

Analyzing and Comparing Energy and Exergy of POXR and SMR Reactors for Producing Hydrogen from Methane Gas

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Abstract

The POXR and SMR methods adopted in producing hydrogen from methane gas are simulated and exergy analysis of both the processes are run for comparison. The effective parameters of the feeding materials ratio and the system temperature for maximizing hydrogen production and increasing efficiency are assessed here. Influenced by the changes in these parameters the unit efficiency is increased up to 76%. The efficiency of POXR and SMR processes are calculated for new ratios. The results indicate that SMR process has higher exergy efficiency than POXR process. Exergy efficiency of SMR and POXR processes are obtained as 73.2 and 66.9, respectively, where the SMR efficiency process is increased by 2.6% because of the changes in the feeding material ratio and temperature. Highest destruction of exergy in methanator reactor in SMR process is due to high temperature of reaction caused by irreversibility from chemical reactions. Exergy destruction is reduced at high temperature and unit molar ratio.

Keywords

Hydrogen production unit, exchange reaction of methane and steam, partial oxidation, modeling, simulation, exergy.

1. Introduction

Exchange reaction of methane and steam has been and is being applied for years as the main method of hydrogen production in industries. Isolation through methane partial oxidation catalytic method is a very common process in producing hydrogen from synthesis gas (Figen & Baykara, 2015).

This issue has become the focus of many studies regarding the performance of hydrogen production units. According to the studies run, hydrogen-making unit of steam partial oxidation modeling is done by 69-76% efficiency which prevents the unit efficiency increase because of H₂ to CO molar ratio output product flow and an increase in greenhouse gases (Starik, Kuleshov, Loukhovitski, & Titova, 2015).

According to thermodynamic rules, methane completely turns into hydrogen at low

temperatures, with a high possibility of coke formation which results in stopping catalyst (Rabenstein & Hacker, 2008). This problem is solved by an increase in the reaction temperature up to 540°C and an increase in molar ratio up to 2.88. An increase in S/C ratio needs higher heat for evaporation and increases energy needed for the pumps. Any molar ratio higher than 4 is not cost effective in hydrogen production.

The efficiency in hydrogen production is assessed from synthetic methane reform through exergy and flow exergy analyses, where the destruction and efficiency are calculated. Exergy efficiency is calculated and the highest exergy destruction is occurred because of irreversibility in chemical reactions and heat convection in which a considerable amount of exergy is wasted in heaters in order to supply the required heat of reaction. The change in input parameters indicate that the

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reverse relation between hydrogen product and the required methane volume for system and reaction temperature.

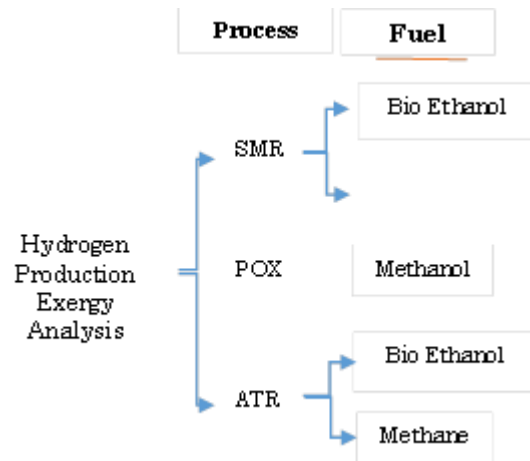
Conversion of carbon monoxide into carbon dioxide at low temperatures inside reactor is modeled here. The analyses of energy and exergy of SMR and POXR processes of methane and steam are run for identifying the thermodynamic defects. The thermal and exergetic efficiencies of previous studies on SMR process are 70% and 65.5% while in this new process, the thermal and exergetic efficiencies are 79% and 69.1%, respectively. In this model one mole of methane gas produces 2.53 moles of H₂, that is, an increase when compared to the previous process where the same is 2.35 (Hajjaji, Pons, Houas, & Renaudin, 2012). In previous studies, the interior and exterior losses of exergy were 91% and 9%, respectively, and the produced hydrogen had the purity of 97-98% (Dincer & Rosen, 2012). In SMR process, methane and steam are converted into H₂ and at 700-850°C and during an endothermic reaction, CO is converted to CO₂ in order to reduce environmental pollutions. In the POXR process, Methane reacts with O₂; in large units of hydrogen production, the efficiency can reach 80-85% and if output steam is reused in the system, total efficiency increases. Small units have lower efficiencies of about 10-15% with higher cost of unit. Production in large reformers with dimensions of 10×3m and applying CCS (Carbone Capture System) technology may increase output efficiency. H₂ cost of natural gas reform is within 10-15\$/GJ-H₂ at large scale and this value reaches 50 \$/GJ-H₂ for small scale; these values change with natural gas price, an effective factor in final cost. The influence of reformer temperature, pressure and the steam to carbon (S/C) ratio in the process and calculating exergetic efficiency indicate that rational selection of these parameters can improve exergetic performance procedure. Exergy analysis is applied in order to have optimal energy consumption for each section of system.

