

Effect of Operating Conditions on Hydrogen Production in Butanol Reforming: A Review

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Abstract—The development of alternative sources of energy is becoming important in this era of diminishing petroleum reserves and increased environmental awareness. Hydrogen production from biomass has attracted great interest because of the potential application in fuel cells and it is considered to be clean energy source. Biomass derived from forest or agricultural residues, energy crops or organic waste streams could partly replace fossil fuels as part of a biorefinery strategy. Such biomass has the potential to be processed for synthesis gas production in order to generate chemicals or fuel. Bio-oil via pyrolysis route can be produced from this bio-mass. Bio-oil produced via this route has number of functional groups like acids, ketones, aldehydes, alcohols etc. Model compounds have been widely used in order to simplify the process and gain further insights into bio-oil and the steam reforming of its water-soluble fraction. Butanol is considered to be one of the compound of bio-oil. Moreover, n-butanol can be produced by fermentation from sugar beet, sugar cane, corn, wheat and potentially lignocellulosic biomass. Using butanol as a source of producing hydrogen is a good possibility. Steam reforming is a promising way to utilize the butanol aqueous solution to produce hydrogen. In comparison with other substrates (e.g. ethanol and methanol), n-butanol exhibits a series of advantages, including higher hydrogen content than ethanol and methanol; lower vapor pressure and greater tolerance to water; and furthermore, n-butanol can be used directly in existing fuel distribution pipelines. Hydrogen can be produced from n-butanol via steam reforming, dry reforming, partial oxidation and oxidative steam reforming reactions.

Keywords— Steam Reforming, Oxidative steam Reforming, Dry Reforming, Hydrogen Production, Butanol.

I. INTRODUCTION

Petroleum and natural gas are expected to become scarce in the coming decades, in this context renewable energy sources has been gaining much importance to cope-up foreseeable scary future. Growing energy demands in a time of dwindling fossil fuel supplies has attracted much attention to hydrogen as an energy carrier. Moreover, use of fossil fuels entails a large CO₂ footprint; their combustion is causing serious environmental problems. Hence, the need for alternative energy sources is becoming urgent. Hydrogen, when produced from renewable substrates, has been identified as an ideal energy carrier to support sustainable energy development. Pure hydrogen can also be used in fuel cells for

the generation of electricity. Hydrogen has approximately three times more energy content than gasoline. Current trend is to produce hydrogen from biomass derived bio-oil. Bio-oil is a mixture of various hydrocarbons having functional groups like alcohol, aldehyde, ketone, etc. To understand behaviour of bio-oil to produce hydrogen, different model compounds have been investigated. Alcohols are one of the larger fraction of bio-oil. Number of researchers have published articles on the hydrogen production capacity of methanol, ethanol and iso-propanol. But there is limited literature available for hydrogen production from n-butanol. It has more hydrogen content than methanol (12.5 wt.%) and ethanol (13.04 wt.%). Hydrogen content in n-butanol is 13.51% by weight. So development of catalyst for selective production of hydrogen from n-butanol will be very interesting research area. Moreover, n-butanol can be produced from lingo-cellulosic biomass via fermentation route also, which can be proved pivotal for a sustainable development in future. n-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.

Competitive techniques for production of hydrogen from butanol are steam reforming, oxidative steam reforming and dry reforming. Above mentioned all processes has its own merits and demerits.

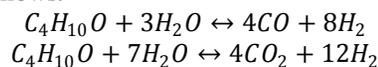
In this review, focus has been given on all reforming processes and operating parameters like temperature, catalyst and steam to carbon molar ratio, oxygen to carbon molar ratio. This study also explains opportunity and challenges in the field of butanol reforming.

II. REFORMING PROCESSES

1. Steam Reforming: The production of hydrogen containing gas from hydrocarbon feed stock with steam in the presence of a catalyst has been established since 1930s[1]. Steam reforming process is endothermic process and main drawback of steam

reforming the poisoning of the catalyst by decomposition of the hydrocarbons [1]. Earlier much of work in the area of hydrocarbon steam reforming was done by ICI (Imperial Chemical Industries Limited) in collaboration with IG Farben and Standard Oil. First reforming plant was commissioned in 1936, in which feedstock was hydrocarbons ranging from methane to butane[1].

