

LIFE CYCLE ASSESSMENT OF THE PROCESS STEAM REFORMING OF METHANE (SMR)

This thesis is submitted in the partial fulfilment of the requirement for
the degree of **Bachelor of Technology** in Chemical Engineering

by

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In guidance of

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2014-15**



**National Institute of Technology
Rourkela
CERTIFICATE**

This is to certify that the thesis entitled “**LIFE CYCLE ASSESMENT OF THE PROCESS STEAM REFOEMING OF METHANE (SMR)**” submitted by **SUSHIL KUMAR (ROLL NO: 111CH0441)** in partial fulfilment of the requirements for the award of Bachelor of Technology degree in Chemical Engineering at the National Institute of Technology, Rourkela is an authentic work carried out by him under my supervision and guidance.

To the best of my knowledge, the matter embodied in the thesis has not been submitted to any other University/ Institute for the award of any degree or diploma.

DATE: 7thMAY, 2015

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ABSTRACT

Life cycle assessment is a process to determine the environmental impact of the product at various stages of its life during the process. The steam reforming of methane is carried out in a methane reformer using ASPEN PLUS simulator at 630 °C temperature and 1.5 atm pressure. Methane at these conditions reacts with steam to produce Carbon dioxide (CO₂), Carbon monoxide (CO) and Hydrogen (H₂). The excess amount of Carbon monoxide is also converted to Carbon dioxide in two steps; High temperature shift conversion (HTS) and Low temperature shift conversion (LTS). Methyl diethanolamine (MDEA) is utilized to retain carbon dioxide from the final stream.

Life cycle assessment is then carried out to find the effect of Carbon dioxide gas in air emission, Greenhouse effect, Energy consumption and Waste water emission at different stages of the process. The outcome demonstrates the increment in weight (%) of CO₂.

Keywords: High temperature shift conversion (HTS), Low temperature shift conversion (LTS), ASPEN PLUS Simulation.

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CHAPTER 1
INTRODUCTION

INTERODUCTION:

The continuously increasing standard of living in developing and developed nations results in higher energy demands. On the other hand the conventional energy supply via combustion of fossil fuels and subsequent emission of large volumes of carbon dioxide has led to one of the most serious global environment problem. Therefore, there is a growing awareness that energy must be produced with significantly lower greenhouse gas emission. Hydrogen is often referred to as a potential free energy carrier, but its advantages are unlikely to be realized unless efficient means are found to produce hydrogen with reduced CO₂ emissions. Biomass which is considered a CO₂ neutral energy source, can be used to produce hydrogen via different thermo-chemical routes (Gasification, fast pyrolysis followed by steam reforming of the bio-oil produced).

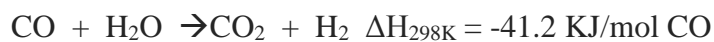
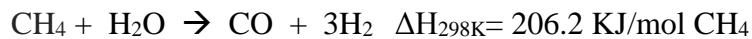
It is likely that the generation of H₂ by means of steam reforming of methane (SMR) will keep on being the prevailing innovation for the following couple of decades, despite of the apparent measure of CO₂ discharged, catalyst deactivation because of coking, need of high temperature metal-lurgies for the reactor development. In addition, due to the increase in hydrogen demand and the importance of synthesis gas as a major feedstock for carbon chemistry. The steam reforming of methane (SRM) is currently the most cost-effective and highly developed method for production of hydrogen at relatively low cost and high hydrogen to carbon ratio are desired. Some late works pointed out the basicity piece of the reinforcement and of the decline conditions in the carbon advancement. In fact, two other factors seem to be important to decrease the carbon deposition; size of metal particles and interactions between the metal particles and the support.

