

## Environment and Economic Assessment of Hydrogen Production from Methane and Ethanol

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### Abstract

Hydrogen is an interesting energy source alternative to fossil fuel which commonly produced from a non-renewable resource such as methane. Alternatively, ethanol is an attractive resource option for producing hydrogen because of its renewability. Assessing both alternatives is important for selection of better and sustainable option. In this work, we perform an environmental and economic assessment of both hydrogen production pathways and compare its performance. In doing that, both processes were modelled and simulated in Aspen Plus V8.6. Sensitivity analysis were performed as well. Life cycle assessment (LCA) ReciPe method was performed to evaluate the environmental performance using GaBi software. Overall, 16 categories impact assessment were evaluated. Economic assessment was based on capital expenditure (CAPEX) of all main equipment and operating expenditure (OPEX) of utilities. From LCA results, three categories were identified as highly significant namely climate change, fossil depletion and water depletion. Methane shows a higher impact on climate change. In contrary, ethanol shows a higher impact on fossil fuel resource depletion and water resources. Economic assessment shows that in term of capital expenditure (CAPEX) methane is 5.2% less compared to ethanol. Whereas, for operating expenditure (OPEX) methane is 12.8% less compared to ethanol. Overall, our findings show that methane outwit ethanol despite the latter uses a renewable source for hydrogen production.

Keywords: Hydrogen production; life cycle analysis (LCA); economic assessment; Aspen Plus

### 1.0 INTRODUCTION

The world energy demand currently depends on fossil fuel as a source. While the population of human increase more than 2% thus increasing energy demand, fossil fuel sources depleted yearly. It is estimated that 25% of the world population consumes 75% of the world energy supply [1]. Today, global demand towards energy consumes more than 85 million barrels of oil and 104 trillion cubic feet of natural gas per day and this consequently release a lot of greenhouse gas to the atmosphere [2]. In the light of this, a new source of energy is needed as an alternative to fossil fuel. The new energy resource however need to be sustainable with minimal impact to the environment. It is found that one of the promising new source of energy is hydrogen. Hydrogen energy is one of the most sustainable energy carrier to reduce the dependence on fossil fuels. Hydrogen is abundant with high reactivity chemically and can be found in water, fossil fuels and other living thing such as animals and plants. In addition, the energy content for hydrogen; 120 MJ/kg, is three times higher compared to gasoline with 44 MJ/kg which shows hydrogen is highly efficient in solving energy crisis [3]. Apart from that, burning hydrogen does not produce carbon emission thus could significantly reduce carbon monoxide and other greenhouse gases.

Currently, hydrogen is mainly produced from methane. In the United States, hydrogen is produced at more than 8 million tons and mostly from fossil fuel such as methane [4]. Furthermore, 97% of hydrogen production was synthesized from methane steam reforming (MSR) of natural gas. However, methane feedstock availability is reduced year by year. Alternatively, renewable

resources can replace methane which could considerably reduce dependency on fossil fuels as fuel sources. One such option is ethanol. Ethanol is a good alternative since the feedstock for producing ethanol is abundant and renewable. Moreover, ethanol has a high hydrogen content, non-toxicity, storage and handling safe and can be produced from renewable sources such as biomass sources, agro plantation waste and municipal solid waste [5].

There are numerous methods to conducted environmental assessment of chemical processes. One of the most widely used is life cycle assessment (LCA). Life cycle assessment (LCA) is a method for assessing various environmental aspects associated with the development of a product and its potential impact throughout a products life from raw material, processing, manufacturing, use and disposal or end of life. LCA allows for characterization of the consequences of possible public policy options or scientific alterations and development of novel sustainable energy resources and technologies [6]. Apart from that, LCA can be used to evaluate the process and product impacts towards the environment as well as helping manufactures and customer to select an environmentally friendlier option. There are several studies conducted on the environmental impact of hydrogen production using life cycle assessment (LCA). Giraldi et al. [7] for example used LCA to analyse the environment burden of hydrogen production focuses on emissions of greenhouse gases. In another work, Verma et al. [8] conducted LCA for hydrogen production from underground coal gasification with and without carbon capture. Their study focused on the global warming impact and greenhouse gas emission. Authayanun et al. [9] conducted LCA for bio-ethanol reforming and proton exchange membrane fuel cell (PEMFC) integrated process fuelled by cassava based bio-ethanol and methane as co-reactant. Their LCA analysis shows that overall mixed bio-ethanol and methane reforming integrated with PEMFC system (BM-PEMFC) has more environmental impact than dehydrated bio-ethanol reforming with PEMFC system (DE-PEMFC). However, the global warming potential (GWP) and photochemical oxidant formation (POFP) impacts of the BM-PEMFC system remain high. In another study, Galera et al. [10] used LCA to assess the environmental impact of supercritical water reforming of glycerol for hydrogen production. Aspen Plus was used as simulator to solve the mass and energy balance. Their finding shows that the process gives a low carbon emission in the greenhouse gas inventory. Christoforou & Fokaides [11] investigate the environmental impact of torrefaction process using LCA. Their results conclude the important of the drying phase of the whole torrefaction system and the potential improvement of olive husk process in terms of energy consumption.

Apart from environment assessment, there are also studies on economic feasibility of hydrogen production. Muellerlanger et al. [12] conducted an economical evaluation on selected hydrogen production processes based on natural gas steam reforming, coal, biomass gasification and water electrolysis. They found out that from an economic viewpoint steam reforming of natural gas is currently the most favourable hydrogen production method compared with other methods. Gasification of coal could be competitive even at present condition but is only sensible if coupled with carbon capture. Hydrogen production from electrolysis is unlikely to be an economically competitive option mainly due to high electricity. Braga et al. [13] performed a technical, economic and ecological analysis of hydrogen production from biogas steam reforming. In their work, they used biogas in MSR as alternative for hydrogen production and claimed that it able to decreased the negative environmental impact compare to natural gas. In another work, Roldan [14] investigated the technical and economic feasibility of adapting an industrial steam reforming unit for production of hydrogen from ethanol. The economic analysis performed indicates that the high market price of pure ethanol makes the process far from viable.

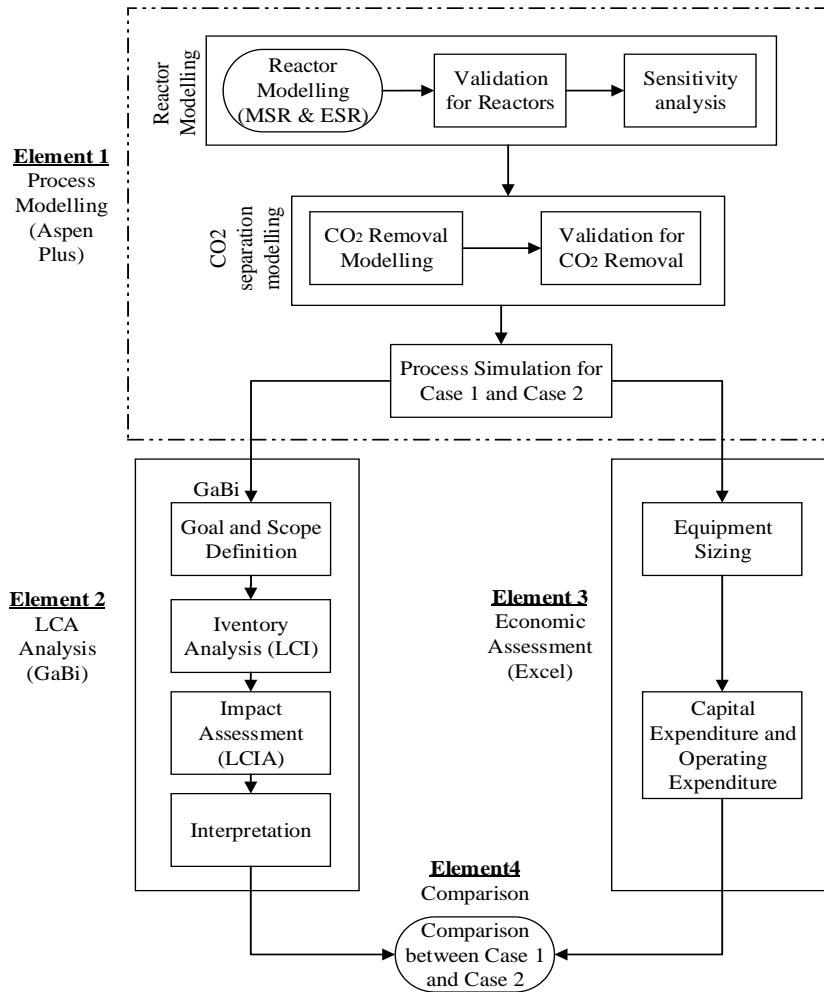
Most of the literature conducted a standalone environmental and economic assessment of different pathways of hydrogen production. While most such assessment focuses on methane, ethanol based hydrogen production receive less attention. Therefore, in this work our main objective is to assess and compare the environmental and economic performance of both processes. The environment assessment was performed using LCA which give details insight the impact to the environment. The economic analysis involves capital cost calculation of each unit operations whereas operating cost calculation involve utilities particularly steam and water consumption. Such work contributes to the depth analysis and insights of both environment and economic assessment and comparison. Overall, this study will help decision makers or stake holders to understand the environmental and economic impacts of hydrogen production which could mitigate undesired impacts and ensure the sustainability to attract community, government and investor interest and support.

