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Influence of the Water Phase State on the Thermodynamics of Aqueous-Phase Reforming for Hydrogen Production

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Hydrogen is a promising renewable energy source that can be produced from biomass using aqueous-phase reforming (APR). Here, using data obtained from AspenPlus and the literature, we evaluated the phase state, temperature-dependent enthalpy, and Gibbs free energy for the APR of small biomass model substrates. Phase equilibrium studies reveal that, under typical APR reaction conditions, the reaction mixture is in the liquid phase. Therefore, we show for the first time that the water-gas

shift reaction (WGSR), which is the second main reaction of APR, must be modeled in the liquid phase, resulting in an endothermic instead of an exothermic enthalpy of reaction. A significant implication of this finding is that, although APR has been introduced as more energy saving than conventional reforming methods, the WGSR in APR has a comparable energy demand to the WGSR in steam reforming (SR).

Introduction

As the world population and its energy demands continue to increase, and as conventional fossil fuel sources are depleting rapidly, research into alternative and renewable energy resources is gaining increasing attention. Hydrogen is both an attractive and clean energy vector: it has a high energy density and does not produce harmful products during combustion.^[1–3] Hydrogen can be produced from natural gas or coal,^[4,7] but these sources are neither renewable nor are their processing methods sustainable. Using biomass waste streams, however, as a resource would valorize otherwise discarded materials.^[5,6] Current hydrogen production methods include liquefaction, pyrolysis, and steam reforming (SR). All these methods require temperatures above 473 K and, for liquefaction and pyrolysis only, pressures up to 200 bar (1 bar = 100 000 Pa).^[7–11] In 2002, aqueous-phase reforming (APR) was introduced by the Dumesic research group as an alternative method to reform oxygenated carbohydrates with a C/O ratio of 1:1 into H₂ and CO₂ using milder reaction conditions.^[12] Although many gaseous- and

Cracking

WGSR

Scheme 1. Two main steps in APR: the substrate is first cracked into CO and H₂. Next, the formed CO is converted into CO₂ and an additional amount of H₂ in the WGSR.

liquid-phase intermediates and products are formed by complicated and not yet fully understood reaction mechanisms, APR proceeds in two main reactions (Scheme 1). The substrate in the aqueous phase is first cracked into CO and H₂. Next, CO is converted into CO₂ in the water-gas shift reaction (WGSR), while forming an additional amount of H₂.

To prevent evaporation of the reaction mixture, an elevated pressure must be applied, as determined by the vapor–liquid equilibrium (VLE) of the system. APR is typically performed at temperatures up to 550 K and pressures up to 55 bar.^[11] Previous thermodynamic studies have shown that the WGSR is favorable for hydrogen production at temperatures approaching room temperature.^[13,14] Water has a dual role: it acts both as a solvent for the whole process and as a reactant for the second main reaction of APR. Here, we only considered water as a reactant in the WGSR, unless specified otherwise.

Although the APR reaction conditions are a great improvement over the previously mentioned conventional hydrogen production methods, elevated temperatures and pressures are still needed. Herein, we evaluated the reaction thermodynamics of APR of a selection of low-molecular-mass substrates to explore the feasibility to perform APR closer to ambient conditions to make the process even more sustainable. In the ideal case, elevated temperatures and pressure would no longer

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be necessary to execute the process, saving a considerable amount of energy. The enthalpy and Gibbs free energy of reaction were evaluated as a function of the temperature at atmospheric pressure using data obtained from the literature and from the AspenPlus database. Next, to determine the lowest pressure required to maintain the reaction mixture in the liquid phase, the VLE and the saturated pressure (P^{sat}) were modeled as a function of both the temperature and the substrate mole fraction using AspenPlus.

Results

Ethylene glycol, glycerol, xylose, and xylitol were selected as biomass model substrates to study the APR reaction thermodynamics (Figure 1). Ethylene glycol and glycerol have been widely reported as APR substrates in the literature^[15–18] and

Figure 1. Biomass model substrates used in this study. Ethylene glycol and glycerol act as benchmark substrates, whereas xylose and xylitol were selected to study the potential of hemicellulose derivatives as APR feedstock.

act therefore as benchmark substrates. Xylose (the main component of hemicellulose) and xylitol were considered to study the use of hemicellulose derivatives as potential future APR feedstock.^[19]

Although in APR many side reactions can take place, of which methanation is the most prominent,^[18,20] we limit our study to the two main reactions as presented in Scheme 1. Scheme 2 indicates if the enthalpy of these reactions is posi-

Cracking

WGSR (g)

WGSR (l)

Scheme 2. Main APR reactions: cracking and WGSR where water as a reagent is either in the gas (g) or liquid phase (l). The endothermic or exothermic character is indicated by $+\Delta$ and $-\Delta$ respectively.

tive and if the reaction is therefore endothermic ($+\Delta$) or if the enthalpy is negative and the reaction exothermic ($-\Delta$) under standard conditions ($T=278.15\text{ K}$; 1 bar).