In order to assess possible options for the future energy strategy of interest for the evaluation of hydrogen energy. Popular methods used in the evaluation of the power system are: the thermodynamic method, estimate the cost of energy and the Life Cycle Assessment (LCA). Each method is based on the optimization features reflecting a single indicator in the assessment of individual design options power. Since the production of energy in the power system based on different physical principles, each version of the system power will reflect the importance of various parameters optimization. In addition, each version of the power supply system will use another source of energy that transform the final energy and will impose a different interaction with the environment. In this project, LCA is used to calculate life cycle emissions of the air and greenhouse effects of carbon dioxide and methane.

CHAPTER 2
LITERATURE REVIEW

2.1 STEAM METHANE REFORMING PROCESS (SMR):

The continuous but complex multistep SMR process can be replaced by a much simpler single step process which employs a bed packed with an admixture of catalyst and sorbent for the selective removal of CO₂. The latter is known as sorption enhance reforming (SER) in which the highly exothermic carbonation reaction of the sorbent is included in the reaction scheme. The main reactions are the following:



The concept of sorption enhanced steam reforming is based on Le Chatelier's principle, according to which the conversion of reactants to products and the rate of the forward reaction in an equilibrium controlled reaction can be increased by selectively removing some of the reaction products (say CO₂) consumed in reaction.

