles of the species in the system and the number of atoms involved, represented by the Lagrange multipliers. The non-linear algebraic system was solved in MATLAB (R2010b) using the in-built routine fsolve and the code newtons.[20] In addition, a subroutine was developed to calculate the fugacity coefficients of each species in the gas mixture using the Soave-Redlich-Kwong equation of state. The convergence in some conditions was not straightforward and therefore strategies such as scaling up/down the initial guesses and the subsequent rescaling of the solutions were applied.[20]

To validate the non-stoichiometric methodology used here, comparison was made with published experimental equilibrium data. Recently Graaf et al.[21] reported a comprehensive survey of experimental data involving forward and reverse water gas shift and methanol decomposition and synthesis. In particular, the authors identified studies where high quality experimental Kp values were reported for the WGS reaction.[22,23,24] The experimental equilibrium data (Kp) at temperatures and pressures relevant for the present work (473-1200 K, 1-70 barg) were compared with our computed values, Figure 3a. The non-stoichiometric calculations for WGS show good agreement with the experimental data. For methanol synthesis, values of Kp can be obtained from experimental measurements.[22,25,26,27,28] Comparison of experimental data for methanol synthesis with the calculated values is given in Figure 3b, where good agreement is again observed. In the case of methanol-to-shift (without CO$_2$ removal), the calculated equilibrium composition is in acceptable agreement with the product distribution reported by Nielsen et al.[1] from experiments carried out at very low space velocity (conversion close to equilibrium), Table 1. Further validation of the non-stoichiometric methodology is shown in Figure 4. Only small differences with respect to experimental equilibrium compositions reported by Stevens Jr. et al.[12] for SEWGS with complete CO$_2$ removal ($f = 0.99$) and without CO$_2$ capture ($f = 0$) are observed. Equilibrium data obtained with our model for the SEWGS also showed good agreement with data produced in Aspen Plus by Stevens Jr. et al.[11] (Figure S1).

\section*{2.2 Species in WGS and MtoS}

During water gas shift and methanol reforming, some compounds can be formed as by-products such as methane, dimethyl ether, formic acid and methyl formate.[7] Methane, in particular, is a very favourable species in terms of thermodynamics and its formation needs to be prevented by means of an adequate selection of the catalyst used. The commercial Cu/ZnO/Al$_2$O$_3$ based catalyst for medium temperature shift is reported to be very selective towards H$_2$ and CO$_2$ even in the presence of methanol, and by-products are only detected at trace levels.[1,29]

The free energy minimisation approach described in section 2.1 requires the specification of the species that are in chemical equilibrium in the system, i.e. methanol,
carbon monoxide, carbon dioxide, hydrogen and water. If a well-designed catalyst is used, the by-product formation can be kinetically controlled and maintained at trace levels, as reported for commercial catalysts. Consequently, the formation of by-products is not expected to contribute significantly to the overall heat of the reaction and is not included in the present analysis. It is worth mentioning that the methane present in the feed to the water gas shift reactor (Table 2) is treated as an inert.

2.3 Description of the simulated shift stage

The shift stage consists of an equilibrium reactor in which water gas shift alone or in combination with methanol steam reforming takes place. To assess the energy efficiency of the section, besides the energy balance of the shift reactor, the heat that is removed from the effluent of the reformer and transferred to the water or methanol streams if they are co-fed to the reactor are included, Figure 2. In the sorption-enhanced cases (WGS and MtoS), a heat of adsorption of 17 kJ mol\textsuperscript{–}1 CO\textsubscript{2} was assumed. The value was measured by Ding et al.[30] from CO\textsubscript{2} Langmuir-adsorption isotherms at 673 K and 753 K (in the Henry’s region) under wet conditions for layered double oxides, which are promising adsorbents for sorption-enhanced H\textsubscript{2} production.[30,31,32] As discussed in section 2.1, the equilibrium calculations presented in this study assume that CO\textsubscript{2} is the only species that is adsorbed on the surface. It is known that water also adsorbs and improves the performance (capacity and stability) of relevant solid adsorbents.[30,33,34] However, some authors have observed that the partial pressure of water has little effect on the CO\textsubscript{2} capacity of the adsorbents and therefore non-competitive adsorption calculations provide a good approximation to the real adsorption systems.[30,35,36]

