

THERMO DYNAMIC ANALYSIS OF HYDROGEN PRODUCTION BY STEAM REFORMING OF ETHANOL

¹AHMED BSHISH, ²ZAHIRA YAAKOB, ³ALI EBSHISH

¹Department of Chemical and Process Engineering, Faculty of Engineering and Built Environment,
University Kebangsaan Malaysia, 43600 Bangi, Selangor, Malaysia

²Department of Chemical and Petroleum Engineering, El-Mergib University, Alkhoms, Libya
E-mail: ¹ahmedbshish@gmail.com, ²zahira65@yahoo.com

Abstract - Hydrogen production varies significantly according to the operating conditions such as pressure, temperature and feed reactants ratio. The thermodynamic analysis provides important knowledge about the effects of those variables in ethanol reforming. A thermodynamic equilibrium analysis was performed over the following variable ranges: pressure 1–50 atm, temperature 300–900 K, and water-to-ethanol feed ratio 3:1-12:1. The present work was aimed at analyzing the thermodynamic steam reforming of ethanol based on the equilibrium constant and minimization of the Gibbs energy methods. For this purpose, EXCEL SOLVER software was used for calculating ethanol conversion, and a THERMOSOLVER software are used to find the number of moles of each species at equilibrium via a minimization technique. The equilibrium concentrations of different compounds were calculated by the method of direct minimization of the Gibbs free energy. Results show that ethanol conversion can be completed at temperatures equal to or higher than 600 K at any value of pressure and molar ratio. Hydrogen production is thermodynamically favored at high temperature, high ethanol-to-water molar feed ratio, and low pressure, while the thermodynamic of CO formation is preferred at high temperature, low ethanol-to-water molar feed ratio, and low pressure. The result also show that, in order to avoid coke formation, temperature and water-to-ethanol feed ratio equal to or higher than 500 K and 3:1, respectively is required.

Keywords - Thermodynamic Analysis; Ethanol Steam Reforming; Hydrogen

I. INTRODUCTION

The thermodynamic aspects of the ethanol steam reforming system have received great attention among researchers working in this area. Operating conditions such as temperature, pressure, water-to-ethanol molar ratio, and residence time play important roles to maximize hydrogen production. Thermodynamic analysis can provide useful and rapid guidance of the proper or optimal zone for these operating conditions [1]. In the published literature, many studies regarding the thermodynamic analysis of the reforming process of alcohols and hydrocarbons have been discussed [2],[3], [4], [5], [6], [7], [8]. In an earlier study conducted by García et al. [9], it was found the optimum conditions to maximize hydrogen production and minimize carbon monoxide and methane formation were temperatures above 700°C, atmospheric pressure, and 10:1 water-to-ethanol molar ratio. Freni et al. [10] found that, by increasing the temperature from 600°C to 700°C, the amount of hydrogen produced increased from 46.8 % to 58.95 %. Undesirable products such as carbon monoxide, carbon, and methane could be reduced by a high water-to-ethanol molar ratio in the feed. The use of a high water-to-ethanol molar ratio resulted in high selectivity for hydrogen, reducing the amount of CO and CH₄ generated as well as preventing carbon deposition on the catalyst [11]. Ethanol reforming can also be carried out using two-stage process.[12][13][14] The main advantages of the combined method were reduced coke formation and lower energy demand. In the this work, A thermodynamic analysis for H₂ production by steam

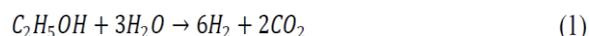
reforming of ethanol was performed. Thermodynamic ethanol conversion was calculated based on the equilibrium constants, and the number of moles of products was calculated based on minimizing the Gibbs free energy. The influences of the reaction conditions such as the temperature, pressure, S/C ratio on ethanol conversion and H₂, CO, CO₂, and CH₄ yields were theoretically investigated using the thermodynamic approaches.