2. Research History

Hydrogen is obtained from water electrolysis, biomass and fuels like coal, crude oil or natural gas. Now, 98% of all produced hydrogen all over the world is obtained from fossil fuels. Light hydrocarbons, methane in specific, are the main hydrogen production resources because of their cheap production cost in large gas reservoirs throughout the world. Analyses of similar

energy processes are run to assess the exergy consumption in the related processes.

Figure 1. Studies Run on Exergy Process Based on Fossil Fuels



Exergy destruction of thermodynamic irreversibility in reactor is specified at higher temperatures and S/C molar ratio. Since SMR is an endothermic reaction, heat must be supplied from internal or external heat source for beginning and continuation of the reaction (Chein, Chen, Zhu, & Chung, 2012). For a multi-partial gaseous flow in reactor, total exergy is of three parts: Chemical (Ex,chem), physical (Ex,phy) and the exergy from mixing components ($\Delta Ex, mix$) (Ortiz, Ollero, Serrera, & Galera, 2012).

Thermodynamic analysis of hydrogen production process is run based on energy and exergy analyses. In order to assess the operation of process, the heat efficiency is calculated. Thermal efficiency is the outcome of energy divided on energy. Input includes the consumable energy divided by its obtaining cost.

$$\eta_{Thermal} = \frac{m_{H_2} \times LHV_{H_2}}{m_{CH_4} \times LHV_{CH_4}} \quad (1)$$

where, m_i and LHV_i are the mass flow and low heat value for specified input, respectively. Analysis of energy is run based on first law of thermodynamics (Hajjaji, Baccar, & Pons, 2014). There exist many methods to perform methane-steam reforming reaction among which the most commonly method applied for reaction is the De Groot and Froment where nickel catalyst bed reactor is applied, Fig. (2).

