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COMPARISON OF VARIOUS REFORMER TYPES BY USING EXERGY ANALYSIS METHOD

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Abstract

Exergical analysis of four reforming processes comprising two stand-alone autothermal reformers (ATR) and top fired reformers (TFR) plus their combination forms as a parallel and series arrangements have been investigated in the present article. The coupled mathematical code in the Visual Basic program and Aspen HYSYS process simulator linked together in order to calculate physical and chemical exergies of industrial plants streams. Four distinct key parameters including dry productivity, exergy loss to dry productivity ratio, fuel consumption, and CO_2 emission have been considered to compare all the reformers arrangements together. The maximum and minimum dry productivity among all reformers belongs to TFR (86058 kg/hr) and parallel mode (73220 kg/hr), respectively. The exergy loss to dry productivity ratio for TFR, ATR, series and parallel modes is 1.88, 0.46, 0.73 and 0.57, respectively. It was shown that, although single ATR has minimum exergy loss to dry productivity ratio, no undesirable CO_2 emission and does not consume fuel, but it utilizes high cost O_2 as an oxidant agent which demand separate oxygen plant. Also, parallel reformer arrangement has consumed around 57% more fuel than series arrangement. Furthermore, it was concluded that high consumption of steam rate in processes would increase the possibility of exergy loss.

Keywords: : Synthesis gas; Aspen HYSYS; Exergy analysis; Reformer arrangement; ATR.

1. Introduction

Nowadays, environmental pollution and public health problem caused by fossil-fuel burning challenge scientist to find alternative environmentally friendly fuel resources. No pollution emissions, production from diverse primary energy sources, such as hydrocarbons, biomass, water or solar energy have introduced hydrogen as an attractive alternative energy source in recent decades [1]. Petroleum refining and petrochemical industries especially ammonia and methanol production plants are the largest sectors that consume hydrogen as a feedstock. Various processes such as coal and biomass gasification, water electrolysis, photo-electrolysis, photo-dissociation and biological operation can produce hydrogen. Among these procedures, steam methane reforming (SMR) is one of the most promising and commonly used processes for large hydrogen production with more than 80 years of history [2]. At the steam reforming unit synthesis gas, i.e., mixture hydrogen and carbon monoxide, is produced. Generally, the process scheme comprises reforming, water-gas shift, CO_2 removal by amine solution and methanation units. The synthesis gas production from hydrocarbon resources is accomplished by two well-known primary and secondary reformers. Steam methane reforming (SMR) and autothermal reforming (ATR) are two industrial examples of primary and secondary reformers, respecttively [3]. Generally, the different routes of producing syngas are: autothermal reforming (ATR), steam methane reforming (SMR), a combination of ATR and SMR which is called combined reforming, and heat exchange reforming involving series and parallel arrangements. It is obvious that combination of both primary and secondary reformers enjoys the benefits of an individual reformer as it is commercialized in ammonia manufacturing plants. Combination of these reformers has been installed for synthesis gas production in facilities such as Mossel Bay (South Africa), Bintulu (Malaysia), Oryx (Qatar), Pearl GTL (Qatar), and Escravos (Nigeria) [31]. The high initial investment cost is the problem of combination process. High productivity, low energy uses or consumed fuel, and minimum release of a component such as carbon dioxide are the important factors which should be considered in synthesis gas production units. Progress and optimization in synthesis gas production processes are essential for large scale production of these valuable materials as a feed for gas to liquid (GTL), ammonia or methanol production plants [4].

Thermodynamic analysis, particularly exergy analysis, appears to be an efficient tool to evaluate the sustainability of a process, system design, analysis and optimization of industrial systems. Totally, exergy analysis is used to recognize the location, magnitude, and sources of thermodynamic deficiencies, and to optimize the usage of energy resources regard to economic and environmental aspects [5].