II. SIMULATION METHODS

The equilibrium of chemical reactions is generally solved by two methods. Ethanol conversion was obtained based on the equilibrium constants, while the minimization of the Gibbs free energy method was used to study the effect of temperature, pressure, and molar ratio on gaseous product yields. The operating parameters used were temperature, pressure, and S/C molar feed ratio.

Thermodynamics equilibrium constant (K_p)

The thermodynamic analysis was performed based on the reforming reaction:



The equilibrium of a chemical reaction is strongly dependent on its temperature, pressure, and initial composition, whereby its temperature dependence is usually expressed as the equilibrium constant (K_p). According to Equation (2), K_p of a reaction is simply calculated from its Gibbs free energy of

reaction (ΔG^0). Since (K_p) is given by the reaction quotient of the products and reactants in the reaction, a high value of ($K_p \gg 1$) indicates that the reaction occurs in the forward direction, whereas the reverse reaction occurs when ($K_p \ll 1$).

$$\ln(K_p) = -\frac{\Delta G^0}{RT} \quad (2)$$

The relation between the equilibrium constant and the composition of reaction species are given in the following equation:

$$\prod_i (y_i \phi_i)^{V_i} = \left(\frac{P}{P_0}\right)^{-v} K_p \quad (3)$$

With,

$$v = \sum_i V_i \quad (4)$$

Where, ϕ_i is the fugacity coefficient of species i , y_i is the mole fraction of species i , P_0 and P are the standard and operating pressure respectively, K_p is the reaction equilibrium constant, and V_i is the stoichiometric number of species i (V_i is the stoichiometric coefficient of species i (with a sign: '+' for products but '-' for reactants). Equation (3) was used to evaluate the effect of composition in the calculation of equilibrium constant. Considering that the behavior of equilibrium mixture is ideal $\phi_i = 1$. For an ideal mixture $\phi_i = 1$, $P = 1$ bar, Equation (3) becomes as follows:

$$\frac{(y_{CO_2})^2 (y_{H_2})^6}{(y_{C_2H_5OH})^1 (y_{H_2O})^3} = (1)^{-4} K_p \quad (5)$$

In order to calculate the mole fraction of species i , y_i can be eliminated as a function of the extent of reaction with the use of (6):

$$y_i = \frac{n_i^0 + V_i \varepsilon}{n_0 + V \varepsilon} \quad (6)$$

Minimization of the Gibbs free energy

The minimization of Gibbs free energy method as a powerful tool with the set of strong mathematical bases can easily predict product distribution at equilibrium condition. This method used to solve the equilibrium composition through minimization of the total Gibbs energy of the system. First a formula relates the j elements in our system to the species i was introduced in Equation (7).

$$\sum_{i=1}^m n_i \beta_{ij} = b_j \quad j = 1, 2 \dots 1 \quad (7)$$

Where, n_i = the number of moles of species i , $i = 1, 2 \dots m$; β_{ij} = formula coefficient matrix, and b_j = all elements that are present in the system, e.g., C, H, O, .

The Gibbs energy of the system as described in Equation (8) can be formulated as:

$$G = \sum_{i=1}^m \mu_i n_i \quad (8)$$

Where, G = Gibbs energy, μ_i = Chemical potential of species i , and n_i = Moles of species i .

The aim is to calculate the different values of n_i which minimizes the Gibbs energy function. In order to do that, Gibbs energy function (Equation 8) will be subjected to the constraint function (Equation 7) by the introduction of the Lagrangian multiplier, λ_j .

$$G' = \sum_{i=1}^m \mu_i n_i + \sum_{j=1}^1 \lambda_j \left(\sum_{i=1}^m n_i \beta_{ij} - b_j \right) \quad (9)$$

To find the composition at which this function is a minimized, set its derivative with respect to n_i to zero as follow:

$$\left(\frac{\partial G'}{\partial n_i} \right) = 0 = \mu_i + \sum_{j=1}^1 \lambda_j \beta_{ij} \quad (10)$$