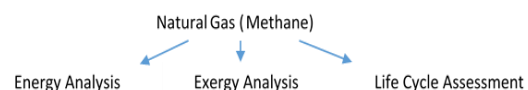


Figure 2. The Studies R on Methane Gas

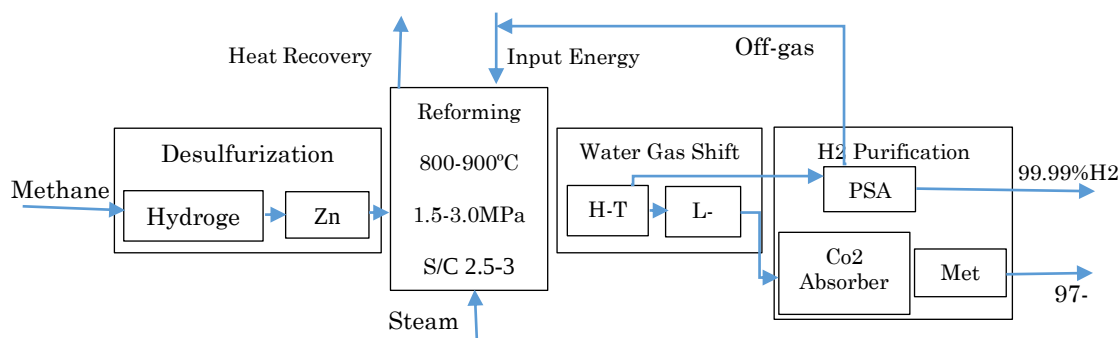


Figure 3. The Block Diagram for Steam-Natural Gas Reforming Reaction

The reaction is supported by nickel catalyst which includes 15-25 wt% of Nickel oxide catalyst on a carrier like Al_2O_3 , aluminosilicate or magnesia. If there is a lack of oxidation reactions, the heat input for endothermic reaction in reformer is performed by indirect heating. In general, a heat efficiency of 81% is expected for reformer and thermal losses is applied as thermal recovery from output flow heat for producing steam which eventually affects the unit size (Izquierdo et al., 2012).

3. Introducing the Process

The main role of steam in the conversion reactions through steam (SMR) is that balance conducts towards the production of CO and H_2 , and according this balance of reaction, reaction products more hydrogen molecules by decreasing pressure. This reaction is highly endothermic and must be performed in conditions at high temperature and low pressure for producing more hydrogen and carbon monoxide. Pressure is usually constant; therefore, an increase in temperature leads the reaction towards hydrogen production. For supplying such high temperature (about 800 to 900 °C), the reactor in which the reaction occurs is located in radiant section of an oven. In case a higher methane conversion is needed, a secondary converter (partial oxidation exchange) can be applied, where, a certain volume of oxygen or air reacts with output gas of the first converter in the vicinity of catalyst. This reaction causes gas oxidation thus; higher percentage of methane is converted to hydrogen, that is, by applying the secondary converter 99.6% of methane is converted to hydrogen. The advantage of combined steam converter and partial oxidation on steam converter is that there is no performance needed by the first steam converter in hard situation at high temperature. In the dual-converter system, the first converter of steam performs at lower

temperature, thus an increase in efficiency and the amount of conversion and a decrease in cost of apparatuses and equipment is decreased.

4. Process Explanation

Methane (the main element of natural gas) involved in balance reaction with steam and the main product of the reaction is mainly hydrogen and carbon dioxide. Schematic of SMR is shown in the fig 4. The equations of reaction for performing SMR process which occur in this unit are shown in the table 1:

Table 1. Reactions of Steam Reforming Process- SMR

Reaction Name	Reaction	Reaction Type
Reform 1	$CH_4 + H_2O \leftrightarrow CO + 3H_2$	Equilibrium
Reform 2	$CO + H_2O \rightarrow CO_2 + H_2$	Equilibrium
Shift 1	$CO_2 + H_2 \leftrightarrow CO + H_2O$	Equilibrium
Meth 1	$CO + 3H_2 \leftrightarrow H_2O + CH_4$	Conversion

The main role of steam in the reaction of conversion with steam is that it maintains the balance in CO and H_2 production, and allows for more number of hydrogen molecules to be produced by a decrease in pressure. This reaction is endothermic and for having more production of hydrogen and carbon monoxide, the reaction must be performed at high temperature and low pressure where; pressure is usually constant. Therefore, an increase in reaction temperature leads the reaction towards hydrogen production.

The remainders of chemical processes are preferably applied for production of hydrogen and carbon monoxide. The stoichiometry coefficients for reaction components are tabulated in Table 2. The conditions for partial oxidation of methane (POXR) are as following and schematic is shown in the fig 5:

Table 2. Reactions of Partial Oxidation Process of Steam POXR

Reaction Name	Reaction	Reaction Type
POX	$O_2 + CH_4 \leftrightarrow CO + H_2$	Equilibrium
METH.	$CH_4 + H_2O \rightarrow CO + 3H_2$	Equilibrium
SHIFT	$CO + H_2O \leftrightarrow CO_2 + H_2$	Equilibrium
POXR	$\frac{1}{2}O_2 + CO \rightarrow CO_2$	Conversion

Partial oxidation process is a catalytic process which does not need cleaning of the materials like sulfur derivatives. High operational temperatures introduce various problems for this process in small scales. Applying catalysts cause the process temperature to be reduced which is named catalytic partial oxidation process.