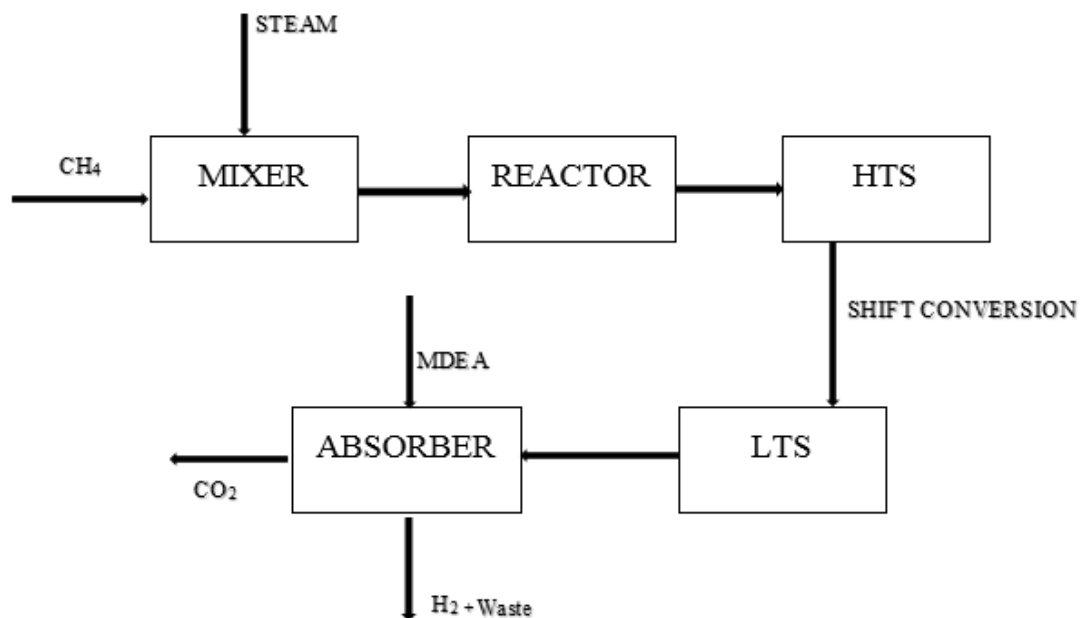


Figure 1: Block Diagram of Steam Methane Reforming Process

2.2 LIFE CYCLE ASSESSMENT (LCA):

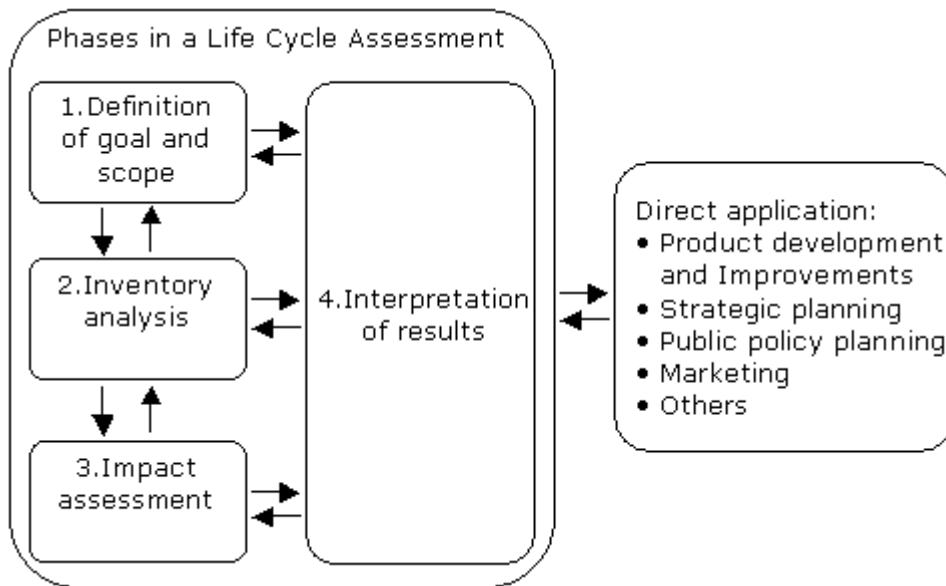


Figure 2: Concept of Life Cycle Assessment (LCA)

LCA concept simply means that the inputs (energy, materials, etc.) and outputs (energy waste, etc.) are estimated at each stage of the product life cycle. LCA analysis can have a positive impact on human health, ecosystems and natural resources. In particular, the LCA systematic method that uses four steps to evaluate the potential impacts associated with a product or process: I) Defining the objectives and scope of the study, II) life cycle inventory, III) life cycle impact assessment, IV) Interpretation of the results. It establishes a context in which the estimate is to be made and identifies the impact on the environment. Inventory identify and quantify energy, water and materials use and emissions into the environment (eg. air emissions, solid waste, waste water and discharge). The impact of human and environmental consequences of energy, water and materials use and emissions into the environment identified in the inventory analysis. Interpretation of the results of the analysis evaluates the inventory and impact assessment, to select the preferred product, process or service with a clear understanding of uncertainty and assumptions.

2.3 RISK BASED LIFE CYCLE ANALYSIS:

Risk based Life cycle is carried out on the premise of a methodology of measuring arrangement options and determination of the most suitable method. For this, it observes human wellbeing, ecological security and economic impacts quantitatively or qualitatively. It incorporates material and energy stream in the outflow from the framework and in the inflow to the framework. It characterizes the environmental impacts of all exercises inside the limits of the arrangement of generation of material for processing, transportation, construction, creation and decommissioning of the plant.

2.3.1 Scope and Boundary:

RBLCA defines the scope and limits of the study joint systems. This involves reversing the traditional system of raw materials in their natural state, which are available at any environmental penalty. Various other process to produce the same quantity of goods to be included within the boundaries defining the global system that gives the advantage that inputs, together with their paths, can be explained in the total emission of the waste. It should be noted that, although this definition is consistent with conventional LCA, it does not include the process routes and stages after ending a process.

2.3.2 Life Cycle Inventory (LCI):

Analysis of life cycle inventory takes place for the collection and measurement of the data and the load on environment by balancing matter and energy for each transaction in the system. If the information is incomplete, the received data used in the analysis should be conservative and clearly revealed. Data quality varies depending on the source, therefore, the choice of the best available source must be provided.

The principle for considering LCI is, all the inputs and waste streams in the system must be assigned to the respective output without waste streams. For the next stage when output stream becomes input stream it consists Els with it. Therefore, the amount of end products assigned raw materials, energy and waste and the total Els in the process chain.