The feed to the water gas shift reactor considered as case study corresponds to the effluent from a heat exchange reformer operating at 20 barg and 1173 K with a steam to carbon ratio 2.5:1, Table 2.[2] This inlet composition is in the range of conditions that are typical in modern hydrogen plants. As mentioned in the introduction, the HTS and LTS stages are performed on an industrial scale in a temperature range from 573 – 773 K and 483 - 543 K respectively. Industrial WGS shift converters operate at total pressures ranging from 3 to 40 barg depending on the requirements of the units downstream.[37] In this study, the effect on the equilibrium product distribution of the standard and sorption-assisted WGS and MtoS processes is examined between 450 and 750 K, and at three relevant operating pressures (5, 20 and 35 barg). The amount of water in the syngas generator effluent is above the stoichiometric ratio 1:1 with respect to CO. However, in some of the simulations more steam is added to the WGS feed to assess the effect of water on the H\textsubscript{2} productivity. For MtoS and SEMtoS cases, either pure methanol or mixtures of methanol and water are co-fed to the equilibrium reactor. The methanol feed flow added was in the range (0-62 Nm\textsuperscript{3}/h), which is expected for a plant with a natural gas flow of 100 Nm\textsuperscript{3}/h, Table 2, and includes that needed for autothermal operation.[1]

3 Results and discussion

This section presents a thermodynamic analysis of the WGS and MtoS reactions alone and with in situ CO\textsubscript{2} adsorption (SEWGS and SEMtoS). Equilibrium calculations of the WGS and SEWGS reactions have been reported previously[6,11] although in some of the cases studied the inlet compositions, temperatures and pressures are not relevant for
industrial application. Conversely, this study is performed in a range of operating conditions that is typical in hydrogen plants. The WGS and SEWGS analyses reported in section 3.1 also allow for a direct comparison with the systems in which methanol is present (section 3.2), where it is shown that co-feeding methanol in the MtoS and SEMtoS processes enhances the H₂ productivity and the energy efficiency of the shift section, and allow autothermal operation.

3.1 Water gas shift and sorption-enhanced water gas shift

Water gas shift

Water gas shift is an exothermic reaction that is thermodynamically limited under typical industrial conditions. Hydrogen formation is favoured at low temperatures but the minimum temperature (around 473 K) is dictated by the dew point of the feed to the reactor and by the activity of the catalysts used. The effect of temperature on the equilibrium product distribution is presented in Figure 5 (5, 20 and 35 barg) for the inlet composition given in Table 2. It is observed that above 543 K the amount of unreacted CO becomes significant (> 1 mol %) to the detriment of the H₂ produced. The operating pressure, on the other hand, has little impact on the product distribution since there is no change in the number of moles during the reaction.

From a thermodynamic point of view the amount of hydrogen produced by WGS can be enhanced either by increasing the partial pressure of the reactants, i.e. addition of steam, or by removing of the products in situ. Adding steam to the syngas has the advantage that part of the steam produced while cooling the effluent from the reformer can be utilised, which improves the energy efficiency of the WGS section, (see Figures 6a, 6b). However, while there is an increase in the H₂ productivity as the amount of steam co-fed increases, the benefit of steam addition is not very pronounced and may not compensate for the impact that the higher partial pressure of water will have on the catalyst performance, i.e. faster deactivation by hydrothermal sintering.[2]

