

Efficient Hydrogen Production via Butanol Steam Reforming: Thermodynamic Study

Ronak Patel^{1*}, Milind H. Joshipura², Sanjay Patel³

^{1*} Assistant Professor, Chemical Engineering Department Institute of Technology, Nirma University, Ahmedabad, India, 382481

² Professor, Chemical Engineering Department Institute of Technology, Nirma University, Ahmedabad, India, 382481

³ Professor, Chemical Engineering Department Institute of Technology, Nirma University, Ahmedabad, India, 382481

Abstract— In the era of dwindling resources of fossil fuels and increased concern related to environment, there is strong need to find next generation energy source which is environment friendly and can be obtained renewably. Moreover procedure to obtain next generation energy source should be economical for sustainable development. Hydrogen obtained from renewable sources of biomass can be answer to all these challenges. Bio-butanol can be obtained from fermentation of biomass, like bio-ethanol, and can be produced renewably. Bio-butanol is also one of the key components of bio-oil. Butanol has more hydrogen content compared to other members of alcohol family like methanol, ethanol and propanol. Extraction of hydrogen from biologically derived butanol can be attractive alternative for hydrogen production. Hydrogen can be extracted from butanol by various techniques like steam reforming, partial oxidation, oxidative steam reforming and dry reforming. Out of all these techniques steam reforming reaction has greatest potential to extract hydrogen, because of its high selectivity towards hydrogen. In current thermodynamic study, emphasis was given to analyse effect of operating conditions on butanol steam reforming. Simulations were conducted with the help of ASPEN HYSYS 2004.2 software.

Keywords— Steam Reforming, Hydrogen Production, Butanol, Thermodynamic study, Simulation.

I. INTRODUCTION

Fossil based energy sources like petroleum and natural gas are likely to exhaust in the coming decades, in this context renewable energy sources has gained attentions of researchers and engineers to explore next generation energy source [1-5]. Moreover, use of fossil based fuels emits large amount of carbon dioxide in environment; which is prime culprit for greenhouse effect [2]. Hydrogen, obtained from renewable biomass, can be answer to these problems. As combustion of hydrogen only leads to generation of water [1, 3]. Various research articles have been published in the area of hydrogen production from different resources like bio-oil [6-8], bio-ethanol [9], glycerol [10, 11] etc. via steam reforming reaction, due to high selectivity of steam reforming reactions towards hydrogen production [9]. Butanol, like bio-ethanol, can be produced by fermentation of biomass. Moreover, it is one of the key constituents of bio-oil. Butanol has more hydrogen content than its alcohol family members like methanol, ethanol and propanol. Hydrogen content in n-butanol is 13.51% by weight, compared to 12.5% and 13.04% by weight of

methanol and ethanol respectively. Butanol has various properties that makes it relatively better fuel compared to other alcohols like methanol and ethanol. It is having lower vapour pressure at atmospheric pressure compared to ethanol and methanol. It has greater tolerance to water content. Due to these properties butanol can be handled with more ease than methanol and ethanol in fuel distribution pipelines [12]. Despite all these advantages, there are limited studies published in the area of butanol steam reforming reaction. In this study, we have investigated effect of operating conditions like temperature, pressure and steam to butanol molar ratio on steam reforming of butanol. Thermodynamic study was performed with the help of ASPEN HYSYS 2004.2 software. Simulations showed equilibrium composition, which may differ in case of actual experimentation. Because selected model (Gibbs' reactor) gives equilibrium composition of all constituents based on process conditions like temperature, pressure and composition of reactants involved, while actual composition also depends on additional factors like kinetics and activity of catalyst involved. But these study gives insights to researchers related to maximum achievable thermodynamic hydrogen yield.

II. COMPUTATIONAL THERMODYNAMIC ANALYSIS

Equilibrium chemical compositions can be predicted by either calculating the equilibrium constant or minimization of the total Gibbs free energy. In case of reactions involving solid components, equilibrium composition prediction by calculation of equilibrium constant is difficult. Moreover, information regarding stoichiometry of the involved reactions are also required. While, method of minimization of the total Gibbs free energy can be easily applied to the reacting system including condensed components and non-reacting components. Moreover, it simply requires inputs like temperature, pressure and initial composition of reactant. Information regarding stoichiometry of the reaction is also not required in case of minimization of the total Gibbs free energy method. Therefore, the Gibbs free energy minimization method was selected for thermodynamic study. Detailed method is discussed elsewhere [5]. In this study, we have investigated effect of operating conditions like temperature, pressure and steam to butanol molar ratio on steam reforming of butanol. Thermodynamic study was performed with the

help of ASPEN HYSYS 2004.2 software. Gibbs' reactor was selected and Soave Redlich Kwong (SRK) property package was selected. Sample flowsheet is shown in Figure 1.