To perform the analysis, both case studies are model in Aspen Plus. From our literature review, there are few works on modelling and simulation of hydrogen production from methane and ethanol. Boyano et al. [15] for example, model a hydrogen production process by adding a combustion chamber (COMBRET) before the MSR reactor to provide heat required by the MSR reaction. The reactions were simulated using a non-kinetic based approach. In another work by Antzara et al. [16], hydrogen production process was modelled to analyse the thermodynamic effect of hydrogen production in situ with carbon dioxide capture. In this work, the MSR and WGS reactions were modelled using non-kinetic model namely RGibbs and RStoic block model. Sensitivity analysis were also performed for several parameters such as temperature, pressure, feed ratio, carbon capture efficiency and NiO/CaO ratio. In another work, Gutiérrez-Guerra et al. [17] simulated a catalytic ethanol steam reforming in Aspen HYSYS using Peng-Robinson thermodynamic method. The ESR reactor were model as fractional conversion reactor while WGS and COMPROX reactors were simulated as equilibrium reactors. To obtain the desired hydrogen purity, a membrane unit is used. In another work, Rossetti et al. [18] simulated an ethanol based hydrogen production process for modified combined heat and power (CHP) generation unit. In this work, Peng-Robinson thermodynamic method was used particularly suited to describe light gas mixture in wide temperature and pressure range. Methanation reaction in the reactor (COMET) is considered when methane is present in the process due to the side reactions in the ESR reactor. Both WGS and methanation used Gibbs reactor model. Most of the simulation work on hydrogen production were mainly based on non-kinetic model. For comparable effort, there is a need to simulate this process based on more rigorous kinetic model. Although simplified models were easier to converge, a kinetic based model approach is needed to provide more insights and accurate behaviour of the process. Such rigorous modelling

approach are more accurate and precise. Therefore, in this work both hydrogen production route; methane (Case 1) and ethanol (Case 2), will be simulated using rigorous model in Aspen Plus. The simulation results will then be used for environmental and economic analysis using GaBi Software and Excel spreadsheet respectively.

**2.0 METHODOLOGY**

Figure 1 shows the overall research methodology framework. The framework is divided into four main elements namely (1) Process Modelling (2) LCA Analysis (3) Economic Assessment and (4) Comparison. To aid each element particularly element 1, 2 and 3 computer aided tools were utilized. In element 1 Aspen Plus was used to model and simulate Case 1 and Case 2. GaBi software was used to perform LCA analysis in element 2 whereas in element 3 Excel spreadsheet was utilized to perform economic assessment. Details of each element is discussed next.



**Figure 1.** Research methodology framework

**2.1 Process Modelling**

In the process modelling element, Aspen Plus were used for modelling the main unit operations of the hydrogen production process including reactors, separation columns as well as overall flowsheet of Case 1 and Case 2. In addition, reactor and separation models were validated with experimental data and flowsheet sensitivity analysis were performed to determine the best operating condition. The simulations results which contained information such as stream mass and energy properties, equipment size and utility consumption were then used for environmental and economic assessment.

### 2.1.1 Reactor Modelling

The rate expression used for MSR, ESR and WGS reactions were based on LHHW reaction mechanism. MSR involves reaction between methane and steam to produce hydrogen and carbon monoxide as in equation 1 in a catalytic fixed-bed reactor. The rate expression, R for MSR is describe in equation 2.



$$R_{MSR} = \frac{k_1 \left( \frac{P_{CH_4} P_{H_2O}}{P_{H_2}^{2.5}} - \frac{P_{CO} P_{H_2}^{0.5}}{K_e} \right)}{DEN^2} \tag{2}$$

The term *DEN* is given by,

$$DEN = 1 + K_{CO} P_{CO} + K_{H_2} P_{H_2} + K_{CH_4} P_{CH_4} + \frac{K_{H_2O} P_{H_2O}}{P_{H_2}} \tag{3}$$

Where *P* is partial pressure, *k<sub>1</sub>* is rate constant and *K<sub>e</sub>* is adsorption equilibrium constant. The MSR kinetic parameters is shown in Table 1.

**Table 1** Kinetic parameter for MSR [20]

Parameter	Pre-Exponential factor	Value
<i>k<sub>1</sub></i>	4.2248 × 10 <sup>15</sup> (mol atm <sup>0.5</sup> /g h)	240.1
<i>K<sub>CH4</sub></i>	6.65 × 10 <sup>-4</sup> (atm <sup>-1</sup> )	-38280
<i>K<sub>H2O</sub></i>	1.77 × 10 <sup>5</sup> (atm <sup>-1</sup> )	88680
<i>K<sub>H2</sub></i>	6.12 × 10 <sup>-9</sup> (atm <sup>-1</sup> )	-82900
<i>K<sub>CO</sub></i>	8.23 × 10 <sup>-5</sup> (atm <sup>-1</sup> )	-70650
<i>K<sub>e</sub></i>	7.846 × 10 <sup>12</sup> (atm <sup>2</sup> )	220200

The reaction for ethanol steam reforming (ESR) on the other hand involve ethanol and steam to produce hydrogen and carbon monoxide as shown in equation 4. ESR reaction can also undergo several other reactions such as dehydrogenation, dehydration and cracking to produce side products such as carbon dioxide, methane, carbon monoxide and coke [11]. There are several researches that modelled a simplified ESR reaction [19,20,21]. Han et al. [21] for example developed a simplified power law kinetic model based on their investigation of Ni/Al<sub>2</sub>O<sub>3</sub> catalyst for hydrogen production from ethanol. The proposed model and its kinetic parameters is shown in equation 5 and adopted in this work.



$$R_{ESR} = k_2 \exp\left(-\frac{E}{RT}\right) (P_{EtOH})^a (P_{H_2O})^b \tag{5}$$

Where *R* is universal gas constants and *T* is temperature. The activation energy for this rate expression is 23 kJ/mol, the reaction order; *a* and *b*, for the partial pressure, *P* of ethanol and water are 0.711 and 2.71 respectively. *k<sub>2</sub>* is 4.39 × 10<sup>2</sup> mol (min g-cat)(atm) [20]. To reduce undesired CO and increase H<sub>2</sub> yield in both MSR and ESR reactions, these reactions products undergo a two stage water gas shift (WGS) reactor operating at temperature between 200-400 °C and 127-177 °C usually in presence of copper/zinc oxide/alumina catalyst [15,22,23].

The reaction for WGS is shown in the equation 6 in which CO react with excess steam to produce CO<sub>2</sub> and H<sub>2</sub>. The WGS rate of reaction expression was proposed by Amadeo and Laborde [24] and Mendes et al. [25] by using LHHW kinetic expression as shown in equation 7. The constant parameter in the rate equations 7 were based on Mendes et al. [25] as shown in Table 2.



$$R_{WGS} = \frac{k_3 P_{CO} P_{H_2O} \left( 1 - \frac{P_{CO} P_{H_2}}{P_{CO} P_{H_2O} K_e} \right)}{\left( 1 + K_{CO} P_{CO} + K_{H_2O} P_{H_2O} + K_{CO_2} P_{CO_2} + K_{H_2} P_{H_2} \right)^2} \tag{7}$$

**Table 2** The kinetic parameter for WGS

Parameter	Pre-Exponential factor	Value
$K_3$	0.92 (mmol g <sup>-1</sup> s <sup>-1</sup> atm <sup>-2</sup> )	4080
$K_{CO}$	2.21	-910
$K_{H_2O}$	0.4	-1420
$K_{CO_2}$	0.0047	-24720
$K_{H_2}$	0.052	-14400

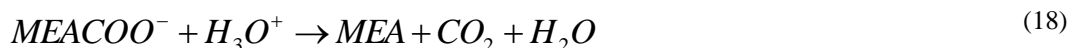
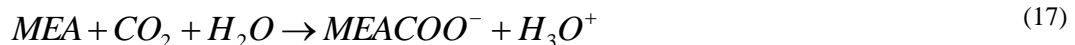
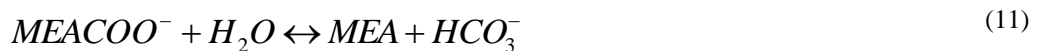
The MSR, ESR and WGS were modelled using RCSTR model block. Separate reaction ID were defined for each reaction. Reaction class of LHHW were selected for each reaction. However, the rate expressions describe previously for MSR and WGS cannot be used directly in Aspen Plus. Therefore these equations were rearranged using natural logarithm (Ln) [26]. For MSR the newly rearranged equation is shown in equation 8. The term DEN is given by equation 2 whereas equation 9 is the rearranged rate expression for WGS reaction. All models for MSR, ESR as well as WGS were validated with experimental data from Singh et al. [27], Mathure et al. [20] and Amadeo & Laborde [24] respectively using the same reactor operating and design conditions.

$$R_{MSR} = \frac{k_1 K_1 \left( K_1 \frac{P_{CH_4} P_{CO}}{P_{H_2}^{2.5}} - P_{H_2}^{0.5} P_{CO} \right)}{DEN^2} \quad (8)$$