Sorption-enhanced water gas shift

The removal of products in situ can be carried out by separating H₂ from the reacting media using membranes (e.g. palladium-ceramic membranes)[38] or by SEWGS removing CO₂ using a solid adsorbent. The product distribution in the presence of a CO₂ solid adsorbent shows higher conversions of CO in the whole range of temperatures studied, Figure 7a (5 barg). However, the benefit of sorption enhancement is more noticeable as the operating temperature increases and the WGS reaction becomes more limited. SEWGS would therefore benefit from higher reaction rates and more favourable thermodynamics between 543 K and 673 K. On the other hand, pressure has minimal influence on the equilibrium production of H₂ for a given temperature and fraction of CO₂ removed, (Figure 7b, 20 barg). Nevertheless, higher operating pressures would result in smaller reactors as higher adsorption capacities would be obtained. Although in the SEWGS process the heat from the reformer effluent cannot be recovered and reutilised, there is a significant increase in the H₂ production in the presence of a CO₂ adsorbent, Figure 8. Compared to the improvement in the productivity of hydrogen due to higher H₂O partial pressures, Figure 6a, the enhancement due to CO₂ adsorption is more significant (e.g. at 513 K, the productivity of H₂ is enhanced by 2.04 Nm³/h when adding 100 Nm³/h of steam and by 3.57 Nm³/h when
95% of CO₂ is removed in situ). As a consequence higher productivities can be achieved with lower H₂O contents if the sorption assisted process is implemented. In addition, a CO₂ rich stream is produced for sequestration while the process stream is almost CO₂ free, which may simplify the subsequent hydrogen purification section.

3.2 Methanol-to-shift and sorption-enhanced methanol-to-shift

*Methanol-to-shift*

The combination of water gas shift and steam reforming of methanol increases the productivity of hydrogen in the range of temperatures relevant in the conventional WGS catalytic process (573-773 K), Figure 9. Methanol is transformed into hydrogen and carbon monoxide, which is then shifted to produce even more H₂. Below 498 K, not all the methanol reacts due to the endothermic character of the methanol steam reforming reaction. As the temperature increases, the hydrogen productivity shows a maximum between 523 K and 593 K, an operation window where both reactions, i.e. WGS and methanol steam reforming, are thermodynamically favourable. Higher temperatures result in a decrease in H₂ productivity as the exothermic WGS reaction becomes increasingly equilibrium limited, and the endothermic methanol steam reforming is no longer limited.

As mentioned above, the operating pressure has little impact on the equilibrium product distribution of the WGS since there is no change in the number of moles during the reaction. On the contrary, the thermodynamic constraints on methanol steam reforming at low temperature can be compensated by reducing the operating pressure due to the twofold increase in the number of moles. For example, at 5 barg the equilibrium composition of methanol can be maintained below 0.15 mol % in the whole range of temperatures, Figure 10a, while 1.55 mol% of methanol remains unreacted at 20 barg and 473 K, Figure 10b. This leads to a higher low-temperature H₂ productivity for a given methanol flow when MtoS is conducted at lower pressures, Figure 11. However, for use in hydrotreating units and in other processes downstream, hydrogen needs to be delivered between 30 and 170 bar. In industry, it is more efficient to increase the pressure of natural gas rather than hydrogen, since smaller volumes need to be compressed. Consequently, the optimal operation pressure of a steam-methane reformer is typically around 20 barg.[2]

Since the increase in hydrogen productivity of MtoS compared to WGS stems from the utilization of H₂ and CO molecules produced in the methanol reforming, a major advantage of the MtoS process over WGS is the ability to achieve autothermal operation of the shift unit, which is not possible with the WGS alone. The heat released by water gas shift compensates the heat consumed by the steam reforming of methanol. The H₂ productivity under autothermal conditions between 473 K and 723 K is given in Figure 12a at two different pressures. It is observed that, for a given syngas composition, the amount of hydrogen produced autothermally at equilibrium depends solely on the reactor temperature. This is because the partial pressures of the species have a negligible effect on the equilibrium conversion of WGS so the amount of methanol that needs to react does not depend on the pressure of the system. On the other hand, compared to operation at 20 barg, less methanol needs to be added at 5 barg to achieve autothermal operation due to the more favourable thermodynamics for methanol reforming, Figure 12b.
Slightly higher hydrogen productivities are obtained over the whole range of operating temperatures if the methanol feed to the MtoS reactor (16 Nm$^3$/h CH$_3$OH) is replaced by a mixture of water and methanol (8 Nm$^3$/h H$_2$O, 16 Nm$^3$/h CH$_3$OH), Figure 13. This stems from the decrease in the partial pressure of the species involved in the methanol decomposition, and from the shift of the WGS equilibrium towards CO$_2$ and H$_2$ due to an increased concentration of water. Nevertheless, the benefit of adding water is not very pronounced and may be required only if the H$_2$O content is below the stoichiometric composition.