There are relatively few studies focused on the syngas units comprising of ATR and SMR in series and parallel arrangements. Bakkerud investigates the combination of HTER (Haldor-Topose exchanger reformer) and ATR reformer in series and parallel arrangement for GTL application by changing steam to carbon (S/C) ratio [6]. Since in the series arrangement, all gas passes through the steam reforming unit, and then through ATR, steam reforming catalyst may set for lower S/C ratio. Independent feeding of two reformers in parallel arrangements giving freedom to optimize S/C ratio individually. Rafiee et al. studied the S/C ratio, purge ratio, amount of tail gas recycled to Fisher-Tropsch (F-T) synthesis units and reactor volume in a GTL plant for configurations of SMR-ATR plus ATR-GHR (gas-heated reformers) series arrangement [7]. The optimization results indicate that installing a steam methane reformer in the syngas production unit will reduce the total oxygen consumption and make the oxygen plant smaller. Ebrahimi et al. simulated four cases of a single SMR, a single ATR, combined series and parallel arrangements for industrial case study and optimization issue is applied to the systems for choosing the optimum conditions [8]. It was shown that the important stream is one that connects SMR to the ATR for the optimized production of syngas. Moreover, the series configuration consumes lower fuel and releases lower amount of CO_2 emission compared to the parallel arrangement.

Up to best of our knowledge, an exergetic comparison of various reformer types for production of synthesis gaseous has not been considered in the previous researches. In the present study, a straightforward method for calculating physical and chemical exergy of various streams inside the industrial plant for a different arrangement of primary and secondary reformers (single autothermal (ATR), single top fired reformer (TFR), parallel (ATR-TFR), series (ATR-TFR)) was performed. The mathematical code in Visual Basic programming was linked to Aspen HYSYS process simulator to evaluate exergy analysis for all streams inside flowsheet. Exergy balance is resulting in more insight into the nature of irreversibilities and exergy loss points associated with specific processes. It was shown that the ATR case is preferable reformer due to the low exergy loss object.

2. Exergy-definitions

Exergy is defined as the maximum obtainable amount of work from the mass of fluid which can be obtained as a process is changed reversibly from the given (existing) state to a state of equilibrium (zero) with the environment, or the maximum work that can be obtained from any quantity of energy [9]. Exergy balance relies on the decomposition of input and output streams in material, work, and heat streams. In addition, output streams can be classified into waste and useful streams [10]. The waste stream includes all streams pushed to the environment without recycling or reusing, while useful streams are heat or material used in the downstream process. A General Grassmann representation of a process or generic system studied through exergy balances is illustrated in Figure 1.

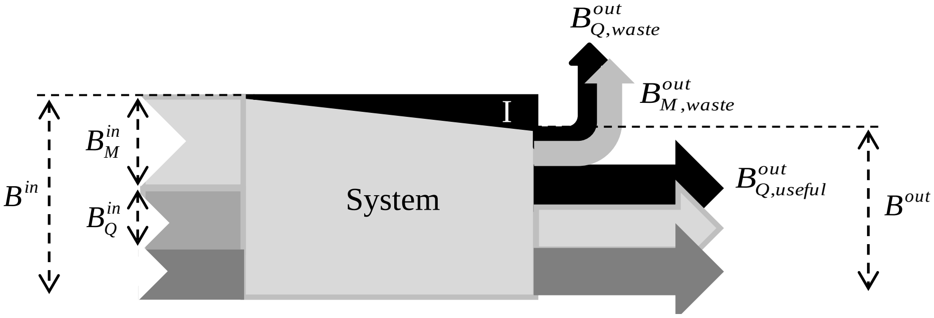


Fig. 1. Overview Grossman diagrams for process or system

In this system that can be either considered as a single unit operation, an energy balance can be written as follows [10]:

$$H_M^{in} + Q^{in} + W^{in} = H_M^{out} + Q^{out} + W^{out} \tag{1}$$

In the above equation, "H," "Q," and "W" are enthalpy, heat, and work respectively. In exergy balance, there is "internal exergy loss" which was shown in Figure 1 by the term I, corres-ponding to the exergy destroyed inside the system because of irreversibilities of the process:

$$B^{in} = B^{out} + I \tag{2}$$

In the above equation, total exergy input (B^{in}) and total exergy output (B^{out}) are respectively given by the sum of input and output exergies associated with material (NS_M streams), work (NS_W streams) and heat streams (NS_Q streams):

$$B^{in} = \sum_{i=1}^{NS_M^{in}} B_{M,i}^{in} + \sum_{i=1}^{NS_Q^{in}} B_{Q,i}^{in} + \sum_{i=1}^{NS_W^{in}} B_{W,i}^{in} \tag{3}$$

$$B^{out} = \sum_{i=1}^{NS_M^{out}} B_{M,i}^{in} + \sum_{i=1}^{NS_Q^{out}} B_{Q,i}^{in} + \sum_{i=1}^{NS_W^{out}} B_{W,i}^{in} \tag{4}$$