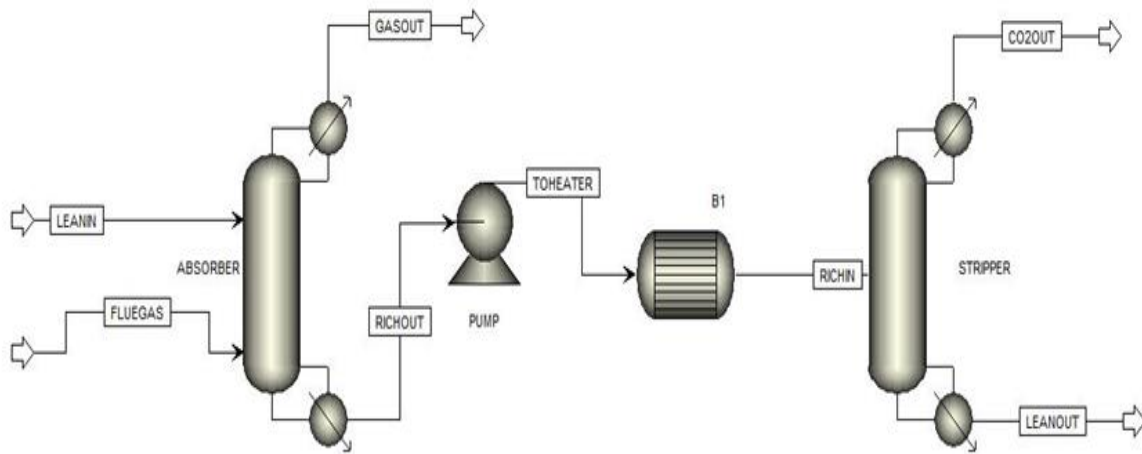
$$R_{WGS} = \frac{k_2 \left( P_{CO} P_{H_2O} - \frac{P_{CO_2} P_{H_2}}{K_e} \right)}{\left( 1 + K_{CO} P_{CO} + K_{H_2O} P_{H_2O} + K_{CO_2} P_{CO_2} + K_{H_2} P_{H_2} \right)^2} \quad (9)$$

### 2.1.2 Separation Modelling

The purpose of separation process in hydrogen production is to increase the purity of hydrogen. In this work, absorption tower and stripper were used to separate carbon dioxide from the reactors to obtain high purity of hydrogen of more than 90 mol%. Aqueous monoethanolamine (MEA) were used as the solvent. Rigorous distillation model, RADFRAC, were used to model the absorption and stripping column. The rigorous model to the liquid and vapour flow in the absorption column were based on the calculation of heat transfer, mass transfer between the phases and chemical kinetics. In total there are 9 chemistry models considered in this work as shown in equation 10 - 18 [28].



In this model, it is assumed NOx and SOx are neglected in the gas stream. In the separation model, the apparent (base) approach component was selected for electrolyte system. The electrolytes system has impacts on physical property calculations and phase equilibrium calculations. The electrolytes system is defined as one in which some of the molecular species dissociate partially or completely into ions in a liquid solvent and some of the molecular species precipitate as salts. These dissociation and precipitation occurs fast enough that the reactions can be assume to be at chemical equilibrium. Reaction 10 – 15 was calculated from the standard Gibbs free energy change whereas reaction 15 – 18 used the general power law expression for the rate-controlled reaction. The kinetic parameters for the reactions were obtained from Li et al. [28]. The flowsheet for CO<sub>2</sub> capture by MEA were developed in Aspen Plus which include absorption column, stripping column and a heat exchanger between the two columns as shown in Figure 2. With regards to the convergence issue, it is assumed that the model has no recycle stream, no mark-up stream for amine and water washing section present in the systems. The model was validated with the work by Li et al. [28] using the same design and operating parameters.



**Figure 2.** The simulation flowsheet for CO<sub>2</sub> removal

### 2.1.3 Overall Flowsheet

The design capacity of the hydrogen production process is 627 kmol/hr with hydrogen purity of 93 mol%. Figure 3 shows the overall flowsheet diagram of the hydrogen production process. Both Case 1 and Case 2 have the same configuration. The only difference is the feed and steam reforming reaction. Ethanol is used instead of methane whereas the reactor involves ESR reaction instead of MSR reaction. This process starts with the feedstock in which methane or ethanol is mixed with superheated steam before entering heat exchanger (E-101) and heated using hot flue gas. The mixed gas then enters the reformer reactor (R-101) reactor. In the reactor, methane/ethanol reacts with steam to produce hydrogen and carbon monoxide using Ni-based catalyst. The reaction products namely hydrogen, carbon monoxide and excess steam are then cooled in heat exchanger (E-102) using cooling water. It is then mixed with steam before going through two WGS reactor; high temperature HWGS (R-102) and low temperature LWGS (R-103), to increase hydrogen yield and reduce carbon monoxide in the stream. After the LWGS reactor, the stream is cooled down in heat exchanger (E-104) using cooling water. After that, the stream is fed into a packed bed absorption tower (T-101) to remove carbon dioxide using MEA solution. The carbon dioxide absorbed by MEA flows at the bottom stream of the absorber which then heated by heat exchanger (E-105) using high pressure steam before entering the stripping column. The heat provided by the stripper reboiler loosen the MEA-carbon dioxide interaction and thus breaks the bonds and therefore releasing the carbon dioxide via top of the stripping tower whereas the MEA solution flows out at the bottom stream. On the other hand, the top product stream of the absorption tower is cooled down in heat exchanger (E-106) before entering a flash column (V-101). In the flash column, hydrogen and water are separated in which 93 mol% hydrogen is obtained at the top of the column. Table 3 summarize the main unit operation design parameters for both cases.



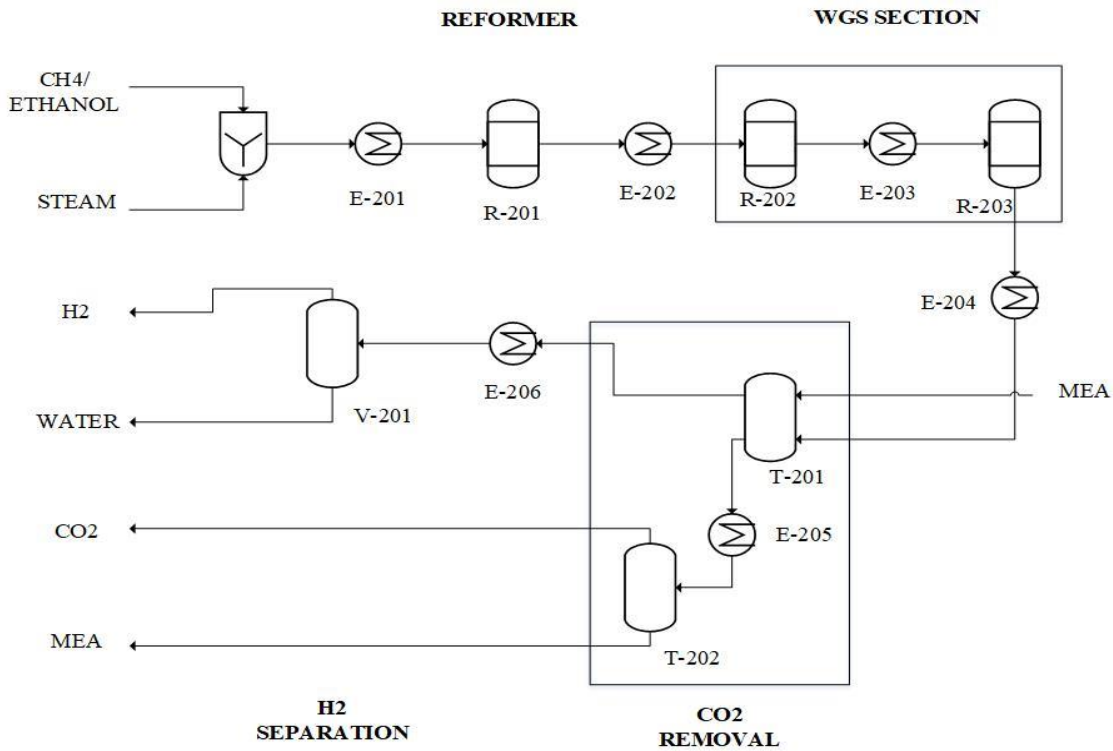


Figure 3. Simplified process flow of hydrogen production (a) Case 1 (b) Case 2

Table 3 Main unit operation design parameters.

Main unit operation	Case 1	Case 2
Reformer reactor (R-101)		
Reaction type	MSR	ESR
Temperature/Pressure	700 C / 1 bar	800 C / 1 bar
Catalyst	Ni	Ni
HWGS reactor (R-102)		
Temperature	400 C/1 bar	400 C/1 bar
Catalyst	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>
LWGS reactor (R-103)		
Temperature	210 C/1 bar	210 C/1 bar
Catalyst	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>	CuO/ZnO/Al <sub>2</sub> O <sub>3</sub>
Absorption column (T-101)		
Temperature/Pressure	40 C / 1 bar	40 C / 1 bar
No. of stages	20	20
Packing type	Flexipac	Flexipac
HETP	0.5 m	0.5 m
Stripper (T-102)		
Temperature/Pressure	100 C / 1 bar	112 C / 1 bar
No. of stages	20	20
Packing type	Flexipac	Flexipac
HETP	0.5 m	0.5 m
Flash column (V-101)		
Temperature/Pressure	25 C / 1 bar	25 C / 1 bar

## 2.2 Environmental Assessment

LCA assessment consists of four phases. Primary phase in LCA is to clarify the goal and scope definition. Defining the goal required to clearly report the reason and intention for carrying out the study while for scope definition it is required to clearly detail the product system to be studied, functional unit, system boundary, assumption, limitation and impact categories. In this work, the LCA objective is to evaluate the environmental impact of hydrogen production for Case 1 and Case 2. The functional unit (FU) which provide a basis for calculating the inputs and outputs were based on 1 kg of hydrogen production. The system boundaries were based on the cradle to grave approach which starts from methane/ethanol feedstock to hydrogen storage. Figure 4 shows the system boundaries which consist of five subsystems namely feedstock (SB1), hydrogen production (SB2), process steam (SB3), solvent absorption (SB4) and process water plant (SB5). Note that, the construction and commissioning phases as well as energy consumptions were excluded from the analysis.