2.3.3 Environmental Impact and Risk Analysis:

The environmental impact and risk analysis examines the potential or actual environmental and human health effects from the use of resources and waste release. It is performed in three stages: i) Classification, ii) Characterization and iii) Valuation.

In classification the results from the inventory are assigned and aggregated into homogenous impact categories that identifying stressors and organizing them with respect to impart on the ecosystem. Examples, stressors like CO, NO_x and CH₄ have the global warming potential (GWP).

Characterization assesses the impacts for each category in order to translate LCI data into impact descriptors. Impact equivalency units are available for subsets of stressors. Where these are unavailable new impact equivalency units must be established.

Valuation assigns relative importance values to different impacts to determine the total score for each product. This involves a structured description of the hierarchical relationships among the problem elements start with an overall goal statement to developing a decision tree.

CHAPTER 3
ASPEN PLUS SIMULATION

ASPEN PLUS simulator is used to simulate and predict the behavior of a process that includes the expansion of its component parts to learning individual operation. It is widely used to study and investigate the influence of different operating parameters on the various reactions.

3.1 ASSUMPTIONS:

The following assumptions were made before Aspen Plus Modeling:

- The methane is pretreated before taking as a feed to overcome the impurities of Sulphur and Nitrogen.
- Carbon dioxide (CO₂) is considered as a product for life cycle assessment.
- The process is isothermal and steady state process.
- Ideal method is used for simulation to overcome all unnecessary calculations during LCA.
- Stoichiometric reactor is used as a primary reactor to find out appropriate conditions for the reaction.

3.2 REACTOR DESIGN:

Initially Stoichiometric reactor is taken with 90% conversion of methane in first reactor since reaction kinetics are unknown.

Model:	RStoic
Description:	Stoichiometric Reactor
Purpose:	Models stoichiometric reactor with specified reaction extent or conversion
Use For:	Reactors where reaction kinetics are unknown or unimportant but stoichiometry and extent of reaction are known

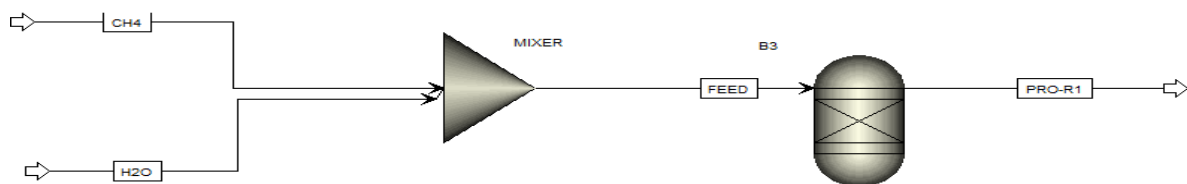


Figure 3: Aspen Plus modelling using Stoichiometric Reactor

Table 1: Parameters used in the reactor design:

Mixer

Temperature (°K)	573.15
Pressure (psi)	14.7

Reactor

Temperature (°K)	573.15
Pressure (psi)	25

Methane

Temperature (°K)	573.15
Pressure (psi)	14.7
Mole Flow (Kmol/sec)	1

H₂O

Temperature (°K)	573.15
Pressure (atm)	14.7
Mole Flow (Kmol/sec)	3.5

3.3 SENSITIVITY ANALYSIS:

Carbon dioxide is the product in this case to run Life Cycle Analysis so flow rate of CO₂ is observed at different temperature and then plotted to find out optimum temperature for the reaction to maximize CO₂ flow rate. It is observed that flow rate of CO₂ initially increases with increase in temperature but after 903 K it starts decreasing again. So 903K is taken as optimum temperature for the reaction and to minimize the Gibbs energy Stoichiometric reactor is replaced by Gibbs Reactor.