The phase expression for the chemical potential for an ideal gas described in Equation (11) as follow:

$$\mu_i = G_i^0 + RT \ln \frac{f_i^{\wedge}}{f_i^0} \quad (11)$$

$$\frac{f_i^{\wedge}}{f_i^0} = y_i p = \frac{n_i}{n} p \quad (12)$$

Where, G_i^0 = standard Gibbs energy of species i , f_i^{\wedge} = fugacity of reaction species i in real equilibrium mixture, f_i^0 = standard state fugacity at 1 bar, and p = reaction pressure. Equation (11) become,

$$\mu_i = G_i^0 + RT \ln y_i p \quad (13)$$

Substitution Equation (13) into Equation (10),

$$G_i^0 + RT \ln y_i p + \sum_{j=1}^1 \lambda_j \beta_{ij} = 0 \quad (14)$$

Substitute the Gibbs energy of formation for the standard Gibbs energy of species i in Equation (13).

$$\Delta G_i^f + RT \ln y_i p + \sum_{j=1}^1 \lambda_j \beta_{ij} = 0 \quad (15)$$

Equations (10) and (15) can be rearranged and manipulated to represent a set of equations that can be solved for the unknown y_i and λ_j . The numeric procedure to solve this set of nonlinear algebraic equations was implemented by Newton-Raphson root finder using Thermo Solver software.

III. RESULTS AND DISCUSSIONS

Ethanol conversion

Figure 4.1a shows the thermodynamic conversions of ethanol as a function of temperature and ethanol-to-water molar feed ratio at atmospheric pressure. As expected for an endothermic reaction, increasing the temperature has a positive influence on ethanol conversion.

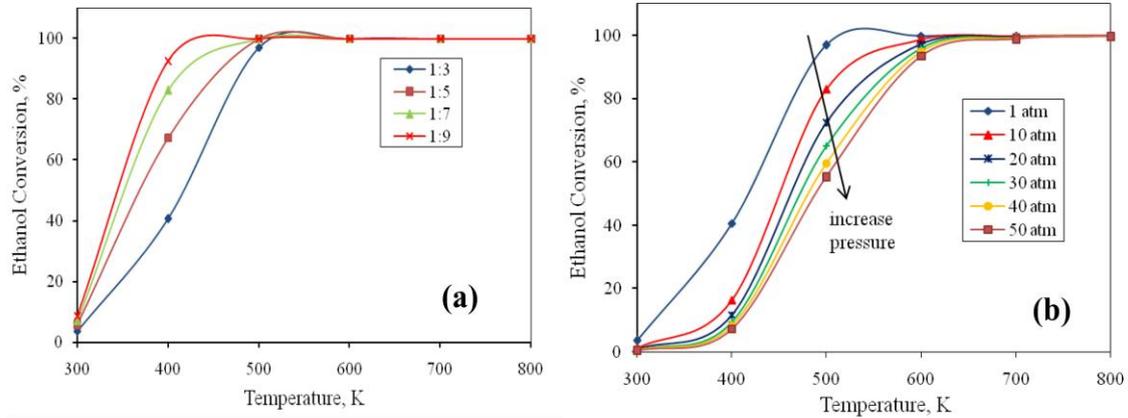


Figure 1. Thermodynamic effects of temperature on ethanol conversion at different (a) water molar ratios and (b) different pressures.

Similar trend was observed regarding the effect of water to ethanol molar ratio. Approximately complete ethanol conversion was achieved as the temperature reached a value of 500 K at all values of ethanol-to-water molar feed ratio. At higher temperatures, ethanol-to-water molar feed ratio has no effect on ethanol conversion. These results are similar to those reported in literature [15]. This suggests that experiments should be conducted at temperatures above 500 K. The effect of pressure on ethanol conversion with reaction temperature ranges from 300 K to 800 K is shown in Figure 1b. Given the difference in molar quantity between reactants and products, total pressure affects the equilibrium of ethanol steam reforming. The strongest effect of pressure appears at low values of temperature ranges from 300 K to 600 K. Within this temperature range,

increasing pressure has a negative effect on ethanol conversion.