SB1 is the feedstock source. For methane it is obtained from natural gas processing plant and assumed transported using pipelines. Ethanol feedstock on the other hand, was assumed obtained from an ethanol processing plant. SB2 consist of reactions and purification section. The reaction section includes MSR/ESR and WGS reactors. The separation section consists of carbon dioxide removal and a separator which aims to purify the hydrogen especially from CO<sub>2</sub>. The system boundary also considers process steam generation section (SB3). This section considers the combustion of hydrocarbon fuel in the boiler to generate steam which is used in the process and also for heating utilities. SB4 is the MEA supply subsystem which supply absorbents for CO<sub>2</sub> removal in the separation process. Finally, the water supply for the reforming process and cooling water were included in SB5. LCI involves the collection and compilation of the simulated data results from Aspen Plus.

The second phase for LCA study is life cycle inventory analysis (LCI) which involve clarification on data sources and principles to use for quantitative computation. The purpose of developing the LCI is to calculate the quantities of input and outputs involved in delivering a specific functional unit of the product system under study [29]. The sources of primary data for the inputs are energy, raw material, ancillary materials and other physical inputs. Meanwhile, the sources of data for output mostly come from product, co-product, emission, waste and other environmental aspects. The input like water, emissions CO<sub>2</sub>, preparation of chemical and electricity used in the different production stage are included in analysis. The upstream impacts of inputs production were based on database from GaBi while the inputs and outputs were obtained from Aspen Plus.

The third phase of the LCA study is life cycle impact assessment (LCIA). This phase provides indicators and basis for analysing the potential contribution of the resource extractions and waste/emission in an inventory to a number of potential impacts. A commercial LCA software, Gabi is used as currently practised by many LCA researchers. The life cycle interpretation occurs at every stage in the LCA study. When the results from LCI and LCIA are interpreted, significant issues shall be identified, uncertainties inherited in the study shall be addressed via uncertainty analysis and sensitivity analysis. The purpose for interpretation step is to reach conclusions and recommendations for the report of the LCA study or LCI study. This stage is important to improve the reporting and transparency of the study. This is important for the LCA final report.

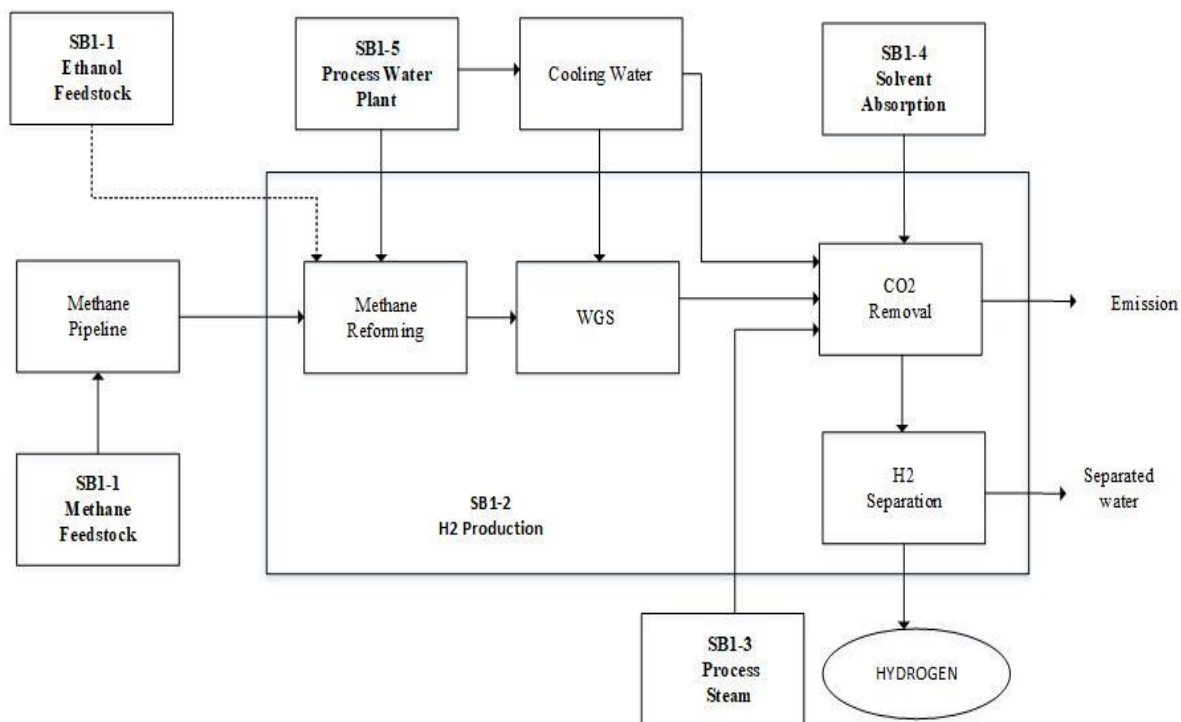


Figure 4. System boundaries for LCA

### 2.3 Economic Assessment

The economic assessment considers capital expenditure (CAPEX) of all main equipments as well as operating expenditure (OPEX) of the process. For CAPEX, bare module cost ( $C_{BM}$ ) which based on the equipment size, operating condition and material of construction (MOC) was considered. Equipment sizing was performed in Aspen Plus. The MOC of equipment was assumed stainless steel. Normally, purchased cost varies yearly due to inflation indicated by the chemical engineering plant cost index (CEPCI). In this work the CEPCI used was 558.3 for June 2017. The OPEX value on the other hand, considers the utilities consumed namely steam and cooling water. Cost for steam and cooling water was considered as \$17.7/GJ and \$0.354/GJ

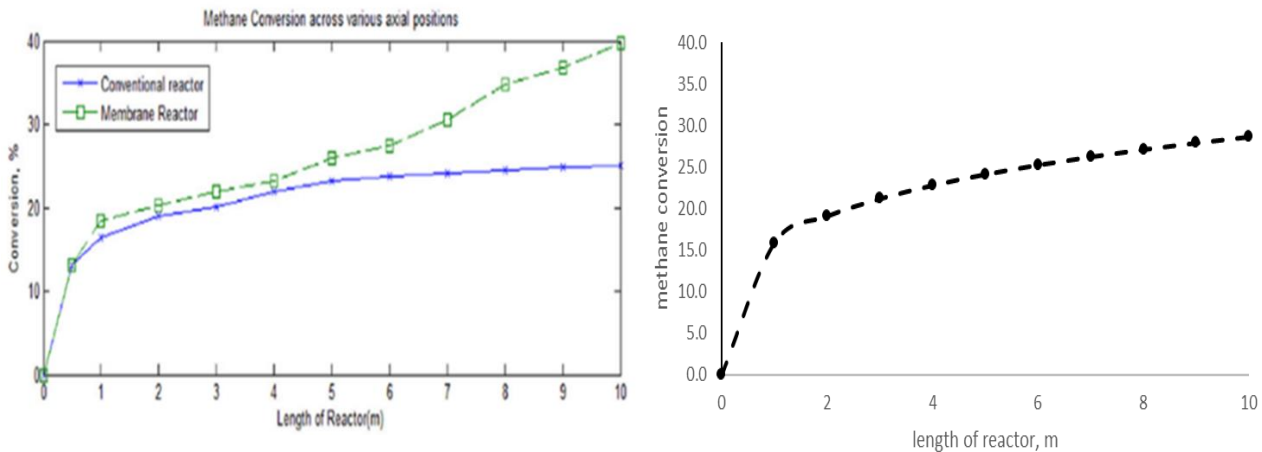


respectively [29]. The utilities consumption data was obtained from the simulated model in Aspen Plus. CAPCOST, an Excel based tools, were used to calculate the CAPEX and OPEX of both cases. Then, in the fourth element comparison were performed on both cases and the results is analysed and discussed.