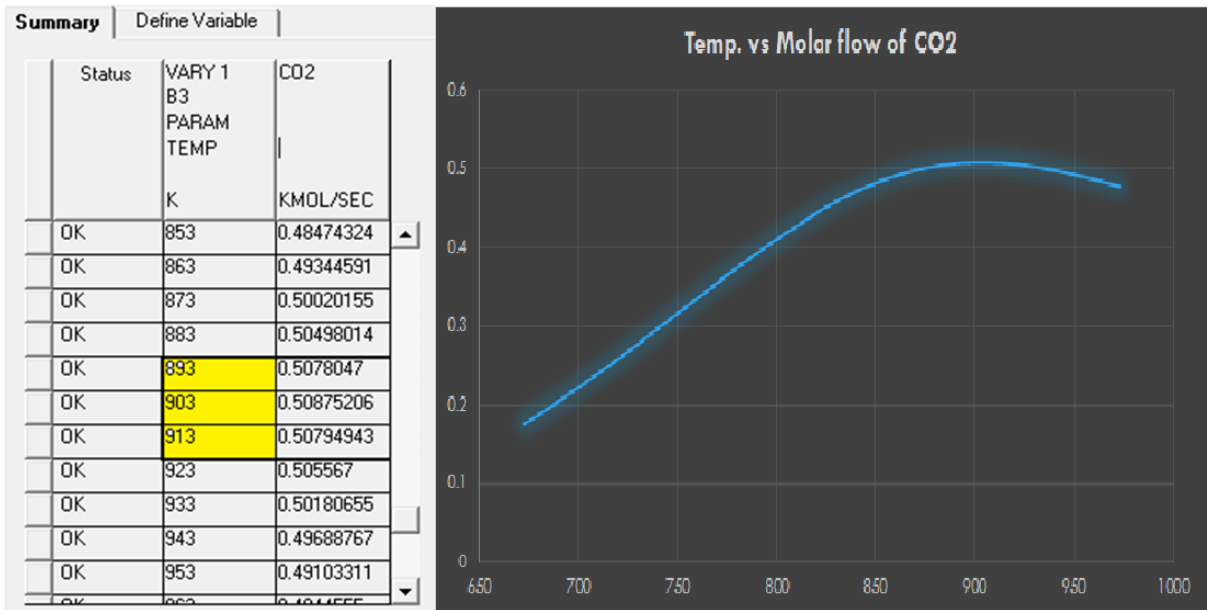


Figure 4: Sensitivity analysis plot of Temperature vs molar flow rate of CO₂

3.4 ASPEN PLUS MODELING:

After reactor design the next step is to design the whole process using Aspen Plus simulator. Final flow sheet is shown below:

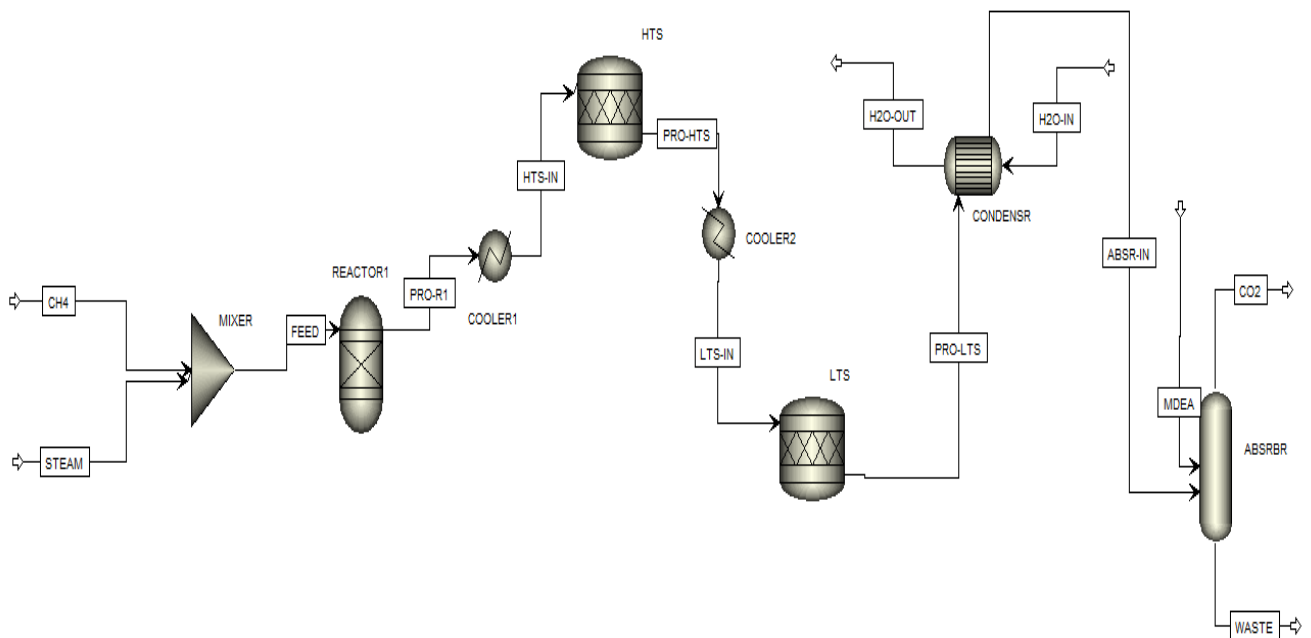


Figure 5: Complete Flow sheet of Aspen Plus simulation

Model:	RGibbs
Description:	Equilibrium reactor with Gibbs energy Minimization
Purpose:	Performs chemical and phase equilibrium by Gibbs energy minimization
Use For:	Reactors with phase equilibrium or simultaneous phase and chemical equilibrium. Calculating phase equilibrium for solid solutions and vapor-liquid- solid systems.

Table 2: Parameters used in Aspen Plus Simulation:

Feed

Temperature (K)		573.15
Pressure (psi)		14.7
Flow Rate(Kmol/sec)	Methane	1
	Steam	3.5

Reactor1 (Primary reformer)

Temperature (K)	903.15
Pressure (psi)	25

High Temperature Shift Reactor (HTS)

Temperature (K)	700
Pressure (psi)	15
Conversion of CO (%)	90

Low Temperature Shift Reactor (LTS)

Temperature (K)	486
Pressure (psi)	15
Conversion of CO (%)	90

Absorber

Temperature (K)	311
Pressure (psi)	5

3.5 FINAL RESULT OF ASPEN PLUS:

Display: Streams Format: FULL Stream Table							
	FEED	PRO-R1	HTS-IN	PRO-HTS	LTS-IN	PRO-LTS	
Mole Frac							
CH4	.2222222	.0309693	.0309693	.0309693	.0309693	.0309693	
H2O	.7777778	.3562898	.3562898	.3119304	.3119304	.3074944	
CO	0.0	.0492882	.0492882	4.92883E-3	4.92883E-3	4.92883E-4	
H2	0.0	.4803350	.4803350	.5246944	.5246944	.5291304	
CO2	0.0	.0831175	.0831175	.1274770	.1274770	.1319129	
C5H13NO2	0.0	0.0	0.0	0.0	0.0	0.0	
Total Flow kmol/sec	4.500000	6.120880	6.120880	6.120880	6.120880	6.120880	
Total Flow kg/sec	79.09624	79.09624	79.09624	79.09624	79.09624	79.09624	
Total Flow cum/sec	211.6369	266.6503	16.69091	344.9087	13.50293	239.1127	
Temperature K	573.1500	903.1500	623.1500	700.9278	477.5944	485.9278	
Pressure N/sqm	1.01325E+5	1.72369E+5	1.90000E+6	1.03421E+5	1.80000E+6	1.03421E+5	