5. Assumptions of Simulation and Parameters of Flows

The software Aspen Hysys 8.4 is applied in order to process the modeling. All assumptions for modeling are based on (Boyano, Blanco-Marigorta, Morosuk, & Tsatsaronis, 2011): Use of methane reactive instead of natural gas.

- All gaseous mixtures are modeled based on inert gas.
- The composition of air includes 21% oxygen and 79% nitrogen.

- Composition is modeled adiabatically in constant pressure.

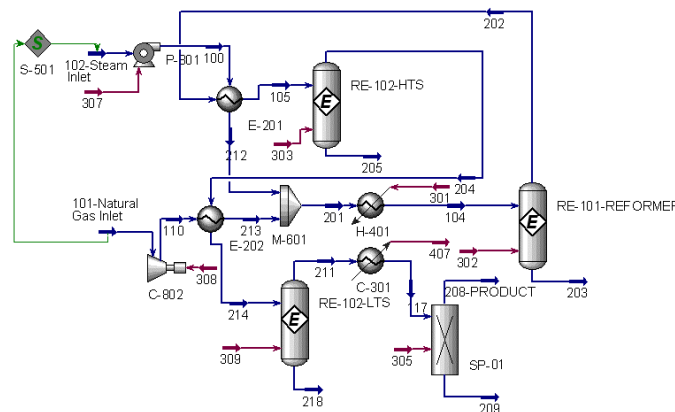
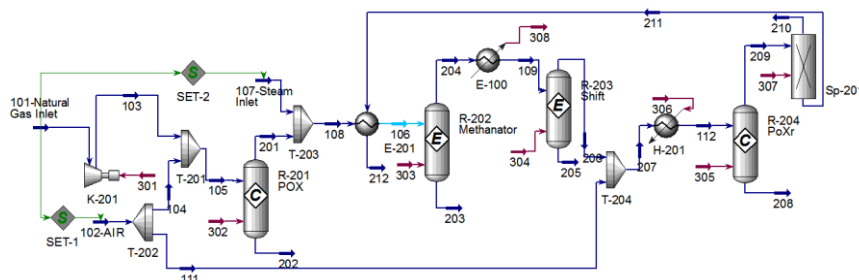
- The steam to methane ratio is $S/C=2.88$, $P_{Reform}=10.13\text{bar}$ and $T_{Reform}=540^\circ\text{C}$.

- Carbon is not deposited.
- Conversion coefficients are 83% and 10% for methane and carbon monoxide, respectively.

5.1. Simulation

State equation of Peng Robinson is applied to implement the simulation. Since some active materials in the reaction are of polar materials and all reactions are performed in gas phase, so state equation is applied. The active materials involved in reaction consist of: methane, carbon dioxide, carbon monoxide, hydrogen and water.

The temperature of output flow of reformer is cooled to appropriate temperature for next reactor by adding cooler. This is essential because of exothermic nature of reaction in this reactor. Amine unit is added to this simulation for removing polluting gases. In this unit, having lower temperature as much as possible is better in order to provide absorption. Heater is used to reach the feed temperature up to methanator reactor temperature.

**Figure 4.** Steam-Methane Reforming Process**Figure 5.** Oxidation Process of Methane-Steam POXR

5.2. Validation

In order to analyze the operation of this performed model, simulation results are obtained through Hysys software and numerical values are shown with basic model adopted for POXR and SMR processes as follows:

Table 3. Primary Results of Flows, Simulation of Aspen Hysys8.4 Software for SMR Reaction

SMR (Model)			
Stream No.	T(°K)	Molar Entropy [kJ/kgmole-C]	Molar Enthalpy [kJ/kgmole]
104	1526	226	-140800
202	1496	180.5	-55610
105	611	149.7	-86420
204	783	154.8	-84820
214	735	152.7	-86460
211	373	121.2	-84170

SMR (Base Case)		
T(°K)	Molar Entropy [kJ/kgmole-C]	Molar Enthalpy [kJ/kgmole]
1253	170.9	-78682
1223	169.2	-73256
338	111.2	-89320
510	142.3	-81370
455	137.2	-98310
465	139.2	-92320

6. Exergy Analysis

Exergy analysis is run based on previous methods and here the calculation of internal/external values of trivial/non-trivial parts of exergy destruction is assessed for

each part. Additional oxygen is consumed in order to lower the effective temperature in the process. The occurred conversion at 550°C is 39% at steam to carbon (S/C) molar ratio of 2.88. Efficiency of H₂ and Co for steam reforming oxidation reaction is calculated in the following. Exergy and heat efficiency from reformer temperature are evaluated in specific S/C ratio.