Regarding the "useful-waste" concept, the equation (2) can be expressed in the following form:

$$B^{in} = B_{useful}^{out} + \underline{B_{waste}^{out}} + I \tag{5}$$

where the underlined term is called "external exergy loss." Assuming that the exergy flow corresponding to work output is always useful exergy, the exergy balance can finally be expressed as follows:

$$\sum_{i=1}^{NS_M^{in}} B_{M,i}^{in} + \sum_{i=1}^{NS_Q^{in}} B_{Q,i}^{in} + \sum_{i=1}^{NS_W^{in}} B_{W,i}^{in} = \sum_{i=1}^{NS_{M,useful}^{out}} B_{M,useful,i}^{out} + \sum_{i=1}^{NS_{M,waste}^{out}} B_{M,waste,i}^{out} + \sum_{i=1}^{NS_{Q,useful}^{out}} B_{Q,useful,i}^{out} + \sum_{i=1}^{NS_{Q,waste}^{out}} B_{Q,waste,i}^{out} + \sum_{i=1}^{NS_W^{out}} B_{W,i}^{out} + I \tag{6}$$

Establishment of exergy balances on a given system needs to evaluate all the terms of above equation precisely. Classification of useful stream form waste ones is an important factor which depends on the recognition of the whole process accurately [10].

2.1. Exergy calculation methodology

Exergy similar to energy can be divided into physical, chemical, potential, and kinetic exergies. In the absence of electrical, magnetic, surface tension and nuclear effects, total exergy of a given system is the summation of four distinct elements [9]:

$$E_{sys} = E_{sys}^{Ph} + E_{sys}^{Ch} + E_{sys}^{Kn} + E_{sys}^{Pt} \tag{7}$$

In the above equation, E^{Ph} , E^{Ch}, E^{Kn} and $E^{Pt}$are physical exergy, chemical exergy, kinetic exergy and potential exergy respectively. Each of these exergies defined as follows:

$$E_{sys}^{Kn} = \frac{1}{2} m\vec{V}^2 \tag{8}$$

$$E_{sys}^{Pt} = mgz \tag{9}$$

$$E_{sys}^{Ph} = (H - H_0) - T_0(S - S_0) \tag{10}$$

$$E_{sys}^{Ch} = \sum_i x_i \varepsilon_i + \int RT_0 \sum_i x_i ln x_i \tag{11}$$

In the equations of (8) and (9), parameters V and z is the velocity of the stream relative to the surface of the earth and altitude of the stream above the sea level respectively [9]. Generally, the share of these two components from total exergy is normally negligible. Hence they can be disregarded. In the Equation (10), parameters h and S are the enthalpy and entropy of the substance at actual conditions, and h_0 and S_0 are the enthalpy and entropy of the substance at reference conditions, respectively. In the present work, the reference temperature and pressure are defined as $T_0 = 298.15$ K and $P_0 = 1.013$ bar. Chemical exergy originates from the difference between the chemical potentials when a substance is changed from reference conditions to the chemical equilibrium state. In the equation (11), x_i is the fraction of species i in the mixture of gases, ε_i is the standard chemical exergy of the same species, and R is the universal gas constant. A comprehensive discussion on various types of exergy calculation is given by Sato [11] and Hinderink *et al.* [12]. In the present article, two types of physical and chemical exergies were considered for each species in the inlet and outlet streams.

Exergy analysis in the field of reforming units has been studied by different researchers. For instance, Atsonios *et al.* [13] studied exergy analysis of a hydrogen-fired combined cycle with pre-combustion carbon capture. Chen *et al.* [14] investigated hydrogen production through SMR from both exergy efficiency and CO_2 emission points of view. Their sensitivity analysis shows a reverse relationship between CO_2 emission and system efficiency. Hajjaji and *et al.* [5] have been used exergy analysis to calculate the energy consumption of an SMR process. Based on the exergetic results and identifying the thermodynamic imperfections of the process, they have proposed a more efficient process by incorporating a third economizer (heat exchanger) to the original process for waste heat recovery. In others work by Simpson and Lutz [15], the performance of hydrogen production via SMR was evaluated using exergy analysis with emphasis on exergy flows, destruction, waste, and efficiencies. Their investigation shows the majority of the exergy destruction occurs due to the high irreversibility of chemical reactions and heat transfer. A brief review on hydrocarbon reforming will be presented in the following section.

