Thermodynamic Modeling of Water-Gas Shift Reaction in Supercritical Water

E. Demirel, N. Azcan

Abstract— **Water gas shift reaction (WGSR) is one of the fundamental reactions which occurs during supercritical water gasification. A stoichiometric thermodynamic model is developed to estimate equilibrium composition of WGSR with reaction temperature, equilibrium constant and Gibbs free energy of reaction. The algorithm is based on Peng–Robinson Equation of State (PR-EoS) formulations and Gibbs free energy minimization. Molar fraction y_i of each species present in equilibrium which is related to degree of reaction is determined using Matlab Software. Model predictions are compared with data found in literature and the agreement is generally satisfying and therefore the correctness of the proposed model is demonstrated.**

Index Terms—**gasification, thermodynamic modeling, supercritical water, water-gas shift reaction**

I. INTRODUCTION

The world's progression towards the hydrogen economy is facilitating the production of hydrogen from various resources. In the carbon based hydrogen production, water gas shift reaction (WGSR) is the intermediate step used for hydrogen enrichment and CO reduction in the synthesis gas [1].

WGSR is a reaction traditionally used for the production of hydrogen from synthesis gas which is further used for ammonia production in the fertilizer industry, petroleum refineries for a variety of operations and recently as fuel for power generation and transportation. It is an old industrial process in which water in the form of steam is mixed with carbon monoxide to obtain hydrogen and carbon dioxide [2]. WGSR is expected to play a key role in the integration of gasification technologies with a H_2 production/recovery unit. The WGSR is an exothermic, equilibrium-limited reaction that exhibits decreasing conversion with increasing temperature and is expressed by,

$$\mathrm{CO} + \mathrm{H_2O} \longleftrightarrow \mathrm{CO_2} + \mathrm{H_2} \quad \Delta\mathrm{H} = -41.1\ \mathrm{kj/mol} \qquad (1)$$

The WGSR is reversible and several correlations for the equilibrium constant have been published [3]. Due to its moderate exothermicity, the WGSR is thermodynamically unfavorable at elevated temperatures. This is illustrated by the continuous decline and eventual sign change in the Gibbs free energy as a function of temperature, and the corresponding decreasing equilibrium constant as temperature increases. Of course, the kinetics of the catalytic reaction is more favorable at higher temperatures. Thermodynamically, the efficiency of the WGSR is maximized at low temperature, high water and low hydrogen concentration [4]. Today industrial realization of WGSR takes place in a series of adiabatic converters where the effluent from the reformer system is converted in two steps with the second at a significantly lower temperature in order to shift the equilibrium towards the favored hydrogen product [2].

In this study, a thermodynamic model for WGSR in supercritical water was formulated using Gibbs free energy minimization to predict the equilibrium composition of each species. Activity coefficient of each species was determined using PR-EoS. Pressure of the reactor was constant as 28 MPa knowing the fact that reaction outputs are nearly independent of pressure. Matlab software is implemented to determine the unknowns in the model. As a result, the effect of reaction temperature on molar fractions of the reactor effluent, reaction equilibrium constant and Gibbs free energy were determined using the proposed computational framework and the results are compared with those in literature.

II. THERMODYNAMIC MODEL FORMULATION

The thermodynamic model proposed in this work is based on Gibbs free energy minimization which implies that the system has reached an equilibrium state. The system under study is depicted in Figure 1.

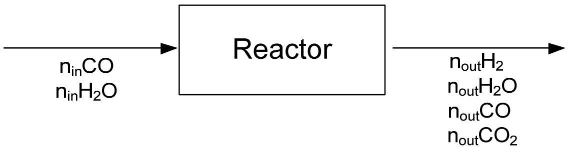

Fig. 1. Scheme of the reactor

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The molar fractions (yi) of the species in the reacting mixture are seen to be functions of the single variable ε (degree of reaction) and are related by:

$$y_{CO} = \frac{n_{in}CO - \varepsilon}{n_{in}CO + n_{in}H_2O} \quad (1)$$

$$y_{CO2} = \frac{\varepsilon}{n_{in}CO + n_{in}H_2O} \quad (2)$$

$$y_{H2O} = \frac{n_{in}CO - \varepsilon}{n_{in}CO + n_{in}H_2O} \quad (3)$$

$$y_{H2} = \frac{\varepsilon}{n_{in}CO + n_{in}H_2O} \quad (4)$$

Thermodynamic description of the system on the basis of the Gibbs free energy minimization is written as:

$$\Delta G^0(T^{reac}) + R * T^{reac} \ln(K) = 0 \quad (5)$$

where Gibbs free energy is computed at atmospheric pressure and temperature of the reactor and is calculated using standard molar entropy, enthalpy of the reaction at reference temperature and temperature dependence of specific heat of each compound [5].

For the equilibrium the thermodynamic constant K satisfies:

$$K\left[\frac{p^{reac}}{P^0}\right]^{-\nu} = \prod_{k=1}^{NS}(y_k \Phi_k)^{\nu_k} \quad (6)$$

where Φ_k , ν_k and P^0 stand for the fugacity coefficient of species k in the reactor effluent, stoichiometric coefficient of species k and atmospheric pressure, respectively. Here k can stand for H_2, H_2O, CO and CO_2.