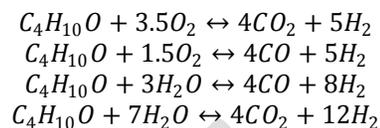
Alcohols is found to be one of the source for the production of hydrogen from catalytic steam reforming. Extensive studies has been carried out on steam reforming of methanol[2,3], ethanol[4,5] and propanol[6]. Several studies has been also conducted in the area of steam reforming of butanol[7-11], it provides advantage of higher hydrogen content but it also suffers from the drawback of poisoning due to coking[9]. Moreover due to endothermic nature of reaction, large amount of energy has to be supplied and it requires high operating temperature. Operating range for steam reforming of butanol is from 500 °C to 700 °C [7,9]. It is considered as complex reaction, where more than one reactions are taking place simultaneously. Main reactions for steam reforming are as follows.



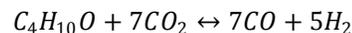
2. Oxidative Steam Reforming: Steam reforming process can extract hydrogen with higher selectivity, but the strong endothermicity is a main concern for the process. Partial oxidation for hydrogen production can be an exothermic process with an appropriate ratio of oxygen in the feed, but the by-products cannot be ignored, especially at a relatively low temperature, which results in a low hydrogen yield. Oxidative steam reforming, which consists of both steam reforming and partial oxidation, can balance the net heat need with a relatively high hydrogen yield by adjusting the ratio of oxygen in feed [12].

Extensive studies on oxidative steam reforming of methanol [13,14], ethanol [12, 15-19], propanol [20,21] has been carried out. Compared to these alcohols, butanol has more scope for the hydrogen production due to more number of hydrogen atoms in the structure. Various researcher also have carried experiments on oxidative steam reforming of butanol [11,22]. Experiments demonstrated that high hydrogen yield can be obtained using noble metal based catalyst at relatively lower temperatures (around 500 °C) compared to steam reforming. It was also found that presence of noble metal reduces coke formation to some extent but still not for longer time that can be implemented for industrial application. So

there is strong need for the development for the catalyst which can perform auto-thermal reforming at relatively low temperature and with prolonged activity. Main reactions for auto-thermal reforming is as follows.



3. Dry Reforming: Dry reforming is considered as reforming with carbon dioxide (CO₂). CO₂ is considered as a potential threat to environment. It is one of the greenhouse gases, which are responsible for global warming. By this dry reforming process, CO₂ can be sequestered in the form of relatively inert carbon nanofibres. So it may be considered as one of the green technology for the production of hydrogen. Various studies has been performed on dry reforming of ethanol [23-25] and methane [26,27]. But to greatest of knowledge, experimental studies on dry reforming of butanol has not been conducted. Thermodynamically dry reforming of butanol is feasible [28], but there will be requirement of the catalyst which will be stable and provide resistance to coking. Main reaction involved in dry reforming is as follows.



III. EFFECT OF OPERATING CONDITIONS

1. Effect of Temperature: Dhanalacet. al. [29], studied effect of temperature on steam reforming of iso-butanol in the temperatures range of 773–923 K. Process conditions were as follows. Iso-butanol = 0.052 mol/hr, H₂O = 0.9 mol/hr, and N₂ = 0.14 mol/hr, Catalyst: 30%Ni on γ-Al₂O₃, Steam to carbon molar ratio = 2.5, WHSV = 7.02 hr⁻¹. Obtained results are tabulated in Table 1.

Table 1. Effect of temperature on steam reforming reaction

Temp., K	H ₂ flow rate, mol/hr	CO flow rate, mol/hr	CH ₄ flow rate, mol/hr	CO ₂ flow rate, mol/hr
773	0.277	0.027	0.04	0.117
823	0.311	0.036	0.033	0.13
873	0.455	0.044	0.03	0.133
923	0.499	0.060	0.011	0.137

They have also observed that carbon conversion to gaseous products (CCGP) has been increased from 89% at 773 K to 100% at 923 K. They have also documented that equilibrium hydrogen yield was increased sharply with increasing temperature and

reached to a maximum then started declining slowly with further increase of temperatures. On the other hand, selectivity to CO was increased and selectivity to CH₄ was dropped with increasing temperature. These observations were justified by researchers as endothermic steam reforming reactions are favorable at elevated temperature; while exothermic water gas shift reaction are favored at lower temperature. At relatively lower temperature (below temperature of maximum of hydrogen yield) with high concentration of methane, contribution of endothermic steam reforming reactions on hydrogen yield were dominating over exothermic water gas shift reaction leading to growing trends of hydrogen yield with increasing temperature. However, at sufficiently high temperatures with very low concentration of methane, steam reforming of methane became unimportant and exothermic water gas shift reaction became sole contributing factor on hydrogen yield leading to slightly declining trends of hydrogen yield with increasing temperatures.