Display: Streams Format: FULL Stream Table							
	H2O-IN	H2O-OUT	ABSR-IN	MDEA	CO2	WASTE	
Mole Frac							
CH4	0.0	0.0	.0309693	0.0	.0340786	1.21169E-5	
H2O	1.000000	1.000000	.3074944	0.0	.2365087	.1019783	
CO	0.0	0.0	4.92883E-4	0.0	5.42462E-4	9.90313E-8	
H2	0.0	0.0	.5291304	0.0	.5824493	1.23983E-5	
CO2	0.0	0.0	.1319129	0.0	.1450680	1.40541E-4	
C5H13NO2	0.0	0.0	0.0	1.000000	1.35281E-3	.8978566	
Total Flow kmol/sec	5.000000	5.000000	6.120880	5.000000	5.560440	5.560440	
Total Flow kg/sec	90.07640	90.07640	79.09624	595.8188	69.74153	605.1735	
Total Flow cum/sec	.0902277	.0906595	235.0121	.5745007	463.5585	.6344325	
Temperature K	293.1500	298.0950	477.5944	298.1500	345.6663	388.1379	
Pressure N/sqm	1.01325E+5	1.01325E+5	1.03421E+5	1.01325E+5	34473.79	41368.54	

CHAPTER 4
LIFE CYCLE INVENTORY

The Life Cycle Inventory analysis is performed to collect data and quantify environmental loads by making material and energy balances. The results of this LCA, including air emissions, Greenhouse gases emission, energy requirement and water emissions. The functional unit, also known as the production amount that represents the basis for the analysis, was chosen to be the net amount of methane charged.

4.1 AIR EMISSION:

In terms of total air emission, Carbon dioxide is emitted in the largest quantity. The next table is a list of the major air emissions:

Table 3: Average air emission

Sl. No.	Gas	Weight (%)			
		Reactor1	HTS	LTS	Absorber
1.	CO ₂	28.34	43.46	44.97	50.96
2.	CO	10.70	1.07	0.11	0.12
3.	CH ₄	3.84	3.84	3.84	4.35

4.2 GREENHOUSE GASES AND GLOBAL WARMING POTENTIALS (GWP):

Although CO₂ is the most important greenhouse gas and is the largest emission from this system, quantifying the total amount of greenhouse gases produced is the key to examining the GWP of the system. The GWP of the system is a combination of CO₂ and CH₄ only since CO is in tress amount.

$$\begin{aligned} \text{GWP relative to CO}_2 : \quad \text{CO}_2 &= 1 \\ (100 \text{ years IPCC value}) \quad \text{CH}_4 &= 25 \end{aligned}$$

Table 4: Greenhouse Gases Emission and Global Warming Potential

	Emission Amount (Kg)	Percent of greenhouse gases (%)	GWP relative to CO ₂	GWP Value (Kg)	Percent contribution to GWP (%)
CO ₂	50.96	92.14	1	50.96	31.91
CH ₄	4.35	7.86	25	108.75	68.09

It is evident that CO₂ is the main contributor, accounting for 92.14 % of the greenhouse gases but due to high GWP value CH₄ contributes more than that of CO₂. However, it is important to note that the natural gas lost to the atmosphere during production and distribution causes CH₄ to affect the system's GWP. Although the amount of CH₄ emissions is considerably less than the CO₂ emissions on a weight basis (50.96 Kg versus 4.35 Kg), because the GWP of CH₄ is 25 times that of CO₂, CH₄ accounts for 68.09 % of the total GWP.

4.3 ENERGY REQUIRMENT:

Energy consumption is an important part of LCA. The energy consumed within the system boundaries results in resource consumption, air and water emissions, and solid wastes. The next table shows the energy consumption at different stages of the process:

Table 5: Average Energy Requirement:

	Reactor1	Cooler1	HTS	Cooler2	LTS	Condenser	Total
Total Energy Consumption (MW)	226.95	60.80	6.196	47.05	0.625	1.83	343.45
Percent of total energy consumption (%)	66.08	17.70	1.80	13.71	0.18	0.53	100

4.4 WATER EMISSION:

The total amount of water pollutants was found to be small compared to other emissions.

$$\begin{aligned}
 \text{Total amount of water pollution} &= 0.102 \text{ kmol/kg of CH}_4 \text{ charged} \\
 &= (0.102 \times 18) \text{ kg/kg of CH}_4 \text{ charged} \\
 &= 0.115 \text{ kg/ kg of CH}_4 \text{ charged}
 \end{aligned}$$

It is very less amount with compare to CO₂ emission (50.96kg).