The fugacity coefficient is calculated from the following equation:

$$\ln\Phi_k = \frac{B_k}{B_m}(Z-1) - \ln(Z-B)\ln\left[\frac{Z+(1+\sqrt{2})B}{Z+(1-\sqrt{2})B}\right] - \frac{A}{2B\sqrt{2}}\left[\frac{2\sum_{j=1}^{NS} x_j A_{kj}}{A_m} - \frac{B_k}{B_m}\right] \quad (7)$$

To describe the thermodynamic behavior of each compound, PR-EoS was adopted for its wide application in the field of supercritical fluid [6]. The PR-EoS can be rewritten as a third-order polynomial with *Z* appearing as the independent variable:

$$Z^3 - (1-B)Z^2 + (A - 2B - 3B^2)Z \\ -(AB - B^2 - B^3) = 0 \quad (8)$$

where A and B are constants which characterize the mixture and are dependent on the critical properties of each compound in the reaction mixture. Critical properties of each compound are given in Table 1 [6]. The PR equation is a third order polynomial equation having three roots. The maximum value of real roots is selected for the gas phase.

Equation (5) is the final nonlinear equation which is solved numerically using Matlab for ε. Then molar fractions and other quantities can be computed from the estimated ε directly.

TABLE I
Critical properties of compounds used in calculations

Compound	T_c (K)	P_c (MPa)	V_c (x10^5 m^3/mol)	Ω
H_2	33.19	1.31	6.42	-0.2320
H_2O	647.13	22.06	5.6	0.3449
CO	132.92	3.5	9.44	0.0482
CO_2	304.21	7.38	9.4	0.420

III. RESULTS

Variation of WGS equilibrium constant and Gibbs free energy with temperature are given in Figure 2 and 3, respectively. Gibbs free energy of the reaction increases with increasing temperature and becomes positive when the temperature reaches around 1100 K. This result shows that reaction becomes thermodynamically unfavorable at elevated temperatures.

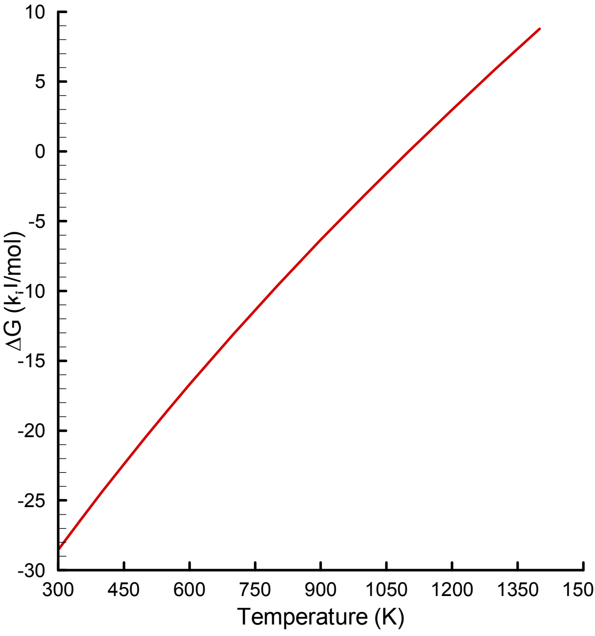

Fig. 2. Variation of Gibbs free energy with reaction temperature

The WGSR equilibrium constant is nearly 60 times greater when the temperature decreases from 1400 to 600 K.

Equilibrium compositions of each species using different initial amounts of CO:H_2O (1:1; 1:2) versus temperature are given in Figure 4 and 5.

Due to the exothermic nature of the WGSR, higher CO conversions and higher hydrogen yields are favored at lower temperatures. Equilibrium amounts of CO and H_2O increase while those of H_2 and CO_2 decrease with increasing temperature. The water content has a strong influence on conversion of CO, hence production of H_2. Therefore, effect of CO:H_2O ratio on equilibrium conversions at different reaction temperatures is determined using the proposed model.

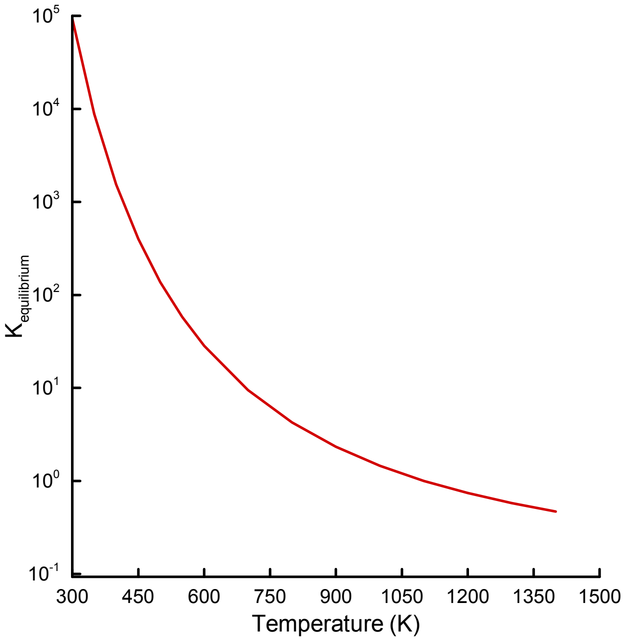

Fig. 3. Variation of equilibrium constant with reaction temperature

According to Figures 4 and 5, it can be concluded that as the amount of water increases in the incoming feed, the reaction will shift to the right. So that concentrations of H_2 and CO_2 (on a water free basis) increase.