Phase studies

As indicated in Scheme 2, the phase state of water during the WGSR is of utmost importance, as it defines whether the WGSR is an endothermic or an exothermic process. Furthermore, the energy released in the WGSR with water in the gas phase can be used for the cracking reaction, resulting in a lower total energy demand. Therefore, a thorough evaluation of the phase equilibrium of the model substrate/water solutions was performed to determine the phase of water under typical APR reaction conditions. For the small substrates studied here, solvation effects were not taken into account. The solvation enthalpy is in the order of 25 and 12 kJ mol^{-1} for xylitol and xylose, respectively, which is negligible compared to the overall reaction enthalpy for APR.^[21,22]

Phase equilibrium studies were conducted for pressures of 1, 22, 30, and 56 bar and temperatures of 298, 498, 538, and 623 K. These APR operating conditions are in accordance with those reported in the literature, as summarized in Table 1, for

Table 1. APR operating conditions reported in the literature and phase state of water at these conditions determined using the calculated VLE diagrams or the saturated vapor pressure (P^{sat}) at $T=498\text{ K}$ and a substrate mole fraction of 0.2.

Substrate	$T\text{ [K]}$	$P_{\text{applied}}\text{ [bar]}$	Calculated phase state ^[a]	$P^{\text{sat}}\text{ [bar]}$	Ref.
ethylene glycol	498	29	liquid	21.9	[12]
glycerol	498	29	liquid	21.1	[12]
xylitol	498	29.3	liquid	22.4	[19]
glucose	538	56	–	–	[12]

the substrates considered in this study. Xylose could not be included in this table as, to the best of our knowledge, it has not been used yet as an APR substrate in experimental work. Glucose was added to the table instead to show typical reaction conditions used for APR of sugars.

The T_{xy} and P_{xy} VLE diagrams were obtained using AspenPlus with a Redlich–Kwong–Soave Boston–Mathias (RKS-BM) model (see the Supporting Information, S1). This model allows calculating the heat duty and is recommended for hydrocarbon processing by AspenPlus. Furthermore, this model has been successfully applied to study biomass reforming, including the reforming of polar compounds.^[23,24] The VLE diagrams indicate that the substrate/ H_2O binary mixtures are in the liquid phase under APR reaction conditions. In these calculations the mole fraction of the model substrate in water could not be accounted for, even though it can influence the phase equilibrium significantly. Therefore, the saturated-vapor pressure as a function of both the temperature and the mole fraction was also evaluated using the same software and model while performing a sensitivity analysis. The results obtained from these calculations confirm that the reaction mixture is in

the liquid phase under APR process conditions (see the Supporting Information, S2). The applied pressure is higher than the calculated vapor pressure at the operating temperature for a substrate mole fraction of 0.2. Altogether, the substrate/H₂O mixture is entirely in the liquid phase under APR. Therefore, the WGSR should be considered in the liquid phase instead of the gas phase as currently reported in the literature.^[11,20] To the best of our knowledge, this is the first time that a study of the reaction thermodynamics of the WGSR is performed with water in the liquid phase, resulting in an endothermic process.

Reaction thermodynamics

To prove the endothermic character of the WGSR in the liquid phase and to evaluate the reaction thermodynamics, the enthalpy and the Gibbs free energy of reaction were calculated from both the enthalpy of formation and Gibbs free energy of formation under standard conditions. Equation (1)^[25] was derived for the temperature-dependent enthalpy of reaction (Supporting Information, S3.3):

$$dH = C_p dT + [1 - \alpha T] V dp \quad (1)$$

where α is the thermal expansion coefficient.

The gases formed during APR (CO, CO₂, H₂) were considered as ideal. Therefore, the pressure dependency of the enthalpy was neglected. The non-ideal gas behavior is expected to have only a small influence on the reaction enthalpy. Both the reaction enthalpy and the Gibbs free energy of reaction were calculated at atmospheric pressure. At 1 bar phase transitions occur while increasing the temperature, which was included in the reaction thermodynamics. In this way, the difference in energy between the liquid phase and the gas phase reaction is more clearly illustrated. Furthermore, our end goal was to explore APR at ambient conditions, which implies to conduct the reaction at atmospheric pressure. The phase transition temperature of the substrates was chosen as the upper temperature limit. The heat capacity (C_p) values for the model substrates were kept constant for the temperature range studied, as to the best of our knowledge, the values of $C_p(T)$ for these temperatures are not available. For the compounds involved in the WGSR, the temperature dependency of the heat capacity was accounted for. The Gibbs free energy of reaction as a function of the temperature was calculated using the Gibbs–Helmholtz