Roy et. al. [8], investigated effect of temperature on steam reforming reaction using 20% nickel on Al₂O₃ and CeO₂ supports. Temperature range was from 184 °C to 216 °C. For all experimental runs 5 wt% butanol was taken and pressure of 1034 kPa were maintained. For both the catalysts, it was observed that selectivity of H₂, CO₂ and CO were increased with increase in the temperature. %C in liquid effluent were decreased with increase in reactor temperature, which clearly indicates that carbon conversion to gaseous products were increased with increase in temperature. This behavior can be justified by the fact that at lower temperature exothermic water gas shift reaction are favored and at elevated temperature endothermic steam reforming reactions are favored. So as the temperature increases steam reforming reaction becomes more dominant over water gas shift reaction.

Harju et. al. [30], studied effect of temperature on steam reforming of n-butanol over Rhodium supported on ZrO₂ catalyst. Experiments were performed at 500 °C, 600 °C and 700 °C on 0.5% Rh (by weight) on ZrO₂. GHSV was maintained at 101,000 h⁻¹. The composition of reaction mixture was 3.1% butanol, 50% H₂O and 47% Ar. It was observed that conversion was increased with increase in temperature. Over the Rh/ZrO₂ catalyst at 700 °C and initially at 600 °C, the main products were hydrogen and carbon oxides. However, the yield of CO was higher than expected based on thermodynamic equilibrium and conversely the CO₂ and H₂ yields are lower than at the equilibrium. This indicates that CO₂ and H₂ are formed via relatively

slow consecutive reaction, converting CO. At 700 °C and also initially at 600 °C, the H₂ and CO₂ yields decrease, while CO yield increases. Above behavior was justified as conversion via homogeneous pyrolysis reactions in the gas phase increases. At higher temperatures, reduction in H₂ and CO₂ yields and increase in CO yield was observed due to decline in water gas shift reaction activity.

Naharet. al. [31], carried out thermodynamic analysis of steam reforming of n-butanol. Simulation studies were conducted for the temperature range (300 °C to 900 °C) at 1 bar pressure and water to butanol ratio 3. At lower temperatures the yield of hydrogen was low. Hydrogen yields of 2.152% and 19.53% with selectivities of 3.53% and 30.44% at 300 °C and 500 °C respectively, were observed. At low temperatures, as methane was the primary product, the selectivity for hydrogen was low. With increases in temperature, the selectivity for hydrogen and carbon monoxide increased. This behavior was defended by authors by tactful arguments. Increase in selectivity of H₂ and CO with increase in temperature is due to the fact that at elevated temperatures steam reforming of methane is becoming more dominant.

Wang et al. [28], carried out thermodynamic analysis of butanol dry reforming reaction. They have investigated effect of temperature on hydrogen, carbon monoxide and methane concentration. They have found that at a given carbon to butanol molar ratio, the concentration of H₂ increases sharply with the increase of temperature. It approaches to 83.12% when the temperature is 1500 K and CBR is 0. This can be explained by the fact that equilibrium constants of equation ($C_4H_{10}O + 7CO_2 \leftrightarrow 7CO + 5H_2$) increase with increasing temperature from 500 to 1500 K.

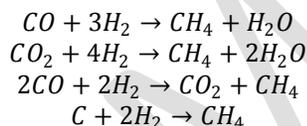
2. Effect of Steam to Carbon molar ratio: Hartley et al. [32], carried out thermodynamic analysis on hydrogen production via butanol oxidative reforming of butanol. They have encountered effect of steam to butanol ratio. With increase in steam to butanol ratio, hydrogen yield increases. This is probably due to addition of water shifting the equilibrium towards n-butanol in the reforming reaction, water gas shift reaction, and coke gasification. They have also demonstrated that steam to butanol ratio of 9–12 was suitable for the steam reforming of n-butanol.

