Influence of the Syngas Composition on the Water-Gas Shift Reaction at Equilibrium Conditions

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Highlights

- The thermodynamic equilibrium limits the reactant conversion to a maximum value.
- The equilibrium conversion decreases with the temperature due to the WGS exothermicity.
- Different feed syngas compositions shift the equilibrium of the WGS reaction.

1. Introduction

Based on the kinetics, a reactor would be operated at the highest possible temperature to maximize the reaction rate. However, the thermodynamic equilibrium limits the reactant conversion to a maximum value, regardless of the catalyst used in the process. Hence, feasibility analyses and operational conditions can be influenced by the chemical reaction thermodynamics. The equilibrium conversion depends on the temperature, pressure, and initial reactant composition.[1]

The Water-Gas Shift Reaction – WGS – is an important reversible exothermic reaction (Equation 1) for the chemical industry due to the increased worldwide hydrogen demand (fuel cells, fertilizers, oil refining, hydrogenation processes, etc.) and the adjustment of the H_2/CO ratio in the syngas obtained from reforming reactions.[1]

$$CO + H_2O \leftrightarrow H_2 + CO_2 \qquad \Delta H^o = -41{,}16\ \text{kJ/mol} \qquad (1)$$

The WGS reaction is dependent on the process technology used for syngas generation such as Steam Methane Reforming (SMR), Autothermal Reforming (ATR), Shell Gasification Process (SGP), Biomass Gasification, Methane Tri-Reforming, among others. Within this framework, this study was carried out to analyze the influence of different syngas compositions on the WGS reaction equilibrium. Table 1 summarizes the syngas compositions considered in the analysis.

Table 1 – Syngas compositions (mol %)

	SMR[2]	**ATR**[2]	**SGP**[2]	**Biomass (dry wood)**[3]	**Tri-reforming***
CO	7	5	1,1	17	24,3
H_2O	32	31	32,4	23	21,9
H_2	41	38	38,2	15	45,3
CO_2	12	21	25,5	11	7,8
N_2	2	2	2,2	33	0,4
CH_4	6	3	0,6	1	0,3

*composition obtained through process simulation

2. Methods

To calculate chemical reaction equilibrium, the REquil pallet from ASPEN PLUS™ was used. Moreover, the Soave-Redlich-Kwong (SRK) Equation of State was used to take into account the non-ideal behavior of the reaction mixture.

3. Results and discussion

Figure 1 presents the equilibrium CO conversion for the WGS reaction at various temperatures and different syngas compositions. From the Le Chatelier's principle, the equilibrium conversion decreases with the temperature due to its exothermicity, favoring H_2 production at lower temperatures.

The equilibrium conversion related to the syngas from biomass showed greater values than the others in about all temperature range studied. This can be explained by its small H_2 content compared to others, shifting the equilibrium towards products. Moreover, both biomass and tri-reforming curves presented greater conversions at higher temperatures in comparison to the other processes because of their large quantity of CO in the feed. However, working at lower temperatures is more economically attractive, besides shifting the WGS reaction to produce further H_2 (exothermic) with higher equilibrium conversion values, which is the case of SMR, ATR, and SGP. Also, it is worth noting that the syngas from SMR has more CO content than from ATR and SGP, providing a shift towards the products and increasing conversion.

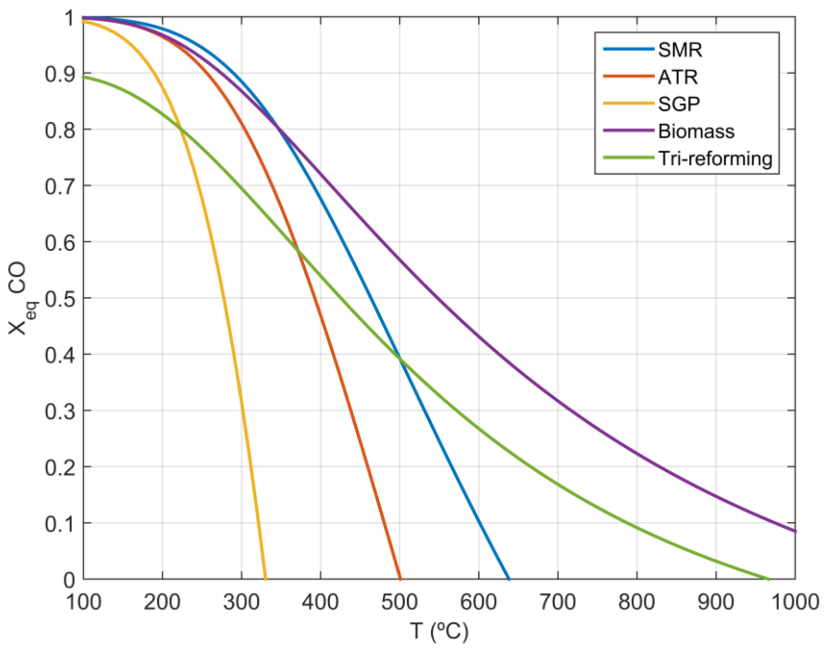

Figure 1. Equilibrium conversion as function of temperature for different syngas compositions.

4. Conclusions

The WGS reaction equilibrium study provides valuable information about the maximum conversions that can be reached with different syngas feed compositions. The equilibrium is shifted towards H_2 production at lower temperatures and with higher CO content in the feed stream. The syngas from biomass presented better conversion values in the studied interval, proving to be a promising route to feed the WGS process.

References

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Keywords

water-gas shift; chemical reaction equilibrium; syngas composition; Le Chatelier's principle.