3. Hydrocarbon reforming

3.1. Primary reformers

As it was emphasized before, SMR is considered as an industrial example of primary reformers [2]. Reforming process produces syngas with an H_2/CO ratio in the range of about 2.2 to 4.848 depending on the feed composition, CO_2 recycle and operating conditions such as pressure and temperature. Generally, steam Methane Reforming proceeds in two steps, the reforming reaction (Eq. 12), which is strongly endothermic (206 kJ.mol^{-1}), and the water gas shift (Eq. 13), which is slightly exothermic (41 kJ.mol^{-1}): [4b,8].

$$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \text{(steam methane reforming, } \Delta H = 206.3\ kJ\ mol^{-1}\text{)} \qquad (12)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \qquad \text{(water gas shift, } \Delta H = -41.2\ kJ\ mol^{-1}\text{)} \qquad (13)$$

The comparison of the heat of reaction values indicates that the net reaction is endothermic. For this reason, additional energy has to be provided by external heating. It means that the tubular catalytic reactor needs a heat source, generated by a furnace. Mostly, industrial furnaces that were used for reforming process were classified into four groups: top-fired, terraced-wall, bottom-fired and side-fired. Usually, the top-fired primary reformer is used for methanol and ammonia plants with large single train capacity containing up to 1000 catalyst tubes. Nickel and cobalt in the form of thick-walled raschig rings with several holes are the best catalysts for SMR, and the overall rate in steam reforming is limited by the heat transfer, at high tempe-ratures. The product of SMR is sent to the product line or enters to the secondary reformer. In the present paper, the primary reformer is presumed SMR with a top-fired furnace.

3.2. Secondary reformers

Generally, the conversion of hydrocarbon feed in primary reformers is not complete, specially, for heavy feed stock such as gasoil or naphtha. Conventionally, the product of primary reformers was sent to other reformers entitled "secondary reformer." Industrial ATR used in the present work consist of two sections: 1) Partial oxidation chamber (POX); 2) fixed bed catalytic reformer. The main reaction occurred in the POX chamber stated below (Eq. 15) [3b]:

$$CH_4 + 0.5O_2 \rightarrow CO + 2H_2O \qquad \text{(Partial Oxidation,} \ \Delta H = -520\ kJ\ mol^{-1}) \qquad (15)$$

Preheated natural gas and oxygen (separated from the air) are fed to the reactor and mixed by a burner and finally react in a turbulent diffusion flame. Due to fast exothermic combustion reactions, all oxygen is consumed with methane completely. In contrast to ATR, SMR has a bulky installation, due to the large SMR furnace with catalyst tubes and large flue gas heat recovery section. However, SMR process is preferred for the production of hydrogen, as a result of the high H_2/CO molar ratio (3-5) compared to ATR (1.6-2.65).

3.3. Combined configuration with different reformer arrangement

Poor economy of scale, large input heat requirement and production of syngas with at least 3:1 hydrogen to carbon monoxide ratio prevent utilizing standalone SMR for large scale industrial application such as GTL [7] Also, high cost feature of the ATR process is not preferable. Adding secondary reformer to primary one could convert the probable un-reacted methane remained from SMR and adjusted the H_2/CO ratio based on the suitable application such as methanol, F-T, and ammonia synthesis. Figure 4 and 5 depict the parallel and series arrangements of SMR and ATR reformers, respectively [7-8,16]. In the parallel type, the hydrocarbon feed such as natural gas is divided into two distinct parts: one part is conducted into primary reformer (TFR) directly, another portion is sent to secondary one (ATR), and finally the output products of two reformers are connected together. In the series form, the output product of TFR and fresh hydrocarbon mix together with relevant ratio and convey to the secondary reformer. In the present paper, exergy analysis of both series and parallel schemes are compared together.