Though, differences in S/C molar ratio show partial influences on efficiency, reformer temperature highly affects efficiency. Because of having high endothermic energy level of SMR process reactors, an endothermic process is restricted to heat transfer. POXR process is an exothermic process. Because SMR process is an endothermic reaction, the required heat for initiating and preparing reaction is supplied from internal and external resources. Therefore, the temperature of oxidation process of steam-from-methane reform is considered as 540K by the assumption of sufficient internal energy and thermodynamic ir-reversibility in small reactors. Among the methods of hydrogen production from natural gas, Steam methane reform (SMR) and partial oxidation of methane (POXR) are assessed in this article, and SMR technology is categorized in endothermic processes and POXR is in exothermic processes (Katiyar, Kumar, & Kumar, 2013). Pressure drop in heat exchanger is assumed as 5 bar.

The process flow is uniform and stable. The RE-101 reactor, diagram 4, Reform1 reaction operate at 760°C range. Temperature range of reactions Shift 1 and Meth 1 is within 280 and 540 °C. When, reaction temperature increases, the amount of methane mixture is reduced, while output hydrogen mole is increased.

The oxygen injected into methane and steam in the catalyst reactor bed leads to steam and methane oxidation in reformer reactor where Co, Co₂ and H₂ are yield.

Exergy is in each flow determined as follows provided that the temperature is in physical balance:

Table 4. Primary Results of Flows, Simulation of Aspen Hysys8.4 Software for POXR Reaction

POXR(MODEL)				POXR(Base Case)		
Stream No.	T(°K)	Molar Entropy [kJ/kgmole-C]	Molar Enthalpy [kJ/kgmole]	T(°K)	Molar Entropy [kJ/kgmole-C]	Molar Enthalpy [kJ/kgmole]
105	294	77	-93634	303	81	-94000
201	687	172	-29103	773	180	-29000
106	1223	199	-25978	1223	199	-26000
204	909	180	-28138	923	195	-28000
109	573	166	-38653	623	172	-38000
206	629	168	-39671	632	173	-38800

Table 5. Values of Chemical Exergy for Participating Materials in Chemical Reaction

Substance	Chemical Exergy (Kj/mol)	Substance	Chemical Exergy (Kj/mol)
$H_2(g)$	235.39	$CH_4(g)$	832.4
$CO(g)$	275.55	$O_2(g)$	3.94
$CO_2(g)$	20.11	$H_2O(g)$	8.58

Table 6. Results of Flows Exergy, Simulation of Aspen Hysys 8.4 Software

SMR				POXR			
Stream No.	Ex. Phys. [KW]	Ex. Chem. [KW]	Mass Exergy [MW]	Stream No.	Ex. Phys. [KW]	Ex. Chem. [KW]	Mass Exergy [MW]
104	89,640	940,001	1,029.8	105	15,200	531,800	547.0
202	115,690	1,084,090	1,200.6	201	48,300	1,222,100	1,270.4
105	71,220	1,084,070	1,155.9	106	73,000	981,800	9,891.0
204	94,510	1,064,090	1,159.4	204	60,200	1,222,400	1,282.6
214	87,600	1,064,080	1,152.4	109	36,500	1,118,500	1,155.0
211	46,020	1,054,010	1,100.2	206	79,700	1,318,500	1,398.2
				112	53,400	1,213,400	1,266.8
				209	34,100	1,010,800	1,044.9

Physical exergy is calculated through Eq. (2):

$$Ex_{phy} = \Delta H - T_0 \Delta S \quad (2)$$

The chemical exergy values and exergy destruction are through Eq. (3 and 4):

$$Ex_{chem} = \sum X_i Ex_{chem,i} + \bar{R}T_0 \sum X_i \ln X_i \quad (3)$$

$$Ex_{dest} = T_0 S_{gen} \quad (4)$$

where, S_{gen} represents the production entropy. The exergy values of input and output flows are calculated for methane, steam and oxygen in input flow and the five components of methane, steam, hydrogen, carbon monoxide and carbon dioxide in output flow. Exergy efficiency is calculated subject to influence of effective operational parameters where reforming temperature and S/C molar ratio of feeding flow are involved, Table 10.