### 3.0 RESULTS AND DISCUSSION

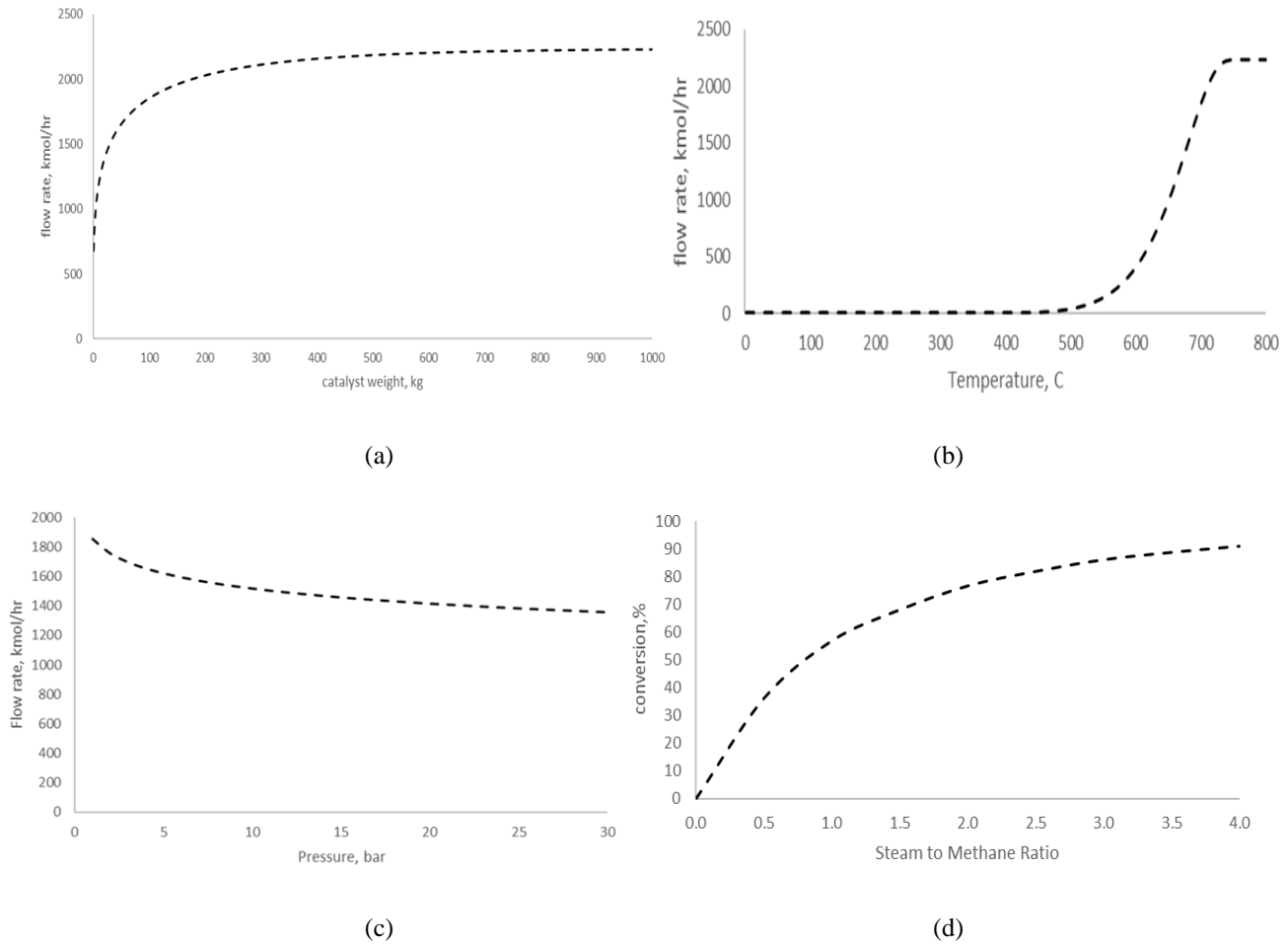
#### 3.1 Model Validation And Sensitivity Analysis

Figure 5 (left) shows the experimental result by Singh et al. [27] which shows that methane conversion increase rapidly at the first meter of the reactor length. After that, the conversion started to resolve. The same trend is also found in the simulated MSR reactor in Aspen Plus as shown in Figure 6 (right). The highest error was at 1 meter with 11.71 % while the smallest error is at 2 m with 0.53 %. Overall the mean error was 3.27 %.



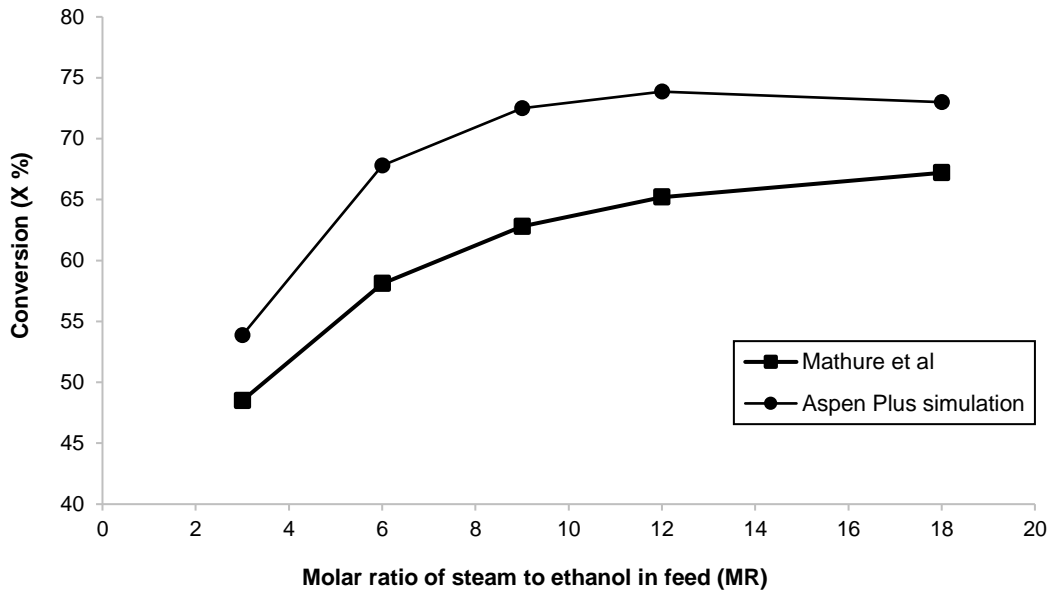
**Figure 5.** The methane conversion effect on length of the reactor (left) Singh et al [29] (right) simulation using Aspen Plus

Sensitivity analysis of the reactor performance was done by changing several operation variables namely catalyst weight, reactor temperature, pressure and steam to methane feed ratio into the reactor to observe and determine the suitable operating condition for MSR. For the sensitivity analysis, the manipulated variables were independently varied while the other design parameters remain unchanged. Figure 6a shows the sensitivity analysis results for variation in the catalyst weight to hydrogen production molar flowrate. It shows that increasing the amount of catalyst in the reformer, increases the hydrogen production especially at the first 100 kg. After about 300 kg, the hydrogen production starts to become constant. Figure 6b shows the response of the hydrogen molar flowrate to MSR reactor temperature. Hydrogen started to produce at temperature of 500 °C and increased drastically until the temperature of 700 °C. After that, hydrogen flow rate started to become constant. Increasing the reactor temperature to 700 °C leads to high reforming reaction rate and thus improved methane conversion and increased the hydrogen yield. Figure 6c shows the changing of reactor pressure in the reformer to hydrogen molar flowrate. It is found that when pressure is increased, the hydrogen molar flow rate shows inverse response where the highest hydrogen produced is at 1 bar. This inverse effect causes methane conversion and yield of the hydrogen to decreases. According to Antzara et al. [16], this due to the Le Chatelier’s effect in which increase in pressure causes inverse effect on methane conversion. Figure 6d shows the effect the methane conversion towards change in steam to methane feed ratio. From the figure when steam feed flow rate is increased, the percentage of methane conversion also increased. This shows that the feed ratio is important to ensure the reaction is pushed to the right side thus increases hydrogen flow rate. Moreover, when steam to methane ratio is increased, the energy requirement for the reformer reaction reduces due to the reduced flow rate of methane. Therefore, for maximum hydrogen production the MSR reactor were simulated using 300 kg of catalyst with operating temperature and pressure at 700 °C and 1 bar respectively and 4 steam to methane feed ratio.