Nahar et al. [31], carried out thermodynamic analysis of steam reforming of n-butanol. They have carried out simulation studies on effect of water/butanol feed ratio. By increasing the water/butanol feed ratio, the yield of hydrogen can be increased with a reduction

in the selectivity for carbon monoxide. This is due to increased activity of water gas shift reaction.

Dhanalaet. al. [29], conducted steam reforming experiments over 30% Ni on γ -Al₂O₃ at 923 K and 6.5 hr⁻¹ WHSV with varying steam to carbon molar ratio in the range of 1.5–3.2. The hydrogen yield was increased with increasing steam to carbon molar ratio for a fixed temperature. The selectivity to CO and CH₄ was however decreased with increasing steam to carbon molar ratio. The maximum of 90% hydrogen yield with less than 3% selectivity to CH₄ was observed experimentally at steam to carbon molar ratio of 3.2. With increase of steam to carbon molar ratio, steam reforming of isobutanol, steam reforming of methane, and water gas shift reaction were favored thereby increasing hydrogen yield and decreasing selectivity to CO and CH₄.

3. Effect of Pressure: Naharet. al. [31], carried out thermodynamic analysis of steam reforming of n-butanol. They have carried out simulation studies on effect of pressure. The effect of pressure on steam-reforming performance was examined at water to butanol molar feed ratio = 3 and at different temperatures from 300 to 800 °C. It was found that increases in pressure did not positively affect the yield and selectivity for hydrogen. Increase in pressure likely shifted the equilibrium towards the methanation reactions and hence a decrease in yield of hydrogen was observed. Methanation reactions are as follows.



Wang et al. [28], carried out thermodynamic analysis of butanol dry reforming reaction. They have investigated effect of pressure on hydrogen, carbon monoxide and methane concentration. The pressure from 1 to 100 atm has no effect on the conversion of C₄H₁₀O, which is already attained 100%. It is attributed to the high equilibrium constants. The increase of pressure decreases the H₂ and CO concentration, but increase CH₄ and H₂O concentration, because the increase of pressure probably shifts the equilibrium to CH₄ and H₂O which is attributed to methanation and carbon oxides reduction, respectively.

4. Effect of Oxygen to Carbon molar ratio: Dhanalaet. al. [29], studied effect of oxygen to carbon molar ratio (OCMR) on oxidative steam reforming of iso-butanol. Process conditions were as follows.

Iso-butanol = 0.052 mol/hr, H₂O = 0.9 mol/hr, and N₂ = 0.14 mol/hr, Catalyst: 20%Ni on γ -Al₂O₃, Steam to carbon molar ratio = 2.5, Temperature = 873 K, WHSV = 7.02, 7.6, 8.3 and 8.9 hr⁻¹ for oxygen to carbon molar ratio of 0, 0.8, 1.7, and 2.5 respectively. Obtained results are tabulated in Table 2.

Table 2. Effect of oxygen to carbon molar ratio on oxidative steam reforming of iso-butanol

OCMR	H ₂ flow rate, mol/hr	CO flow rate, mol/hr	CH ₄ flow rate, mol/hr	CO ₂ flow rate, mol/hr
0	0.406	0.052	0.025	0.107
0.8	0.363	0.043	0.005	0.137
1.7	0.318	0.040	0.003	0.147
2.5	0.183	0.023	0.001	0.179

The carbon conversion to gaseous products was increased from 89% to 98% with increasing OCMR from 0 to 2.5. The increase of carbon conversion to gaseous products was mainly due to enhanced oxidation of isobutanol or intermediate compounds with increasing OCMR. The hydrogen yield and selectivity to CO and CH₄ was however reduced and selectivity to CO₂ was increased continually with increasing OCMR. The hydrogen yield was reduced to just 30% from 73%, while selectivity to CH₄ was dropped to only 0.3% from 13.5% with increase of OCMR from 0 to 2.5. These results suggested that oxidation of hydrogen, CO, and CH₄ into H₂O and CO₂ was promoted with increasing levels of oxygen in the feed thereby decreasing hydrogen yield and selectivity to CO and CH₄.

