



Process Development for Bio-butanol Steam Reforming for PEMFC Application

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Abstract

In current study, process has been developed for hydrogen production from bio-butanol via steam reforming (SR) for proton exchange membrane fuel cell (PEMFC) application. Heat integration with pinch analysis method was carried out to reduce overall heating and cooling utility requirement of energy intensive SR process. Despite of highly endothermic nature of bio-butanol SR, process found to be self-sustained in terms of requirement of heating utility. Heat integrated process for hydrogen production from bio-butanol SR was found to be green process, which can be explored for its hydrogen production capacity.

Keywords: Bio-butanol; Heat integration; Hydrogen production; PEMFC; Steam reforming.

1. Introduction

Proton exchange membrane fuel cells (PEMFCs) shows great potential for next generation energy source for automobiles due to relatively quick start-up, high power density, quick response to load variation, and low functioning temperatures [1]. Moreover, PEMFCs are also environmental benign compared to conventional internal combustion engines, as product from PEMFC is water vapor [2, 3]. PEMFC uses hydrogen and oxygen as fuels to generate electricity [4]. But Storage and transportation of hydrogen limits the use of hydrogen [5]. High purity hydrogen, less than 10 parts per million by volume (PPMV) carbon monoxide (CO), is desired for fuel cell application. Higher concentration of CO leads to deactivation of Pt electrode [6]. On-board production of high purity hydrogen, especially with low CO concentration, from green and renewable hydrocarbon source can be the answer to these problems [7]. On-board hydrogen production from hydrocarbon provides ease in transportation of hydrocarbon, which can be transported in existing fuel distribution pipelines. It also eliminates problems encountered in hydrogen storage. Hydrogen can be produced by various techniques like steam reforming (SR) [8], oxidative steam reforming (OSR) [3,7] and partial oxidation (POX) [9] of various hydrocarbons like methanol [3,8], ethanol [10,11], acetone [12,13], acetic acid [13,14], dimethyl ether [9,15], glycerol [16,17], butanol [18,19] etc. Conventional fuels like natural gas, gasoline and diesel are considered to be lucrative sources for on-board hydrogen production due to ease in transportation and available infrastructure [2]. But due to scarcity of these conventional fossil based sources and environmental related concerns, renewable and green sources like bio-ethanol [20], glycerol (when obtained as a byproduct in the production of biodiesel) [16,17], bio-oil [21,22], bio-diesel [23], bio-butanol [19,24] etc. have gain consideration among the researchers and scientists.

SR has advantage of having highest hydrogen yield compared to OSR and POX processes. But it suffers from drawback of highly endothermic heat of reaction [25]. In order to obtain high purity

hydrogen from SR process, additional units like CO₂ separator and water gas shift (WGS) converter are used conventionally in petroleum processing industries [26]. Few studies also demonstrated use of membrane water-gas shift reactor, which gives advantage of carrying WGS reaction and hydrogen separation in a single unit [27, 28]. With this type of membrane water-gas shift reactor high purity hydrogen can be achieved and thermodynamic equilibrium constraints can be shifted, which ultimately improves yield of hydrogen. Various studies have been conducted to develop process with the aim to produce high purity hydrogen from renewable sources like bio-oil [22], bio-ethanol [23, 29, 30], bio-diesel [23], glycerol [31] and key components of bio-oil [13, 32]. To the best of our knowledge, process development for bio-butanol SR has not been documented. Bio-butanol is obtained from fermentation of renewable biomass [33-35] and it is a mixture of butanol, acetone, ethanol and water [19]. Preliminary product obtained from fermentation of biomass is directly used for simulation purpose in current study. Main objective of this study is to develop a process for hydrogen production, which can be used for PEMFC application. Heat integration is also sought in order to make highly endothermic of steam reforming process self-sufficient in terms of heating requirements.

2. Methodology

Preliminary product obtained from fermentation of biomass was used as bio-butanol feed. Bio-butanol was explored for its hydrogen production capacity. Composition, as documented elsewhere [19] were considered for simulation purpose. Entire process was divided in two steps. In first step, flowsheet was developed using Aspen HYSYS V9 software. And secondly, heat integration of entire process plant was conducted from the stream details obtained from Aspen HYSYS.