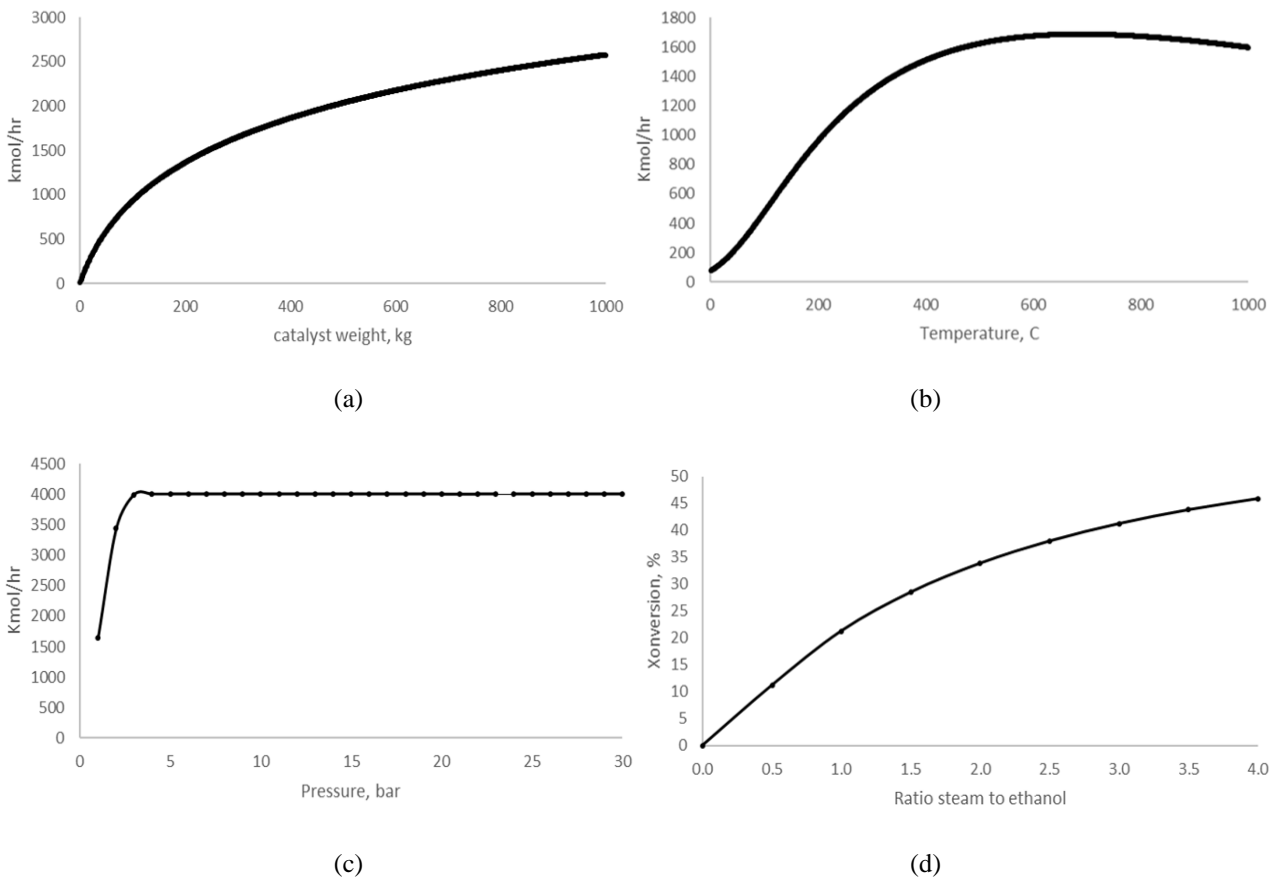


**Figure 6.** Sensitivity analysis of MSR reactor. (a) Effect of weight of catalyst on hydrogen molar flowrate (b) Effect of temperature on hydrogen molar flowrate (c) Effect of pressure on hydrogen molar flow rate (e) Effect of steam feed ratio on conversion of methane

Figure 7 shows the results from Mathure et al. [20] in which the ethanol conversion increased with increased molar ratio of steam. The highest conversion is obtained at 18 molar ratio of steam to ethanol with conversion up to 69%. Figure 7 also shows the comparison results of the simulated model. The highest error was molar ratio at 6 with 14.9% and the smallest error was molar ratio at 18 with 7.3%. the mean error was 12%. The sensitivity analysis for ESR reactor is the same as MSR reactor. Figure 8a shows the effect of increasing the amount of catalyst in the reformer. The graph shows that the molar flow rate of hydrogen is increased continuously when the amount of catalyst is increased. The maximum molar flow rate of hydrogen can be achieved is 2500 kmol/hr at 1000 kg of catalyst. The temperature effect on hydrogen molar flow rate of hydrogen is shown in Figure 8b. From the result obtained, hydrogen flow rate started to increase at 600 C with the maximum flow rate of 1700 kmol/hr. After that, the molar flow rate slightly decreases. Figure 8c illustrates the change of pressure in the reformer to hydrogen flow rate. From the results, it shows that the hydrogen flow rate increased rapidly when the pressure is increased from 1 bar to 3 bar. After that, the flow rate of hydrogen remains unchanged although the pressure is increased from 3 bar to 30 bar. The reason the hydrogen produced is unchanged from the pressure 3 bar to 30 bar because the ethanol has totally reacted with steam and achieved maximum yield of hydrogen. To analyse the effect of steam to ethanol feed ratio, the steam flow rate is increased while maintaining the flow rate of ethanol. Figure 8d illustrates that increase of hydrogen productivity is evident with the increasing water feed. Ethanol conversion is increased to 45% when the steam to ethanol feeding ratio is 4. Therefore, the use of diluted ethanol is effective to improve hydrogen yield because to lower the impact of methanation and other side reaction such as acetaldehyde formation [9]. Overall, for ESR the reactor was simulated using 1000 kg of catalyst with operating temperature and pressure at 600 °C and 3 bar respectively and 4 steam to ethanol feed ratio.

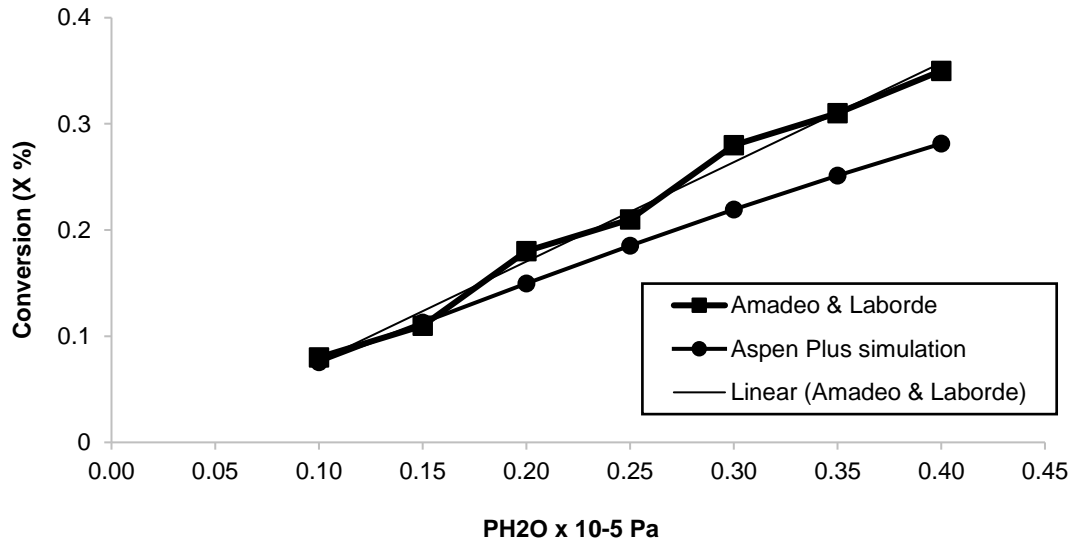


**Figure 7.** The effect of molar ratio of steam to ethanol by Mathure et al [20] and Aspen Plus simulation.



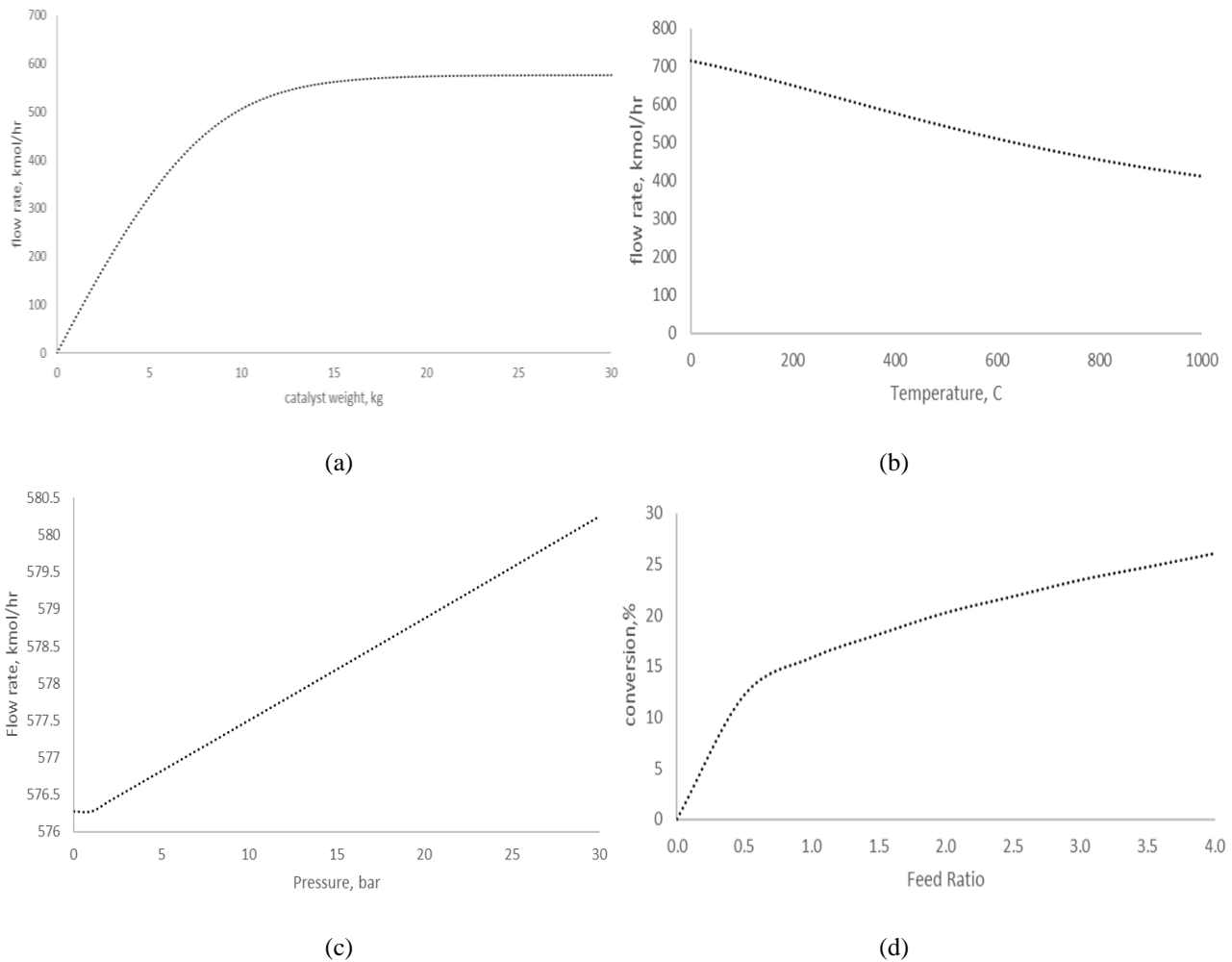
**Figure 8.** Sensitivity analysis of ESR. (a) Effect of catalyst weight effect on hydrogen molar flowrate (b) Effect of temperature on hydrogen molar flowrate (c) Effect of pressure on hydrogen molar flowrate (d) Effect of steam ratio feed on conversion of hydrogen