Hydrogen yield

Figures 2 (a) and (b) depict the H₂ moles and molar fraction at different temperatures and ethanol-to-water molar ratios, respectively. Low temperatures are found to be unsuitable for reaction based on H₂ yield. As shown in Figure (2a), the number of moles of H₂ increases with increasing temperature. Similarly, the number of moles of H₂ increases with increasing ethanol-to-water molar feed ratio. This increase can be attributed to the acceleration of water gas shift reaction (Equation 16), which converts CO to CO₂ and H₂ in the presence of water.

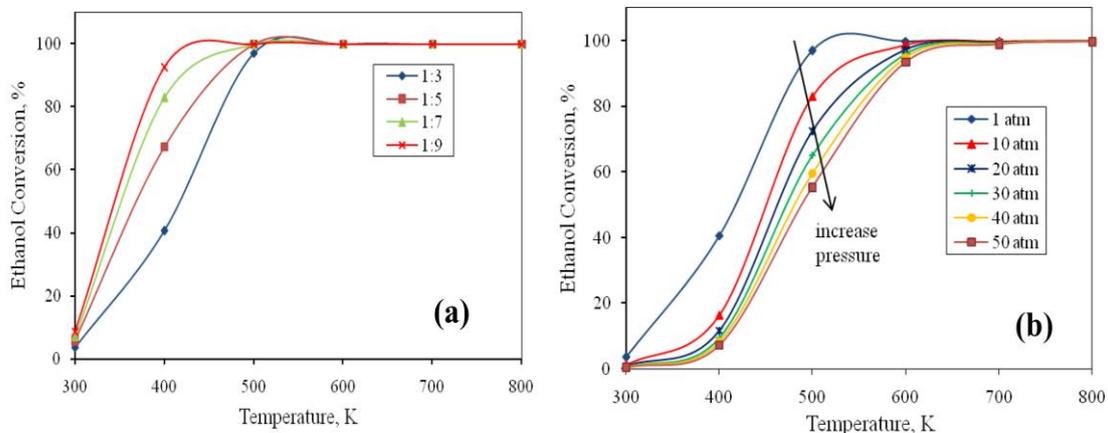
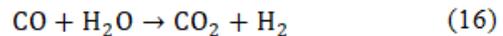


Figure 2. (a) Hydrogen moles vs. temperature at different molar ratios at P=1 atm, (b) Mole fraction of hydrogen vs. temperature at different molar ratios at P=1 atm.

The effect of temperature and ethanol-to-water molar feed ratio on the molar fraction of H_2 is shown in Figure (2b). The molar fraction of H_2 is found to be higher in case of low ethanol-to-water molar feed ratio, which is clearly observed at higher temperature values because a large quantity of unreacted water exists in the product at high ethanol-to-water molar feed ratio. This amount of water diminishes the H_2 mole fraction, but not necessarily the amount of H_2 . The largest amount of H_2 is obtained from excess water at all temperatures. The best conditions for H_2 production are obtained from excess amount of water, but the energy required to evaporate the excess water will be higher.

IV. CONCLUSION

Thermodynamic ethanol conversion was calculated based on the equilibrium constants, and the number of moles of products was calculated based on minimizing the Gibbs free energy. The thermodynamic calculations show that ethanol conversion for temperatures equal or higher than 600 K can be completed at any value of pressure and molar ratio. H_2 yield is favored at high temperature, high ethanol-to-water molar feed ratio, and low pressure.

By contrast, CH_4 formation is favored at low ethanol-to-water molar feed ratio, low temperature, and high pressure, and CO moles are favored at high temperature, low ethanol-to-water molar feed ratio, and low pressure. Seeking a high H_2 yield and a low CO yield is a contradiction because the reaction temperature should be sufficiently high to obtain a reasonable H_2 yield and as low as possible to obtain a low CO yield. Although this thermodynamic calculation indicates an advantage of conducting ethanol reformation at high temperature and high ethanol-to-water molar feed ratio because of the high level of H_2 formed, these conditions lead to an increase in energy requirement for water evaporation. Thus, experiments in this research were run under mild conditions of 400 °C, 1 atm, and 6:1 water-to-ethanol molar ratio.

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