2.1. Development of Process Flow Diagram (PFD)

PFD without heat integration is shown in Fig. 1. Bio-butanol was pumped by pump P-100 to heat exchanger E-1, where it was heated to desired temperature of reformer. Water depending upon desired steam to carbon molar ratio (SCMR) was pumped by pump P-101 to heat exchanger E-2. In E-2, water was heated to desired temperature of reformer. Then bio-butanol and water were introduced into reformer. Gibbs reactor was selected as a reformer, which calculates component flowrate at reformer outlet based on minimization of Gibbs free energy. Reformer was equilibrium based reactor and operated isothermally. For the purpose of this study, 650 °C reformer temperature, 1 atm reformer pressure and 4.5 SCMR were considered. Exit gas from reformer mainly contained gases H₂, CH₄, CO, CO₂ and water vapour. Higher CO concentration is detrimental for PEMFC electrode, so it is very much essential to reduce CO concentration below 10 PPMV. This can be achieved by employing water gas shift (WGS) reactor. But due to high concentration of CO₂ and H₂ in reformer exit stream, reverse water gas shift (rWGS) reaction becomes predominant over water gas shift reaction and reduces overall hydrogen yield. Therefore it is essential to remove CO₂ from the reformer gases prior to WGS reactor. For removal of CO₂, reformer exit gases were cooled down to 40 °C in heat exchanger E-3. Reduction in exit gas temperature was required in order to favor CO₂ absorption in subsequent step. Exit temperature from E-3 was fixed to 40 °C, in order to facilitate use of cooling water as cooling utility. Exit stream from E-3 was sent to gas-liquid separator Seperator-1, to separate water and other non-condensable gases. From the separator non-condensable gases, mainly CO, CO₂, CH₄, and H₂, and water vapor, were sent to absorber T-100 (absorber is part of sub flow sheet FLOW-1). In absorber, CO₂ was separated with the help of monoethanolamine (MEA, 29% by wt.) solution. From absorber CO₂ lean stream was sent to heat exchanger E-4, in order to achieve desired temperature (250 °C) for high temperature WGS reactor HTS. Water from Seperator-1 was also heated to desired temperature of HTS via heat exchanger E-5. HTS was operated adiabatically and due to exothermic nature of WGS reaction, temperature of exit stream increased. Resulting stream from HTS contained lower concentration of CO. But still this concentration was not tolerable in PEMFC. CO concentration was further reduced in low temperature WGS reactor LTS, by shifting equilibrium of WGS reaction in forward direction. Stream from HTS, at 491 °C, was sent to heat exchanger E-6, where it is reduced to 148 °C. Like HTS, LTS reactor is operated adiabatically and due to exothermic nature of reaction stream leaving LTS is having temperature of 362 °C. This final stream does not contain any measurable amount of CO by PPMV, which can be directly used in PEMFC after reducing its temperature to 40 °C in heat exchanger E-7.

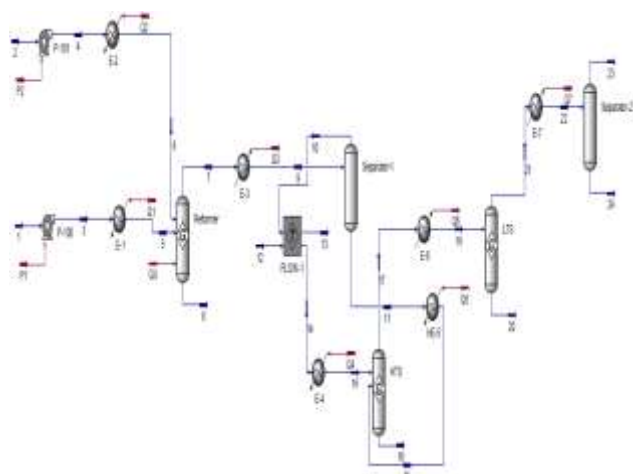


Fig. 1: PFD for PEMFC grade hydrogen production without heat integration.

In development of this PFD, two different fluid property packages were selected. In main flow sheet SRK-Twu, while in sub flow sheet (FLOW-1) Acid gas – chemical solvents package were selected. In process, pressure drop across all equipment was assumed to be zero. This assumption can be justified as this has negligible impact on objective of current study.