Figure 9 shows the experimental results by Amadeo & Laborde [24] for WGS reaction. Using the same reactor parameters by Amadeo & Laborde [24], the result from Aspen Plus simulation shows a good agreement with the experimental data. The highest error in this model was 21.70% at partial pressure of water at  $0.30 \times 10^{-5}$  Pa. For the lowest error was 2.75% at pressure of  $0.15 \times 10^{-5}$  Pa. The mean error for this validation was 13.87%. For sensitivity analysis, Figure 10a shows the effect of catalyst weight to CO<sub>2</sub> flow rate. The increment in catalyst weight causes the carbon dioxide flowrate to increase. The results show that at 50 kg of catalyst produced 580 kmol/hr of carbon dioxide before became constant. Figure 10b shows the effect of reactor temperature. The increase in temperature causes a dropped in carbon dioxide molar flow rate. The hydrogen molar flow rate gradually decreased from zero C until 1000 C. The WGS is intrinsically an exothermic reaction. Based on Le Chatelier’s principle, equilibrium constant decreases with increase in temperature thus lower the conversion of carbon monoxide [31].



**Figure 9.** Partial pressure of water effect on conversion of carbon monoxide (left) Amadeo & Laborde [26] (right) Aspen Plus simulation

Figure 10c shows the effect of reactor pressure. CO<sub>2</sub> flow rate slightly increased when pressure is increased however the increment is small. The molar ratio of steam to carbon monoxide versus the carbon monoxide conversion to carbon dioxide is shown in Figure 10d. The result shows that, diluted carbon monoxide yields higher hydrogen and carbon dioxide flow rate. The maximum conversion was 25% at feed molar ratio of 4. The analysis results were in agreement with the work by Haarlemmer [32] which indicate that pressure play a minor role in the reaction and compare to steam ratio which significantly increase the CO conversion. WGS simulation involves two stage which is high temperature WGS (HWGS) and low temperature WGS (LWGS). Both stages were simulated using 50 kg of catalyst at 1 bar with operating temperature of 400 C for HWGS and 200 C for LWGS while steam to CO feed ratio is four. For the separation process, the results of the simulated model and experimental data by Li et al. [30] are shown in **Error! Reference source not found.**4. Errors were less than 6% except for O<sub>2</sub> in the GasOut stream with 14.37%. The mean error for this simulation was 2.53%.



**Figure 10** Sensitivity analysis of WGS reaction. (a) Effect of catalyst weight on CO molar flowrate (b) Effect of temperature on CO molar flowrate (c) Effect of pressure on CO molar flowrate (d) Effect of ratio steam to ethanol on the conversion of carbon monoxide.

**Table 4.** Comparison of Li et al. [30] and simulation results

Stream	Comp	Li et al. (2016)	Simulation	Error
GasOut	N <sub>2</sub> (kg/kg)	0.798	0.7973	0.08
	O <sub>2</sub> (kg/kg)	0.1085	0.0929	14.37
	H <sub>2</sub> O (kg/kg)	0.0743	7.51E-02	1.07
	CO <sub>2</sub> (kg/kg)	0.0191	0.0191	0.15
	F(kg/hr)	67.03	67.08	0.08
CO2Out	H <sub>2</sub> O	0.0043	4.32E-03	0.57
	CO <sub>2</sub>	0.9943	0.9943	0
	N <sub>2</sub>	0.0011	1.13E-03	3.13
	O <sub>2</sub>	0.0003	2.82E-04	5.88
	F (kg/hr)	4.86	4.86E+00	0.01

### 3.2 Simulation Inventory Data

The overall process flowsheets were simulated based on plant capacity of 627 kmol H<sub>2</sub> /hr. Table 5 summarize the main inventory data per functional unit (FU) of 1 kg of hydrogen. In Case 1, for every kg of hydrogen produced requires 6.4 kg of steam and 2.04 kg of methane and produced 4.68 kg of carbon dioxide and 0.26 kg of carbon monoxide. In addition, the utilities required for heating and cool down the process gas is 6.81 MJ/FU of steam and 386.43 kg/FU of cooling water. In Case 2, for every 1 kg hydrogen, 5.9 kg of CO<sub>2</sub> and 0.14 kg of CO were produced respectively. The cooling water consumed in this process

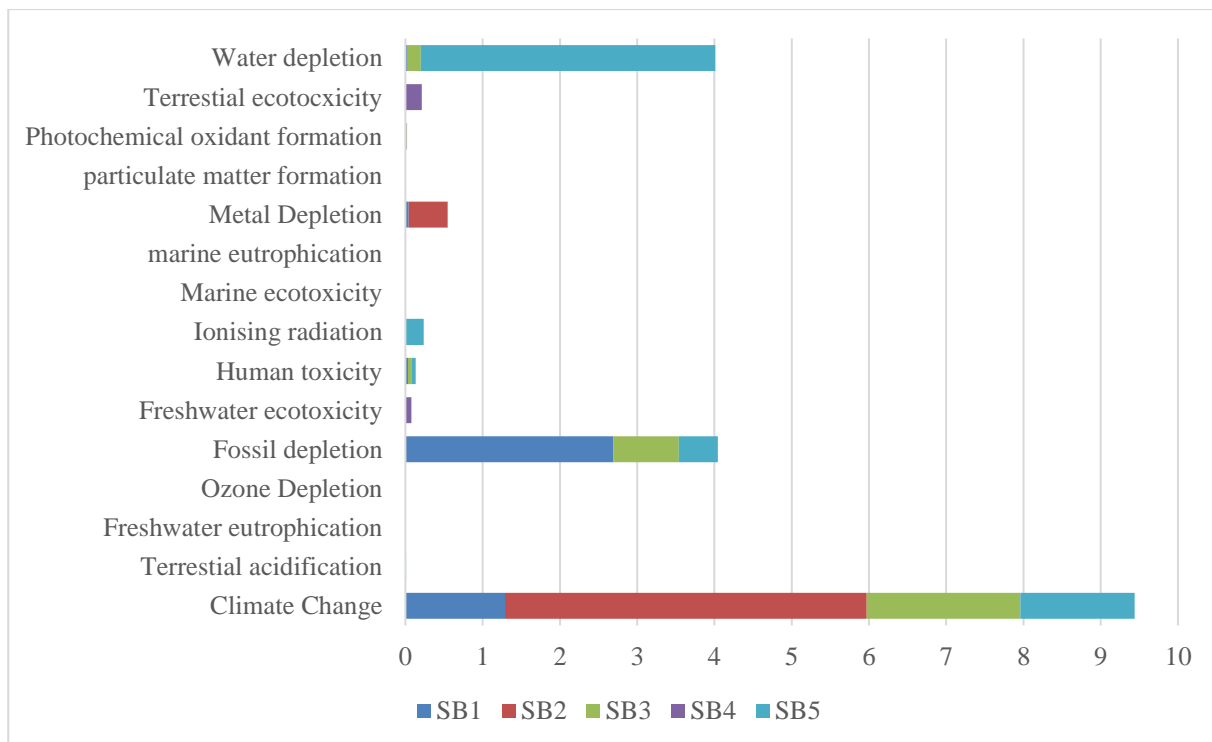
is 2145.65 kg and the net calorific value for the steam used is 50.02 MJ. The ethanol as feedstock used for produced 1 kg of hydrogen is 3.96 kg, meanwhile the steam consumed in the reaction between ethanol with steam is 8.79 kg.