CHAPTER 5
DISCUSSION

Discussion:

Although hydrogen is generally used as a clean fuel, but it is important to understand that its production affects the environment. A complete picture of the environmental problems associated with hydrogen production by steam methane reforming (SMR) was studied at the basis of energy consumption and emissions of a life cycle perspective.

In this operation the emission of the Carbon dioxide from primary reformer to the absorber was taken into account and its mole fraction was noted down at each and every stage of its production. Based on the system, the carbon dioxide emission takes place in large quantities, which is 92.14% by weight of total emissions and 31.91% of the GWP contribution. Though the weight percent of carbon dioxide is more in the product stream but due to high GWP value (25 times of that of CO₂) methane contributes more in Global warming. The energy balance of the system shows that the most of the energy is consumed by the primary reformer since the reaction takes place at higher temperature. Environmental and economic point of view is important to increase the energy efficiency and the relationship of each process. This in turn will reduce emissions of the waste water and energy.

Component Life Cycle Assessment is used to identify opportunities to reduce the environmental impact of the product to the system. From the energy requirement data it is clear that energy efficiency of this process has a great effect on the stress system (resources, emissions, waste and energy consumption), and, therefore, this variable has a large impact on the environment. SMR due to the high conversion ratio is the conventional technology in which many improvements have taken place in the past. However, it is important to note that the hydrogen system must operate efficiently to minimize the impact on the environment.

Reduction of losses of methane is also an opportunity to strengthen and improve the GWP system due to its high global warming potential. The analysis shows that 68.09 % of GWP is the result of methane and it must be reduced to a significant number. Reducing the loss of methane will also improve the energy balance of the system. Water emission is not that significant in this analysis due to its tress amount in the product stream.

CHAPTER 6
CONCLUSION

CONCLUSION:

Life Cycle Assessment of steam methane reforming (SMR) process using Aspen Plus gives the overall review of the process. The main product of this process is hydrogen (H_2) but that does not affect the environment as much as the by-products (CO and CO_2) and the unreacted methane in the process. To find out over all environmental impact of the process the molecular flow of the carbon dioxide is observed at various stages of process.

The steam methane reforming process takes places in different reactors like Primary reformer; where methane reacts with steam at high temperature to produce carbon monoxide and carbon dioxide, High temperature shift conversion; where carbon monoxide is converted into carbon dioxide at high temperature, Low temperature shift conversion; where even tress amount carbon monoxide gets converted into carbon dioxide and the absorber; carbon dioxide is absorbed into MDEA solution. The mole fraction of carbon dioxide increases in each steps and its weight percent of emission is calculated to find out its environmental effect. The effect of the unreacted methane on the other hand is observed relatively with carbon dioxide.

Aspen Plus simulation gives the brief over view of the process. To find out maximum environmental impact of the gas carbon dioxide a sensitivity analysis was performed between flow rate of the carbon dioxide and the reaction temperature. Then process was designed using ideal method to reduce the unwanted thermodynamic calculations and results were observed with the help of life cycle analysis. It is observed that most of the energy (226.95 MW out of 343.45 MW total energy consumed) was consumed by the primary reformer since SMR process takes place at higher temperature and pressure.

Life Cycle Analysis shows that the carbon dioxide has the maximum weight percent (92.14%) in the air emission and causes more in environmental pollution. The second is methane with relatively low weight percent but high global warming potential (GWP) valve because of that it causes more in global warming. The amount of water emission is very low (0.115 Kg/Kg of CH_4 charged) so we can neglect its effect on environment during life cycle assessment.

CHAPTER 7
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REFERENCES:

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