Table 7. Exergy of Equipment Based on Input and Output Exergy

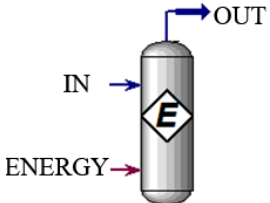
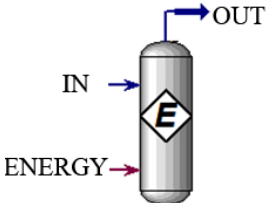
Type	Equipment	Exergy	Exergy efficiency
Shift Reactor		$Ex_f = [m_{in,co} \dot{e}_{in,co} - m_{out,co} \dot{e}_{out,co} + m_{in,H_2O} \dot{e}_{in,H_2O} - m_{out,H_2O} \dot{e}_{out,H_2O} + m_{in,CH_4} \dot{e}_{in,CH_4} - m_{out,CH_4} \dot{e}_{out,CH_4} + m_{in,CO_2} \dot{e}_{in,CO_2} - m_{out,CO_2} \dot{e}_{out,CO_2}]_{ch}$ $Ex_p = [m_{in,H_2} \dot{e}_{in,H_2} - m_{out,H_2} \dot{e}_{out,H_2} + \dot{E}_{out,water} - \dot{E}_{in,water}]$	$\eta = \frac{Ex_p}{Ex_f}$
Reformer & POX Reactor		$Ex_f = E_{energy}$ $Ex_p = Ex_{OUT} - Ex_{IN}$	$\eta = \frac{Ex_{OUT} - Ex_{IN}}{Ex_{in}}$

Table 8. Exergy of Equipment Using Simulated Values for POXR Reaction

Equipment name	Type	Ex-in (MW)	Ex-out (MW)	Ex _{D,K} (MW)	y _K (%)	$\eta = \frac{Ex_p}{Ex_f}$
R-203 Shift	Equilibrium Reactor	2038.2	923.3	1114.9	1.71%	45.3%
R-202 Meth.	Equilibrium Reactor	23.4	8.7	14.7	2.10%	37.1%
R-201 POX	Conversion Reactor	1462.3	291	1171.3	0.08%	19.9%
R-204 POXR	Conversion Reactor	5735.0	2804.4	2930.6	1.11%	48.9%

Table 9. Exergy of Equipment Using Simulated Values for SMR Reaction

Equipment name	Type	Ex-in (MW)	Ex-out (MW)	Ex _{D,K} (MW)	y _K (%)	$\eta = \frac{Ex_p}{Ex_f}$	η (Base case)
RC-101	Equilibrium Reactor	78.056	62.750	15.305	1.38%	80.39%	47.3%
RE-102-HTS	Equilibrium Reactor	177.69	157.09	20.602	1.86%	88.41%	35.1%
RE-103-LTS	Equilibrium Reactor	101.79	90.164	11.626	1.05%	88.58%	48.5%

Table 10. Calculation of Heat Efficiency and Exergetic Efficiency

		POXR		SMR	
		S/C=2.88 930C	S/C=2.55 970C	S/C=2.55 520C	S/C=2.88 540C
Inlet flow (mol/mol H ₂)	Methane	0.46	0.46	0.44	0.34
	Steam	1.32	1.17	1.12	0.97
	Air	0.65	0.62	-	-
Outlet flow (mol/mol H ₂)	H ₂	1	1	1	1
	Outlet gas	5.5	5.3	0.31	0.25
Thermal Efficiency (%)		80.5%	80.03%	78.7%	79%
Exergy Efficiency (%)		69.1%	67.3%	65.9%	67.2%

It is observed that exergy efficiency at high temperature and S/C molar ratio and constant input flow the POXR process is 88.4% with a 53.3% increase in comparison with reference reaction which is assessed as 35.1%. High exergy efficiency is not available in real condition, indicating that in this term and cause the high price to all of the system.