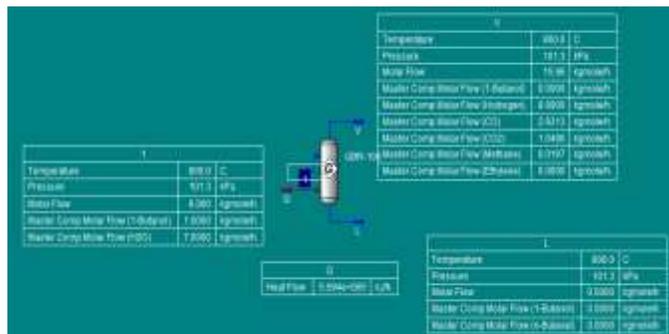


Figure 1. Sample flowsheet of Gibbs' reactor for butanol steam reforming.

Yield of different components are calculated by following equation.

$$Y_i = \frac{F_{iout}}{F_{Bin}} \quad (1)$$

Where, F_{iout} is the molar flow rate of component i leaving the reactor and F_{Bin} is the molar flow rate of butanol introduced in reactor.

Conversion of butanol was 100% for entire range of study due to very high value of equilibrium constants. So conversion was not considered as deciding factor for determination of optimum reaction conditions. Emphasis was given on yield of various components.

III. REACTION INVOLVED IN STEAM REFORMING REACTION

Steam reforming of butanol is accompanied with many series parallel reaction, these reactions also have considerable impact on hydrogen yield. Considered reactions are tabulated in Table 1.

Table 1. Considered reactions in butanol steam reforming [5].

Sr. No.	Reaction	Equation
1	Butanol steam reforming reactions	$C_4H_{10}O + 3H_2O \leftrightarrow 4CO + 8H_2$ and $C_4H_{10}O + 7H_2O \leftrightarrow 4CO_2 + 12H_2$
2	Butanol decomposition	$C_4H_{10}O \leftrightarrow CO + 2CH_4 + H_2 + C$
3	Methane decomposition	$CH_4 \leftrightarrow C + 2H_2$
4	Boudouard reaction	$2CO \leftrightarrow C + CO_2$
5	Water-gas shift reaction	$CO + H_2O \leftrightarrow CO_2 + H_2$
6	Hydrogenation of carbon monoxide	$CO + 3H_2 \leftrightarrow CH_4 + H_2O$ and $2CO + 2H_2 \leftrightarrow CO_2 + CH_4$
7	Hydrogenation of carbon dioxide	$CO_2 + 4H_2 \leftrightarrow CH_4 + 2H_2O$
8	Hydrogenation of coke	$C + 2H_2 \leftrightarrow CH_4$
9	Methane steam reforming	$CH_4 + H_2O \leftrightarrow CO + 3H_2$
10	Methane dry reforming	$CH_4 + CO_2 \leftrightarrow 2CO + 2H_2$
11	Carbon monoxide	$CO + H_2 \leftrightarrow C + H_2O$ and $2CO + 2H_2 \leftrightarrow$

12	Reverse water-gas shift reaction	$2C + 2H_2O \leftrightarrow CO_2 + H_2 \leftrightarrow CO + H_2O$
13	Coke gasification	$C + H_2O \leftrightarrow CO + H_2$
14	Dehydrogenation of butanol	$C_4H_{10}O \leftrightarrow C_4H_8O + H_2$
15	Butyric aldehyde decomposition	$C_4H_8O \leftrightarrow CO + CH_4 + C_2H_4$

IV. EFFECT OF OPERATING CONDITIONS

1. Effect of Temperature: In order to determine effect of temperature, simulations studies were carried out in the range of 450-1100 °C. While pressure and steam to butanol ratio were kept constant at 1 atm pressure and 7 respectively. Effect of increase in temperature on hydrogen, carbon monoxide, carbon dioxide and methane is shown in Figure 2.