**Sorption-enhanced methanol-to-shift**

The maximum in the hydrogen productivity for the MtoS process between 523 K and 593 K (Figure 11, 20 bar), corresponds to the temperature window in which both, water gas shift and methanol reforming are favourable. Methanol decomposition (endothermic reaction) is only slightly limited around 473 K, whereas WGS (exothermic reaction) is significantly limited above 573 K. Therefore, adsorption of carbon dioxide becomes useful above 573 K to overcome WGS equilibrium and to benefit from high reaction rates. When the MtoS process is conducted in the presence of a solid adsorbent, there is a marked increase in the hydrogen productivity as the fraction of CO$_2$ adsorbed, $f$, increases, Figure 14a. For the different values of $f$, the maximum H$_2$ productivity is centred between 523 K and 593 K. The dry-basis equilibrium compositions at 573 K are given in Figure 14b. Increasing the fraction of CO$_2$ removed results in an increase in the concentration of hydrogen in the gas mixture, while the rest of the species decrease. In the ideal scenario in which most of the CO$_2$ is removed, the H$_2$ mole fraction is nearly 1 while for the standard process, i.e. $f = 0$, the H$_2$ mole fraction is approximately 0.7.

The effect of the operating pressure on the H$_2$ productivity of SEMtoS is shown in Figure 15. Above 623 K the amount of hydrogen produced for different values of $f$ is the same at 5 and 20 bar. However, at lower temperatures the production of hydrogen is more favoured at 5 barg due to thermodynamic limitations on the steam reforming of methanol. Under sorption assisted conditions, the heat balance in the MtoS reactor must include the contribution of CO$_2$ adsorption. At 573 K, the enthalpy of reaction for methanol steam reforming is 62.9 kJ mol$^{-1}$ and for water gas shift is -38.4 kJ mol$^{-1}$. If a heat of adsorption of 17 kJ molCO$_2$$^{-1}$ is assumed (see section 2.3),[30] it is evident that for $f = 1$, autothermal operation of the reactor is obtained when the ratio of converted CO to converted methanol is 0.83. It is worth mentioning that typical heats of adsorption of CO$_2$ for layered double oxides (5-25 kJ mol CO$_2$$^{-1}$) were found to make only small differences to this ratio (~10%). This ratio increases slightly in the temperature range relevant for SEMtoS, Figure 16a. However, due to the endothermicity of the steam reforming of methanol, the amount of methanol that needs to be added to the feed increases significantly at low temperatures, Figure 16b. However, this is at a temperature which is below 573 K and therefore is not useful for sorption enhancement. The thermodynamic analyses presented in this work aim to serve as a guideline for future work on methanol-to-shift and other alcohol-to-shift systems assisted by CO$_2$ adsorption. Besides the Cu/ZnO/Al$_2$O$_3$ based catalyst reported by Haldor Topsøe[1], in a previous study we identified a range of Pt-based catalysts that are active for WGS and decompose methanol into CO and H$_2$ with a very high selectivity.[36] Additionally we showed that layered double oxides are promising CO$_2$ adsorbents for the SEMtoS process since they exhibit optimum performance under this operating window. Further studies should
consider the catalytic performance of MtoS and SEMtoS under the actual methanol-to-shift feedstock and operating conditions.