7. Results

Hydrogen efficiency increases by an increase in temperature due to having endothermic process of methane oxidation and exothermic steam reform in methane conversion. Hydrogen efficiency of oxidation reforming process compared to SMR process is lower in similar conditions, and this difference is not considerable. Although, the differences in S/C

molar ratios show partial influence on efficiency, while reformer temperature highly affects efficiency.

A change in the volumes of input temperature and mole, leads to changes in heat efficiency in both processes, Table 10 (Chein et al., 2012), (Tzanetis, Martavaltzi, & Lemonidou, 2012), (Hajjaji et al., 2012).

Exergy destruction decreases at high temperature and unit molar ratio. The highest rate of produced hydrogen occurs at 540°C. An increase in reactor temperature (shift) from 540°C leads to an increase in heat necessary for reaction which in turn, decrease process efficiency. The molar changes of mixing components in terms of temperature increase are shown in Fig. (6).

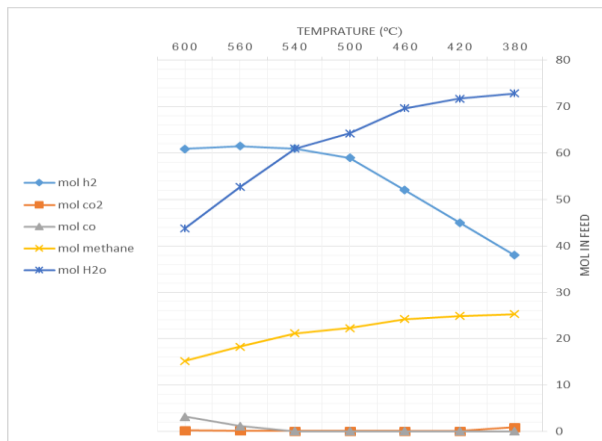


Figure 6. Molar Changes of Mixing Components in Terms of Temperature in SMR Process

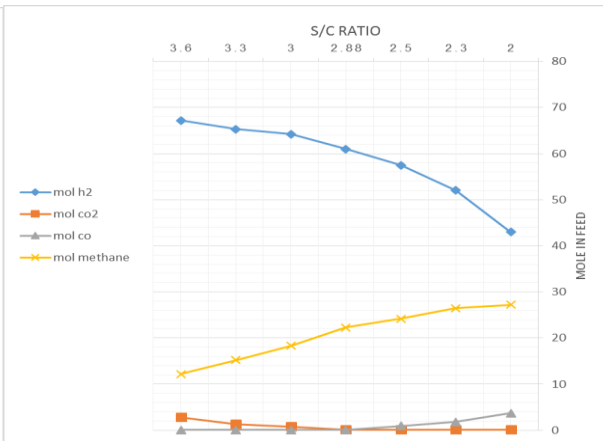


Figure 7. Molar Changes of Mixing Components in Terms of S/C Ratio in SMR Process in Isothermal Conditions

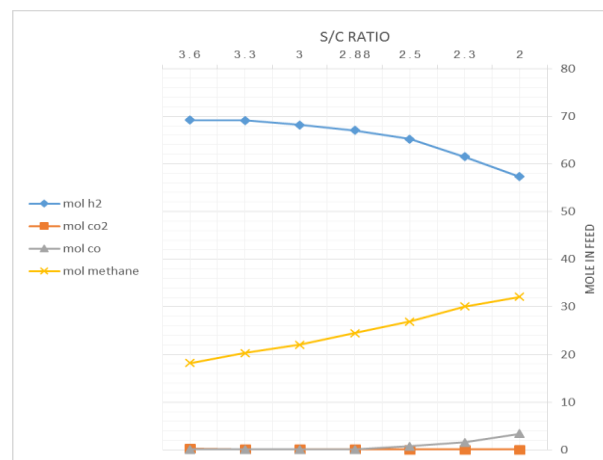


Figure 8. Molar Changes of Mixing Components in Terms of S/C Ratio in POXR Process in Isothermal Conditions $T_{Reactor} = 930^{\circ}\text{C}$, $P_{Reactor} = 1.3 \text{ bar}$