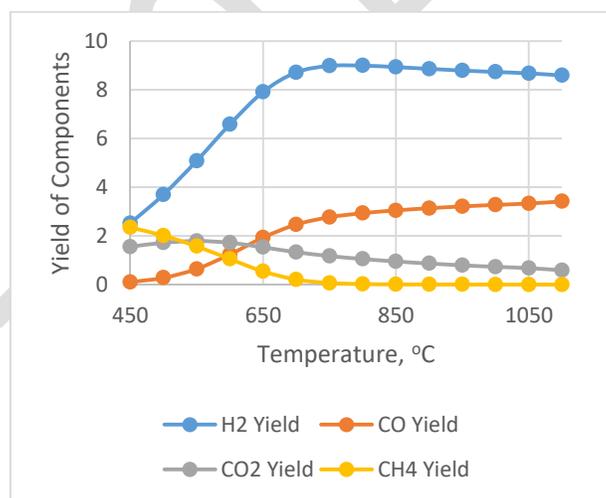


Figure 2. Effect of temperature on yield of various components.

Simulation studies indicated that yield of hydrogen increased rapidly in initial increment of temperature, it reaches to maximum at 800 °C. After that further increase in temperature, reduced yield of hydrogen very slightly. For CO₂ yield decreased with increased temperature, but change in magnitude was not so high. For carbon monoxide yield, it was noted that yield of CO increased with increase in reaction temperature. CH₄ yield found to decrease with increase in temperature. These behavior can be defended by the fact that at lower temperatures (lower than the temperature of maximum of hydrogen yield), influence of endothermic steam reforming reactions on hydrogen yield were controlling over exothermic water gas shift reaction leading to increased hydrogen yield. However, at sufficiently high temperatures and lower methane concentration steam reforming methane became insignificant and exothermic water gas shift reaction became only contributing factor which governs hydrogen yield leading to slightly declining trends of hydrogen yield [13, 14].

2. Effect of steam to butanol molar ratio: Increase in steam to butanol molar ratio has shown following trends.
 - i. Increased hydrogen yield from 7.1298 to 9.9699 by increasing steam to butanol ratio from 3 to 14. Steam to butanol ratio showed similar trend in case of CO₂ concentration. CO₂ yield increased by 97.87%, when changing steam to butanol ratio from 3 to 14.
 - ii. Decreased CO and CH₄ yield.

While investigating effect of steam to butanol molar ratio, temperature and pressure were kept at 800 °C and 1 atm pressure respectively. With increase in steam to butanol ratio, steam reforming of butanol, steam reforming of methane and water gas shift reaction were favored thereby increasing hydrogen and CO₂ yield and decreasing yield of CO and CH₄ [15, 16]. Higher steam to butanol ratio is favorable, if hydrogen to be used in proton exchange membrane fuel cell (PEMFC). As at higher steam to butanol ratio CO production is lesser, which is poison for PEMFCs.

3. Effect of Pressure: Pressure found to show negative impact on hydrogen yield. To investigate effect of pressure on yield of different components like H₂, CO, CO₂ and CH₄, pressure was varied from 1 to 10 atm. Yield of H₂ and CO decreases with increase in pressure from 1 to 10 atm. While yield of CO₂ and CH₄ increases with increase in pressure. Effect of pressure on yield of different components are summarized in Table 2. Temperature and steam to butanol molar ratio were kept constant at 800 °C and 7 respectively.

Table 2. Effect of pressure.

Pressure, atm	H ₂ yield	CO yield	CO ₂ yield	CH ₄ yield
1	8.99	2.9313	1.049	0.0197
2	8.8394	2.8679	1.0589	0.0732
3	8.6278	2.7792	1.0726	0.1483
4	8.3874	2.6791	1.0876	0.2332
5	8.1402	2.5768	1.1024	0.3207
6	7.8963	2.4776	1.1164	0.406
7	7.6677	2.3837	1.1292	0.4871
8	7.4507	2.296	1.1406	0.5633
9	7.2478	2.2147	1.1509	0.6344
10	7.0586	2.1395	1.16	0.7005

This behavior can be justified with the help of Le'chetalier's principle. Increase in total pressure shifts the equilibrium of carbon dioxide, carbon monoxide and carbon hydrogenation reactions in forward direction [17]. As in these hydrogenation

reactions, reactant side moles are more than the product side.

V. CONCLUSIONS

Hydrogen produced from renewable sources is sustainable option from economy and environmental point of view. Thermodynamic study revealed great potential to extract hydrogen from butanol steam reforming reaction. In order to obtain maximum hydrogen yield, process parameters like temperature, steam to carbon molar ratio and pressure needs to be optimized. Following conclusions can be drawn from this study.