relation. The thermodynamic constants for the substrates were collected from several sources, whereas only one source was used for each substrate (Table 2). Unfortunately, no data was found for the Gibbs free energy of xylitol. The temperature-dependent enthalpy values for CO, H₂O, CO₂, and H₂ were obtained from AspenPlus by applying the RKS-BM model. Although only one source was used to acquire data for a single substrate, one should be cautious when comparing the results for different substrates, as there could be inconsistencies between the different sources.

Enthalpy and Gibbs free energy of reaction

Figures 2 and 3 show the temperature-dependent enthalpy and the Gibbs free energy of reaction for APR of all four biomass model substrates and for the WGSR. To establish these graphs, only the water molecules that are acting as a reactant were included in the calculations. These results are in accordance with data previously published for the APR of ethylene glycol and the WGSR (Supporting Information, S4).^[20] The sharp drop in the reaction enthalpy is indicative for the heat of

Figure 2. Enthalpy of reaction for APR and the WGSR as a function of the temperature at standard pressure. The sharp drop is indicative for the phase transition of water.

Figure 3. Gibbs free energy of reaction for APR and the WGSR as a function of the temperature at standard pressure.

Table 2. Thermodynamic data for ethylene glycol, glycerol, xylose, and xylitol. The phase of the reactants at $T = 298.15$ K, liquid (l) or solid (s) is indicated.

Substrate	$\Delta H_f^{[a]}$ [kJ mol ⁻¹]	$\Delta G_f^{[b]}$ [kJ mol ⁻¹]	$C_p^{[c]}$ [J mol ⁻¹ K ⁻¹]	Ref.
ethylene glycol (l)	-451.5	-319.6	149.8	[26]
glycerol (l)	-669.3	-478.3	218.9	[27]
xylose (s)	-1057.84	-744.59	184	[22]
xylitol (s)	-1118.5	-	-	AspenPlus

[a] Standard enthalpy of formation. [b] Standard Gibbs free energy of formation. [c] Heat capacity.

evaporation of the reacting water molecules. In the liquid phase, both the cracking and the WGSR are endothermic, whereas at atmospheric pressure and temperatures above the boiling point of water, the WGSR is exothermic. As the enthalpy does not change much within the temperature range studied, reforming in the liquid phase seems to be highly unfavorable. Furthermore, the reaction is exergonic at temperatures above 310 K not only for the APR of all substrates, but also for the WGSR. The highly positive enthalpy and the negative Gibbs free energy indicate that the entropy has to increase to such an extent that it compensates for the high, positive enthalpy. A gain in entropy can also explain the decreasing Gibbs free energy for higher temperatures. Moreover, a higher temperature would not only be beneficial for the entropy, but it would also increase the rate of reaction. The differences between the substrates can be explained in terms of carbon number. A higher carbon number means a larger APR enthalpy, as more chemical bonds need to be broken. As a result, more H_2 and CO_2 are formed, and a favorable entropy is found for larger substrates. Therefore, APR of larger biomass substrates is preferred in terms of Gibbs free energy.

Discussion

First, based on the calculated Gibbs free energy, APR can be performed at a lower temperature starting from 310 K. The literature APR reaction conditions summarized in Table 1 are all above this minimum temperature needed to perform APR. Similarly, at this temperature, no external pressure has to be applied to maintain the system in the liquid phase. Still, the process is expected to run more efficiently at a higher temperature as a result of the increased entropy and a more negative Gibbs free energy. However, it is unlikely that thermodynamic equilibrium is reached in an experiment. Kinetic parameters such as conversion, reaction rate, and selectivity also depend on the pressure and temperature, which affect the hydrogen yield. Applying a higher pressure might still be beneficial for kinetic reasons, even when it is not required from a thermodynamic point of view: This would be the case when the volume of activation for the specific reaction is positive. Therefore, an additional thorough analysis of the kinetics is also essential to eventually optimize the reaction parameters to maximize hydrogen production. This kinetic study is however beyond the scope of the present work.