The effect of reformer temperature on the concentration in POXR reaction is shown in Fig. 8. Methane and carbon dioxide are the main products at low temperature and the level of produced hydrogen mole is low. With an increase in the temperature of reformer, the level of output methane is decreased, while the level of output hydrogen increase. The highest level of output hydrogen is at 930°C for POXR reaction. An increase in reformer temperature above 930°C decreases efficiency. An increase in S/C ratio generate higher heat for evaporation and required energy for pumps; an increase in hydrogen output is not cost effective in molar ratios higher than 4.

The balance of mass and energy for both processes is presented in Table 10. The results from mass balance reveal that each mole ratio of hydrogen production for other participating materials. The results indicate that for producing one mole of methane gas in POXR process, 1.32 mole of methane is required which is lower compared to SMR reaction with 1.56 value. The amount of consumed methane in generating steam is reduced by a reduction in reform temperature which finally results in an increase in input methane consumption with a decrease in feeding materials' ratio. The heat efficiency of these processes, as observed in Table 10, decrease with a decrease in temperature and the feeding material ratio.

The exergy values of flows for both processes are tabulated in Table 6. The mean input exergy of POXR reaction is 421 kJ/Kg which compared to SMR process with the 970 kJ/Kg in volume is better. It can be deduced that evolutionary studies efforts must focus on decreasing exergy inside reformers, heat converters and recovery of a part of output flow exergy.

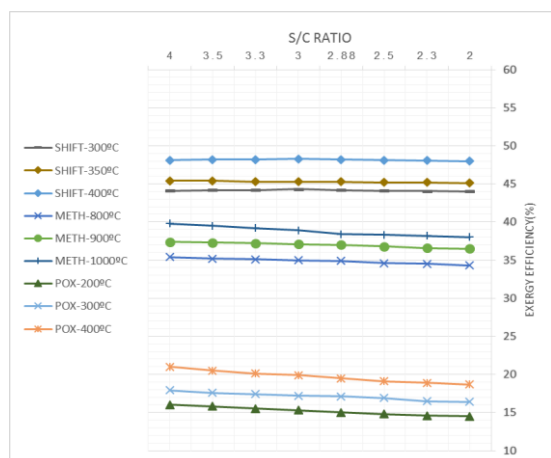


Figure 9. Changes in Exergy Efficiency with the Changes of S/C and Temperature for POXR Process Reactors

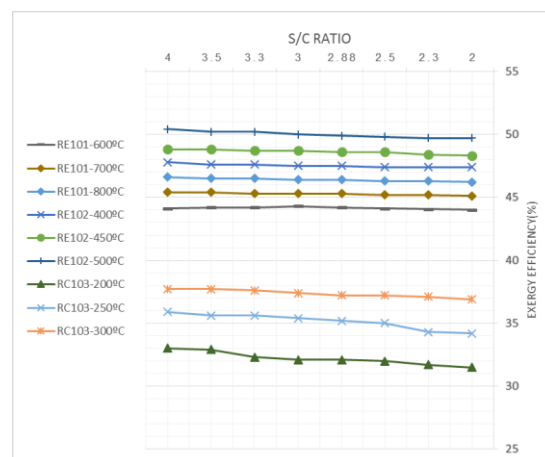


Figure 10. Changes in Exergy Efficiency with the Changes in S/C and Temperature for SMR-Process Reactors

As observed in Figs. (4 and 5) that the changes in S/C have no considerable influence on exergy efficiency.

8. Conclusion

In this article, applications and analysis of energy and exergy are assessed for steam-methane reformer of POXR process. The obtained results indicate that there exist the potential for improving exergy properties in POX and Methanator reactors; therefore, considering exergy efficiency in changes in thermodynamic properties of system deems important.

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