- i. In order to obtain maximum hydrogen yield reaction temperature must be optimized. Operating at higher than optimum hydrogen yield temperature, leads to requirement of high temperature heating medium and costly material of construction for reactor. While operating at lower temperature than optimum temperature, leads to drastic decline in hydrogen yield.
- ii. Pressure has negative impact on hydrogen yield. So to achieve maximum hydrogen yield, reactor should be operated at atmospheric pressure.
- iii. Highest possible steam flow rate should be maintained in reactor to achieve highest hydrogen yield and lowest CO yield.

REFERENCES

- [1] Suh, M.P., Park, H.J., Prasad, T.K., Lim, D.W., (2012). Hydrogen Storage in Metal-Organic Frameworks. *Chem Rev* 112:782-835.
- [2] Balat, M., (2008). Potential importance of hydrogen as a future solution to environmental and transportation problem. *Int J Hydrogen Energ* 33:4013-4029.
- [3] Zhao, Y., Huang, Y., Gao, P., Chen, H., Gonzalez-Cortes, S., Xiao, T., (2016). Hydrogen from bottle-the magic of Pt catalysts for methanol reforming instantly start-up from cold weather. *Int J Hydrogen Energ* 41:10719-10726.
- [4] Bockris, J.O'M., Veziroglu, T.N., (1985). A Solar-Hydrogen Energy System for Environmental Compatibility. *Environ Conserv* 12:105-118.
- [5] Hartley, U.W., Amornraksa, S., Kim-Lohsoontorn, P., Laosiripojana, N., (2015). Thermodynamic analysis and experimental study of hydrogen production from oxidative reforming of n-butanol. *Chem Eng J* 278:2-12.
- [6] Quan, C., Xu, S., Zhou, C., (2016). Steam reforming of bio-oil from coconut shell pyrolysis over Fe/olivine catalyst. *Energ Convers Manage* xxx:xxx-xxx.
- [7] Czernik, S., Evans, R., French, R., (2007). Hydrogen from biomass-production by steam reforming of biomass pyrolysis oil. *Catal Today* 129:265-268.
- [8] Chen, G., Yao, J., Liu, J., Yan, B., Shan, R., (2016). Biomass to hydrogen-rich syngas via catalytic steam reforming of bio-oil. *Renew Energ* 91:315-322.
- [9] Ni, M., Leung, D.Y.C., Leung, M.K.H., (2007). A review on reforming bio-ethanol for hydrogen production. *Int J Hydrogen Energ* 32:3238-3247.
- [10] Papageridis, K.N., Siakavela, G., Charisiou, N.D., Avraam, D.G., Tzounis, L., Kousi, K., Goula M.A., (2016). Comparative study of Ni, Co, Cu supported on γ -alumina catalysts for hydrogen production via the glycerol steam reforming reaction. *Fuel Process Technol* 152:156-175.

- [11] Iriondo, A., Barrio, V.L., Cambra, J.F., Arias, P.L., Güemez, M.B., Navarro, R.M., Sanchez-Sanchez, M.C., Fierro, J.L.G., (2009). Influence of La₂O₃ modified support and Ni and Pt active phases on glycerol steam reforming to produce hydrogen. *Catal Comm* 2009;10:1275-1278.
- [12] Cai, W., Piscina, P.R., Homs, N., (2012). Hydrogen production from the steam reforming of bio-butanol over novel supported Co-based bimetallic catalysts. *Bioresource Technol* 107:482-486.
- [13] Bimbela, F., Oliva, M., Ruiz, J., García, L., Arauzo, J., (2009). Catalytic steam reforming of model compounds of biomass pyrolysis liquids in fixed bed: Acetol and n-butanol. *J Anal Appl Pyrolysis* 2009;85:204-213.
- [14] Dhanala, V., Maity, S.K., Shee, D., (2015). Oxidative steam reforming of isobutanol over Ni/ γ -Al₂O₃ catalysts: A comparison with thermodynamic equilibrium analysis. *J Ind Engg Chem* 27:153-163.
- [15] Dhanala, V., Maity, S.K., Shee, D., (2015). Roles of Supports (γ -Al₂O₃, SiO₂, ZrO₂) and Performance of Metals (Ni, Co, Mo) for Steam Reforming of Isobutanol. *RSC Adv* 2015;5:52522-52532.
- [16] Dhanala, V., Maity, S.K., Shee, D., (2013). Steam Reforming of Isobutanol for Production of Synthesis Gas over Ni/ γ -Al₂O₃ Catalysts. *RSC Adv* 3:24521-24529.
- [17] Nahar, G.A., Madhani, S.S., (2010). Thermodynamics of hydrogen production by the steam reforming of butanol: Analysis of inorganic gases and light hydrocarbons. *Int J Hydrogen Energ* 35:98-109.