3.3 Conclusions

Thermodynamic analyses show that methanol-to-shift (MtoS) and sorption-enhanced methanol-to-shift (SEMtoS) are promising strategies to enhance the productivity of hydrogen while the energy efficiency of the water gas shift section is improved. The amount of H₂ produced in the MtoS and SEMtoS processes shows a maximum between 523 and 593 K, an operating window where the WGS and methanol steam reforming reactions are thermodynamically favorable. For both MtoS and WGS, the adsorption of CO₂ in situ enhances the H₂ productivity more than other strategies to shift equilibrium (e.g. increasing the amount of steam in the feed or reducing the pressure of the MtoS units). A major advantage of the MtoS and SEMtoS is the ability to achieve autothermal operation of the shift unit which is not possible with the WGS alone. The heat released by WGS and CO₂ adsorption is compensated by the heat consumed in the steam reforming of methanol. At 573 K and under the conditions of this work, autothermal operation for MtoS and SEMtoS is obtained when the ratio of converted CO to converted methanol is 1.64 and 0.83 respectively, assuming a heat of adsorption of 17 kJ molCO₂⁻¹, which is typical for oxide adsorbents. This ratio was not very sensitive to variations of the heat of adsorption of CO₂. The thermodynamic studies presented in this work serve as a guideline for future work on methanol-to-shift and more generally, on alcohol-to-shift processes enhanced by CO₂ adsorption. Experimental work is required to prove the feasibility of the sorption enhanced methanol to shift process using CO₂ adsorbents, especially layered double oxides. It is worth mentioning that the MtoS and SEMtoS are attractive technologies to meet the increased demand for extra hydrogen from refineries but they are applicable to a hydrogen plant on any scale.

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Nomenclature

\( A_j \) Total number of atoms \( j \) in the system  
\( a_{ij} \) Number of atoms \( j \) in the molecule \( i \)  
\( f_i \) Fraction of CO₂ removed by adsorption  
\( G \) Gibbs free energy  
\( \Delta G_i^f \) Standard Gibbs free energy of formation of species \( i \)  
\( \lambda_j \) Lagrange multipliers  
\( HTS \) High temperature shift  
\( LTS \) Low temperature shift  
\( n_i \) Number of moles of species \( i \)  
\( P \) Pressure  
\( R \) Universal gas constant  
\( T \) Temperature  
\( \phi_i \) Fugacity coefficient of species \( i \)  
\( \mu_i \) Chemical potential  
\( MtoS \) Methanol-to-shift reaction  
\( SEMtoS \) Sorption-enhanced methanol-to-shift
WGS Water gas shift reaction
SEWGS Sorption-enhanced water gas shift reaction

Tables

Table 1 Equilibrium molar flows in MtoS. Comparison between present work and experimental data reported by Nielsen et al. [1] near equilibrium conditions (process developed by Haldor Topsoe, see exit streams). The corresponding inlet compositions are also given (operating conditions a and b).

<table>
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<th>Nielsen et al. (586 K, 25 bar, 15.1 g catalyst)</th>
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Molar flows (mol/h), exit streams

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<th>Present work (Modelling)</th>
<th>Nielsen et al. (Experimental data)</th>
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Table 2 Operating conditions and feed composition to the shift section (WGS or MtoS)

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<th>Compounds</th>
<th>Composition (mole %)</th>
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<th>Steam</th>
<th>Inlet SMR</th>
<th>Outlet SMR</th>
<th>Feed Shift (WGS or MtoS)</th>
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</tbody>
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Figures

Figure 1 Typical stages of the process of hydrogen production from natural gas (reforming) or coal (gasification)
Figure 2 Simplified methanol-to-shift process based on Nielsen et al.\cite{1}

Figure 3 Comparison between thermodynamic model used in the present work and experimental Kp values reported in the literature. (a) Reverse water gas shift: Oki and Mezaki\cite{23} (WGS, 740-795 K, <1.013 bar), Neumann and Kohler\cite{24} (WGS, 568-1200 K, 1.013 bar) and Graaf et al.\cite{22} (methanol synthesis, 472-539 K, 10-73 bar). (b) Methanol synthesis from CO/H₂: Struis and Stucki\cite{25} (473 K, 4.3 bar), Hilmen et al.\cite{26} (560-593 K, 45 bar), Graaf et al.\cite{22} (472 K-539 K, 10-73 bar), Chen and Yuan\cite{27} (473-500 K, 10 bar) and Sakurai et al.\cite{28} (523-623 K, 8-50 bar).