Harju et. al. [30], studied effect of oxygen to carbon molar ratio on auto-thermal steam reforming of n-butanol over Rhodium supported on ZrO₂ catalyst. Experiments were performed at 500 °C on 0.5% Rh (by weight) on ZrO₂. GHSV was maintained at 101,000 h⁻¹. The composition of reaction mixture was 3.1% butanol, 50% H₂O and 47% Ar. They have observed that increasing oxygen to carbon molar ratio slows down the decline of conversion and the final conversion is also higher. This could be because of higher stability of catalyst due to reduction of coke deposition on catalyst surface. They have also compared experimental yield of hydrogen with equilibrium yield and concluded that thermodynamic equilibrium was not achieved, as otherwise the H₂ yield would have collapsed with increasing oxygen to carbon molar ratio. They have also showed that increasing the oxygen to carbon molar ratio increases the CO₂ yield, due to enhanced oxidation of CO.

Hartley et al. [32], carried out thermodynamic analysis on hydrogen production via oxidative reforming of butanol over Rh and Ni supported on alumina catalyst. They have investigated effect of oxygen to butanol ratio on oxidative steam reforming of butanol. Similar trend was observed. Hydrogen and CO yield was decreased and CO₂ yield increased with increase in oxygen to butanol ratio because of oxidation of hydrogen, CO, and CH₄ into H₂O and CO₂. They have also showed that with increase in oxygen to butanol ratio, reduces the coke deposition on catalyst surface due to combustion of carbon to carbon monoxide and carbon dioxide. Results are summarized in Table 3.

Table 3. Effect of oxygen to butanol molar ratio (OBR) on the degree of carbon formation

Catalyst	OBR	Carbon formation (mm/gm catalyst)
Rh/Al ₂ O ₃	2.5	2.9
Rh/Al ₂ O ₃	2.7	1.4
Rh/Al ₂ O ₃	3.0	0.8
Rh/Al ₂ O ₃	3.2	0.2
Ni/Al ₂ O ₃	2.5	5.7
Ni/Al ₂ O ₃	2.7	2.2
Ni/Al ₂ O ₃	3.0	1.0
Ni/Al ₂ O ₃	3.2	0.2

- Effect of Catalyst: Different type of catalyst affect conversion and selectivity of H₂ to varying extent. For selection of suitable catalyst for any reforming reaction, iterative procedure followed by characterization and activity test needs to be performed. Generally noble metal based catalyst is used for all kind of reforming reaction. Noble metals like Ni and Rh supported on Al₂O₃, ZrO₂, CeO₂, ZnO, TiO₂ are reported in literature for reforming reactions. Bimetallic catalyst like Co-Ru, Co-Rh, Co-Pd, Co-Ir supported on ZnO were also investigated, which demonstrated activity upto 100 hr in aqueous phase reforming reaction [9]. Selection of support, noble metal, method of preparation of catalyst, additives affects activity and stability of catalyst to greater extent. All catalyst suffers from drawback of deactivation by coke deposition at prolonged stage. In absence of noble metal catalyst loses its activity earlier comparatively due to poisoning [30].
- Effect of Carbon dioxide to Butanol molar ratio: Wang et al. [28], carried out thermodynamic analysis of butanol dry reforming reaction. They have investigated effect of carbon dioxide to butanol molar ratio (CBR) on hydrogen, carbon monoxide and methane concentration. The increase of CBR

first sharply decreases the H₂ concentration and then slightly decreases it at temperatures above 1000 K, but slightly decreases the H₂ concentration at temperatures below 1000 K. For example, the concentration of H₂ decreases from 80.58% to 30.41% with the increase of CBR from 0 to 5 at 1100 K, but it slightly decreases from 46.88% to 17.87% with the increase of CBR from 0 to 5 at 800 K.

IV. CONCLUSION

Production of hydrogen from renewable sources is sustainable option from economy and environmental point of view. Reforming reactions have great potential to extract hydrogen from butanol. For obtaining maximum yield of hydrogen at minimum expense of energy requires development of suitable catalyst and optimization of various parameters like temperature, pressure, oxygen to carbon molar ratio, steam to carbon molar ratio, carbon dioxide to butanol molar ratio.

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