IV. CONCLUSIONS

This work deals with thermodynamic modeling of WGSR. Thermodynamic equilibrium analysis of WGSR gives us some information concerning operating conditions. Composition of the reactor effluent is mainly influenced by temperature and feed concentration. 300 K reaction temperature and 1:2 CO:H_2O ratio gave the highest H_2 composition according to used thermodynamic model. Found results are in good agreement with the data stated in literature [4].

Nomenclatures

$n_{in,CO}$: Molar flow rate of incoming CO (mol/s)
n_{in,H_2O} : Molar flow rate of incoming H_2O (mol/s)
n_{out,H_2} : Molar flow rate of H_2in the effluent stream (mol/s)
n_{out,H_2O} : Molar flow rate of H_2O in the effluent stream (mol/s)
$n_{out,CO}$: Molar flow rate of CO in the effluent stream (mol/s)
n_{out,CO_2} : Molar flow rate of CO_2in the effluent stream (mol/s)
T^{reac} : Reactor temperature (K)
P^{reac} : Reactor pressure (Pa)
T^{ref} : Reference temperature (K)
P^0 : Atmospheric pressure (Pa)
Z : Compresibility factor
ε : Degree of reaction
Φ_k : Fugacity coefficient of species k
y_k : Molar fraction of species k
ν_k : Stoichiometric coefficient of species k
K : Equilibrium constant of the reaction
ΔG^0 : Gibbs free energy of the reaction (J/mol)

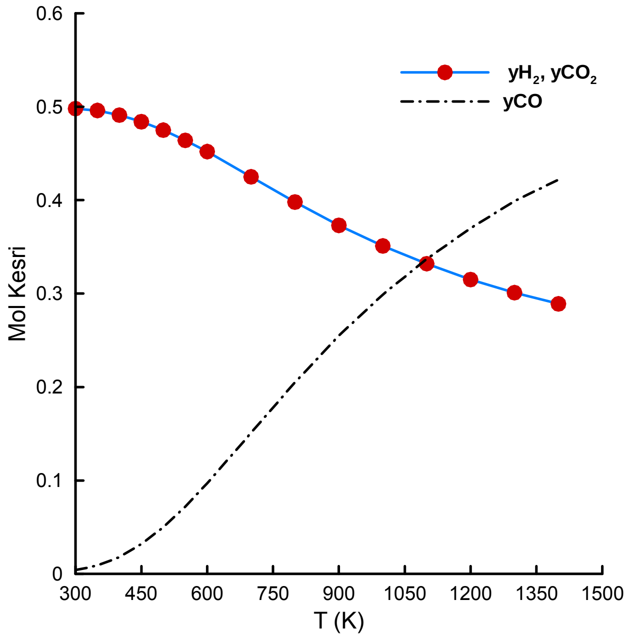

Fig. 4. Equilibrium compositions of gaseous mixture versus reaction temperature on water free basis (1 mol CO+1 mol H_2O)

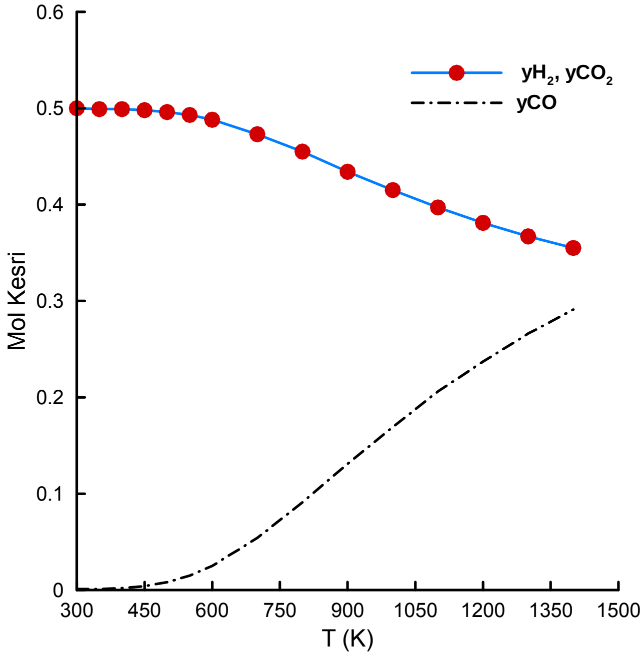

Fig. 5. Equilibrium compositions of gaseous mixture versus reaction temperature on water free basis (1 mol CO+2 mol H_2O)

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