Figure 4 Equilibrium data showing the relationship between CO conversion and temperature in SEWGS with complete CO₂ removal (f = 0.99) and without CO₂ capture (f =0). Comparison between present work and experimental equilibrium data reported by Stevens Jr. et al.\cite{11} (conditions: 1 atm, feed gas composition of CO = 15%, H₂O = 18% and He = 67%).
Figure 5 Effect of temperature on the equilibrium product distribution of the WGS at 5 barg, 20 barg and 35 barg (the data are superimposed), (H$_2$O:CO feed ratio = 2.12, the inlet composition is given in Table 2)

Figure 6 Effect of co-feeding steam with syngas on the (a) hydrogen productivity and (b) on the energy efficiency of the WGS (20 barg, steam was added to the inlet composition given in Table 2)

Figure 7 Effect of temperature on the equilibrium H$_2$ mole % and CO mole % of the SEWGS at different fractions of CO$_2$ adsorbed (a) 5 barg, (b) 20 barg, (H$_2$O:CO feed ratio = 2.12, the inlet composition is given in Table 2, f is the fraction of CO$_2$ adsorbed)
Figure 8 Effect of temperature on the H\textsubscript{2} productivity of the SEWGS at different fractions of CO\textsubscript{2} adsorbed (20 barg, H\textsubscript{2}O:CO feed ratio = 2.12, the inlet composition is given in Table 2, \( f \) is the fraction of CO\textsubscript{2} adsorbed)

Figure 9 Effect of methanol addition on the hydrogen productivity of MtoS (20 barg, CH\textsubscript{3}OH was added to the inlet composition given in Table 2)

Figure 10 Effect of temperature on the equilibrium mole % of MtoS (a): 5 barg, CH\textsubscript{3}OH, 16 Nm\textsuperscript{3}/h, was added to the inlet composition given in Table 2, (b): 20 barg, CH\textsubscript{3}OH, 16 Nm\textsuperscript{3}/h, was added to the inlet composition given in Table 2
Figure 11 Effect of temperature on the hydrogen productivity of MtoS (5 and 20 barg, CH$_3$OH, 16 Nm$^3$/h, was added to the inlet composition given in Table 2).

Figure 12 (a) CH$_3$OH required for autothermal operation (5 and 20 barg, the amount of CH$_3$OH required for autothermal operation was added to the inlet composition given in Table 2) (b) H$_2$ productivity under autothermal conditions of MtoS (5 and 20 barg, the amount of CH$_3$OH required for autothermal operation was added to the inlet composition given in Table 2).

Figure 13 Effect of mixtures of water and methanol on the H$_2$ productivity of MtoS (20 barg, mixture of CH$_3$OH/H$_2$O added to inlet composition given in Table 2).
Figure 14 (a) Effect of temperature on the H₂ productivity of SEMtoS at different fractions of CO₂ adsorbed (b) Equilibrium compositions of SEMtoS at different fractions of CO₂ adsorbed (20 barg, 573 K, CH₃OH, 16 Nm³/h, was added to the inlet composition given in Table 2, f, is the fraction of CO₂ adsorbed)

Figure 15 Effect of pressure on the H₂ productivity of SEMtoS at different fractions of CO₂ adsorbed (CH₃OH, 16 Nm³/h, was added to the inlet composition given in Table 2, f, is the fraction of CO₂ adsorbed)

Figure 16 (a) Ratio of CO converted to CH₃OH converted of SEMtoS and (b) CH₃OH added to the feed of SEMtoS, (20 barg, the amount of CH₃OH required for autothermal operation was added to the inlet composition given in Table 2, fraction of CO₂ adsorbed: f = 0.95)
References


Graphical Abstract