3. Heat Integration

SR is highly endothermic reaction, which makes this process very energy intensive. To improve overall economy of the process, pinch analysis and heat integration of entire process plant is required. It was found from steady state simulation that heating and cooling utility requirements, without heat integration, were 359.97 kW and 314.56 kW respectively. In order to maintain reformer temperature to 650 °C, 66.84 kW of heating utility was required (shown as energy stream QU in Fig. 1). This stream was not considered in heat integration, after heat integration this stream was added in minimum heating utility requirement. For heat integration, minimum temperature approach (ΔT_{\min}) of 10 °C was considered. Due to very large change in temperature and phase change in many of the heat exchangers, heat capacity was not remained constant with temperature. In order to account for this change in heat capacity, enthalpy-temperature diagram was divided in linear segments. For single segment, heat capacity can be approximated as constant. Fig. 2 shows hot composite curve (HCC) and cold composite curve (CCC) for said process and pinch was situated between 90 °C and 80 °C.

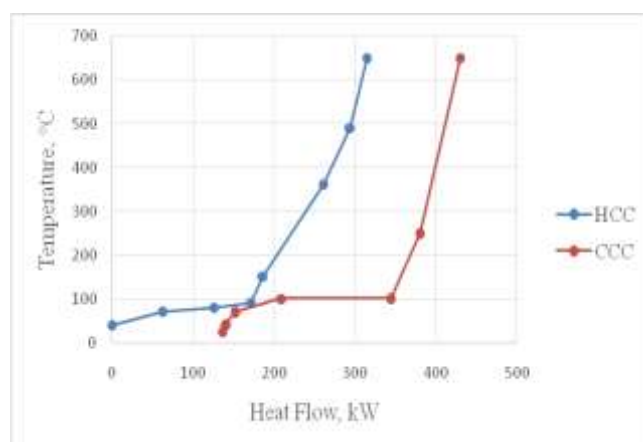


Fig. 2: Hot and cold composite curves for $\Delta T_{\min} = 10$ °C. These composite curves do not include energy stream QU

After heat integration, heating and cooling utility requirements were found to be 114.82 kW and 136.44 kW respectively. After adding 66.84 kW of energy as heating requirement, total minimum heating utility requirement became 181.66 kW. Heat integration reduced overall heating and cooling requirements by 49.5% and 56.6% respectively. Fig. 3 indicates PFD with heat integration. Membrane separator, employed after Seperator-2, can give high purity hydrogen. Methane from membrane reactor was then sent to combustion reactor, where it was used as a fuel. Air was supplied to combustion reactor and heat generated due to exothermic nature of combustion reactor was used as heating utility in plant. Combustion of only methane can't suffice overall heating requirement. Therefore, 0.4505 kmol/hr of hydrogen was diverted to combustion reactor to meet overall heating requirement of the process. Remaining high purity hydrogen was sent to PEMFC for generation of electricity. Energy generated from combustion reactor can be used as heating utility, wherever it is required in plant. Temperature of stream 28 was adjusted to 670 °C based on highest temperature requirement of reformer, i.e. 650 °C.

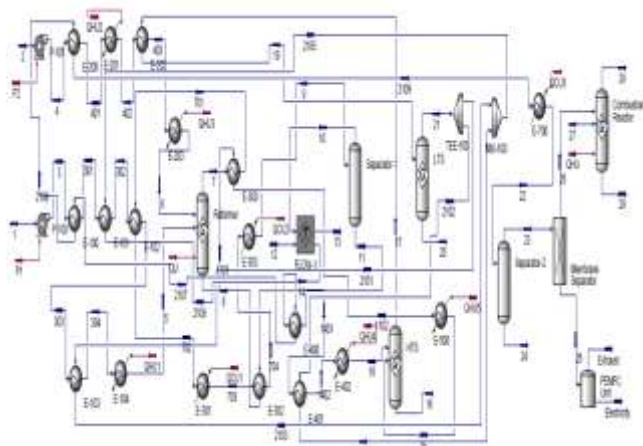


Fig. 3: PFD for PEMFC grade hydrogen production with heat integration.

4. Conclusion

For PEMFC application, on-board production of hydrogen from SR of bio-butanol is a new sustainable option. Heat integration of plant showed great energy saving opportunities. Heating and cooling requirements reduced by 49.5% and 56.6% respectively. Use of product stream as a heating utility makes entire process self-sustaining, which eliminates use of additional heating utility.

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