**Table 5.** Main inventory data for the Case 1 and Case 2

Input	Value		Output	Value	
	Case 1	Case 2		Case 1	Case 2
Iron (catalyst), kg	0.5	0.5	CO <sub>2</sub> , kg	4.7	5.9
Nickel (catalyst), kg	0.13	0.24	CO, kg	0.3	0.1
MEA, kg	14.8	27.4	Catalysts, kg	0.6	0.8
Methane, kg	2.0	-	Flue gas, kg	3.2	19.2
Ethanol, kg	-	4.0	H <sub>2</sub> , kg	1.0	1.0
Nickel (catalyst), kg	0.13	0.24	MEA, kg	14.8	27.4
Heating steam (MJ)	6.8	50.0	Waste water, kg	0.4	0.4
Process steam, kg	6.4	8.8	Water for MEA	88.2	163.6
Water for MEA	88.2	163.6	Cooling water, kg	1545.2	2145.7
Cooling Water, kg	386.4	2145.7			

### 3.3 LCA Analysis

The overall results for Case 1 is given in Figure 11 which shows the individual contribution of the impact category to each of the boundary analysis. Overall the most significant impact category is climate change with total of 9.44 kg CO<sub>2</sub> eq. The most affected system boundaries with regards to climate change is SB2 with 4.68 kg CO<sub>2</sub> eq and it cover 49.48% of the total impact. This is due to the MSR and WGS reactions that produced significant amount of carbon dioxide. This result is in agreement with the work by Galera and Ortiz [10] and Hajjaji et al. [33]. It is then followed by SB3 with 1.99 kg CO<sub>2</sub> eq or 21.08%. SB3 is the process steam boundary in which fossil fuel is burned to generate the heating and process steams. SB5 and SB1 contribute the least with 1.48 kg CO<sub>2</sub> eq and 1.29 kg CO<sub>2</sub> eq respectively. Fossil depletion is the second most significant impact category with total of 4.044 kg oil eq. SB1 contributes the most with amount 2.694 kg oil eq or 66.62 %. This is expected since methane is a type of fossil fuel and used as a feedstock in the hydrogen production. It is then followed by SB3 with amount 0.845 kg oil eq or 20.90 %. In SB3, natural gas is used as raw material to generate heating steam used for heating. The third most significant impact category is water depletion with total of 4.01 kg m<sup>3</sup> eq. SB1-5 contributed the most with amount of 3.81 m<sup>3</sup> eq and covers 95.01% of the total water depletion impact. This is obvious since water is used as process water for the process steam generation and cooling water. It is then followed by SB1-3 with amount 0.03 m<sup>3</sup> eq or 4.24%. The other impact categories have a value less than 1 kg eq.



**Figure 11.** Environmental impact results for Case 1



Figure 12 shows the overall results for Case 2 which also indicate that climate change is the most dominant with total of 26.91 kg CO<sub>2</sub> eq. This value is almost three times higher than Case 1. Detail insight shows SB5 is the most affected system boundaries with regards to climate change with 8.1 kg CO<sub>2</sub> eq and it cover 30.79% of total impact followed by SB3 with 7.9 kg CO<sub>2</sub> eq or 26.26% of the total impact. Both boundaries cover 57.05% of total climate impact. This is caused by large amount of fuel burned in the boiler to obtain the heating and process steams which in return released CO<sub>2</sub>. The second-high impact category is the water depletion with total of 25.51 m<sup>3</sup> eq. SB5 contributes the most with amount 20.91 m<sup>3</sup> eq. and cover 89.55%. This is expected since large amount of water was supplied into the process for process steam generation and cooling. However, the value is almost seven times higher compared to Case 1. The third most significant impact category is fossil depletion with total of 12.54% kg oil eq. This value is lower than Case 1 due to the source for which Case 1 uses methane which is a form of fossil fuel. This is in consistent as SB1 contributed to the highest fossil fuel depletion with amount of 6.42 kg oil eq and covers 51.17% of the total impact. It is then followed by SB3 with 3.36 kg oil eq or 26.76%. Note that, the other impact categories that have a value less than 1 kg eq. These values exhibit minor environmental impact of the process. The reason is mainly due the nature of the process which mainly involve chemical processing and combustion.

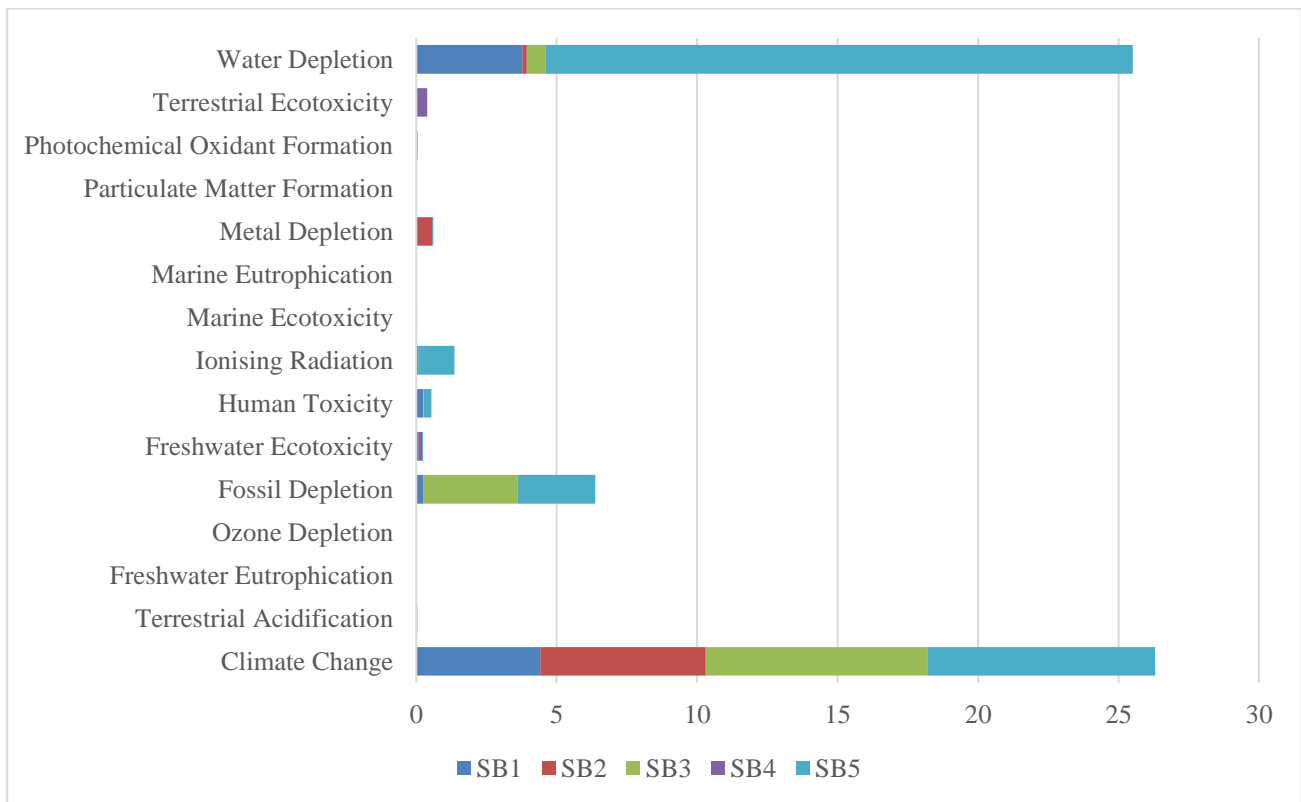


Figure 12. Environmental impact results for Case 2

### 3.4 Economic Assessment

The CAPEX results for both cases is shown in Table 6. For Case 1, the bare module cost,  $C_{BM}$ , was estimated to be \$4,282,327 whereas Case 2 was \$4,504,628. The total bare cost of Case 2 was 5.19 % higher than Case 1. Table 2 also compares the utilities consumption. The result shows that steam cost in the Case 1 is \$ 12,461,000. Meanwhile, the steam cost for the Case 2 is 12.3% higher with total of \$13,994,000. On the other hand, the cooling water cost for the Case 1 is \$ 97,200 and for Case 2 is \$ 171,200 with difference of 76.13%. Overall, the total utilities cost for the Case 2 is higher compared to Case 1 with difference of 12.8%. The high utilities were used in case 2 because the heat duty required for heat transfer in heat exchanger in case 2 is high. In conclusion, overall Case 1 is more economic in the term capital and operating cost compared to the Case 2.

**Table 6.** The comparison of the CAPEX and OPEX between Case 1 and Case 2

CAPEX	Case 1	Case 2	Comparison (%)
Bare module cost, $C_{BM}$ (\$)			
- Heat exchangers	2,255,526.68	2,228,628.30	
- Reactors	1,250,000.00	1,250,000.00	
- Columns	776,800.00	1,026,000.00	
- Total	4,282,327	4,504,628	5.19
<b>OPEX</b>			
Steam (\$)	12,461,000	13,994,000	
Cooling water (\$)	97,200	171,200	
Total (\$)	12,558,200	14,165,200	12.8

#### 4.0 CONCLUSION

The main highlights of this work is to assess and compare the environmental impact and economic feasibility of hydrogen production from methane (Case 1) and ethanol (Case 2). Both case studies were simulated in Aspen Plus 8.6 using a modified kinetic based reaction models for MSR and WGS reactions whereas RADFRAC model were used for CO<sub>2</sub> separation. The modified reaction models and separation model shows good agreement with results found in literature. The flowsheets were then used for sensitivity analysis as well as environmental and economic assessment. Environmental analysis was performed in LCA GaBi software. It is found that three categories namely climate change, fossil depletion and water depletion were the most significant environmental impact compared to the other categories. Methane shows a higher impact on climate change whereas ethanol shows a higher fossil fuel resource depletion and water resources compared to methane. The economic assessment on the other hand, Case 1 were 5.2% and 12.8% less compared to ethanol in term of CAPEX and OPEX respectively. Overall, our findings show that methane (Case 1) is more environmental friendly and economically feasible than ethanol (Case 2) despite the latter uses a renewable source for hydrogen production. This study will help stake holders to understand the environmental and economic impacts of hydrogen production as such helping them to make viable decisions that could mitigate undesired impacts and ensure the sustainability to attract community, government and investor interest and support.

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