Furthermore, based on these findings, the WGSR in the liquid phase is not as energetically favorable as in the gas phase, which is the phase in which the WGSR is currently considered to take place in both APR and SR. This is particularly the case when the reaction enthalpy and Gibbs free energy of reaction are considered. When the energy demand of the WGSR in SR is calculated from steam and gaseous CO, the enthalpy of reaction is lower than for APR as a result of the exothermic WGSR in SR. However, in SR and in the gas-phase WGSR, the reacting water molecules have to be vaporized first and this heat of evaporation has to be added to the energy balance. The heat of evaporation of water—as reactant—is exactly the same as the energy later gained in the exothermic

Figure 4. Schematic comparison of the WGSR reaction enthalpy between APR and SR when including the heat of evaporation of water as a solvent.

WGSR. In other words, the reaction energy demand for the WGSR in APR and SR is the same (Figure 4).

There is still one significant difference between the two reforming approaches; the state of the reaction mixture. For SR, the reaction mixture must be vaporized, including water that is acting as solvent, which has not been included in this study. This additional energy requirement for the evaporation of water as a solvent results in an overall higher energy demand for SR than for APR.

Finally, we propose that the phase state of the reactants would have implications for the reaction mechanism. Both SR and APR comprise the same main reactions: cracking of the substrate followed by the WGSR (Scheme 1), but the phase state of the reactants is different for SR and APR. In the case of SR, all the reactants are in the gas phase and both the cracking and the WGSR are two-phase reactions between the gaseous compounds and the heterogeneous catalyst. In APR, the cracking reaction is again a two-phase reaction, but this time between the substrate in the aqueous phase and the solid catalyst. The WGSR, however, is a three-phase reaction, as concluded from our thermodynamic study, with water as a reactant in the liquid phase, CO in the gas phase, and the solid catalyst. Therefore, water has to come in contact with both the solid catalyst and the gaseous CO and the reaction takes place at the gas–liquid–solid interface (Figure 5). Further research is however needed to clarify the exact reaction mechanism of the WGSR.

Conclusions

Here, the reaction thermodynamics for aqueous-phase reforming (APR) of ethylene glycol, glycerol, xylose, and xylitol was studied to investigate the possibility of performing APR closer to ambient conditions. Based only on thermodynamic considerations, APR of the studied substrates could be performed at a temperature as low as 310 K without additional external pressure. For the first time, we have demonstrated that the water-gas shift reaction (WGSR) should be modeled in the

Figure 5. Schematic interpretations of the WGS reaction mechanisms for SR and APR showing the phase state of the reactants. For SR, the WGS is a two-phase process as all compounds are in the gas phase and a heterogeneous catalyst is used. However, in APR water in the liquid phase reacts at the solid–gas–liquid interface with CO in the gas phase present in bubbles formed during the cracking step.

liquid phase when calculating the reaction enthalpy and the Gibbs free energy for APR. The enthalpy shows little variation with the temperature and the WGS proves to be endothermic in the liquid state, which, at first sight, makes APR thermodynamically unfavorable compared to steam reforming (SR). However, when including the heat of evaporation of water as a reagent to calculate the energy demand of the WGS in SR, the energy requirement of this reaction in APR and SR is exactly the same. The phase state of water as a reactant also has implications for the mechanism of the WGS; the WGS in SR is a two-phase reaction, compared to a reaction at a gas–liquid–solid interface in APR.

Experimental Section

Phase studies were conducted using AspenPlus V8.4 software while applying the Redlich–Kwong–Soave equation of state with an alpha Boston–Mathias extrapolation (RKS-BM). Parameters were derived from the critical temperature and pressure of the components and a quadratic mixing rule was used. For the phase diagrams, a binary analysis was performed to obtain both T_{xy} and P_{xy} graphs with varying water mass fraction. To study the influence of the substrate mole fraction, a sensitivity analysis was performed in which the temperature, pressure, and substrate mole fraction were varied in a Flash 2 separator. Thermodynamic trends for ethylene glycol, glycerol, xylose, and xylitol were calculated using the standard enthalpy of formation and the Gibbs free energy of formation data as reported in the literature. For these compounds, the heat capacity was maintained independent of the temperature while calculating the temperature-dependent enthalpy. The thermodynamics for the WGS was modelled in AspenPlus V8.4, which allowed inclusion of the temperature-dependent heat capacity. The temperature-dependent Gibbs free energy was obtained by applying the Gibbs–Helmholtz relation.

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Conflict of interest

The authors declare no conflict of interest.

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Influence of the Water Phase State on the Thermodynamics of Aqueous-Phase Reforming for Hydrogen Production

The reaction thermodynamics was evaluated to investigate the aqueous-phase reforming (APR) for hydrogen production from biomass. APR has a similar energy demand as steam reforming when neglecting the heat of evaporation of water as a solvent. Based on these results, the phase of the reactants would determine whether the water-gas shift reaction (WGSR) is a two-phase reaction or a three-phase reaction at the gas–liquid–solid interface.