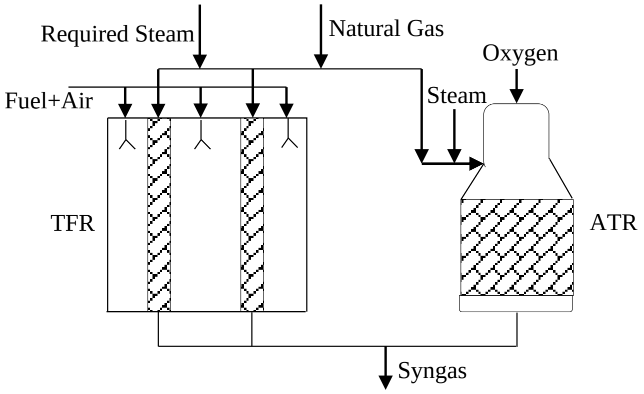


Fig. 2. Schematic diagram of parallel reformers arrangement

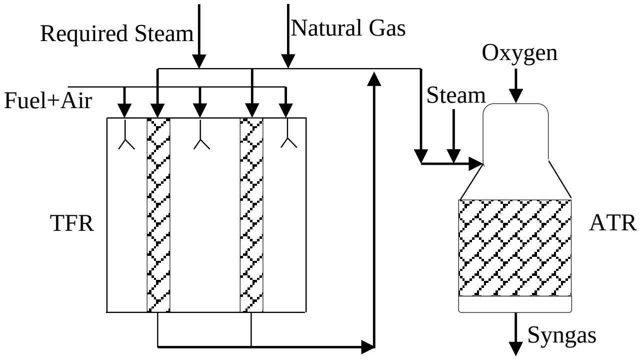
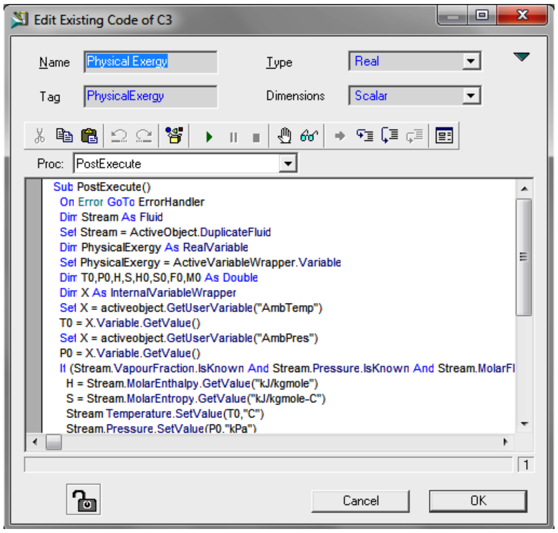


Fig. 3. Schematic diagram of series reformers arrangement

4. Exergy as New User Property in Aspen HYSYS

Process simulator software such as Aspen HYSYS does not calculate any form of exergy in the main stream flowsheet, hence, the mathematical code in visual basic programming provided and linked to Aspen HYSYS as a new user variable worksheet [17].

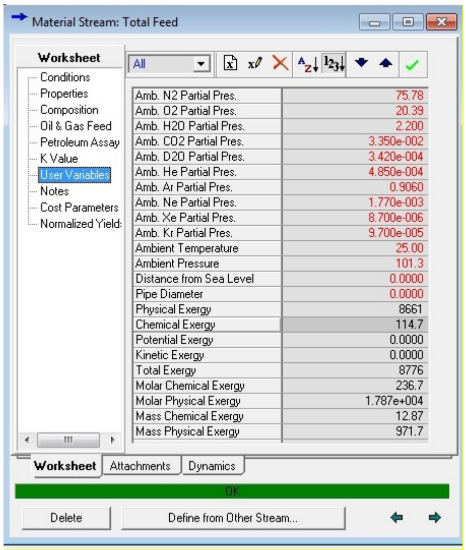
Figure 4 and 5 shows the overview of visual basic codes environment related to the user variables entitled "Chemical Exergy," "Physical Exergy," Kinetic Exergy" and "Potential Exergy." Neglecting the kinetic and potential exergies, total exergy of the specific stream would be the sum of the physical and chemical exergies.



Name: Physical Exergy
Type: Real
Tag: PhysicalExergy
Dimensions: Scalar
Proc: PostExecute

```
Sub PostExecute()
 On Error GoTo ErrorHandler
 Dim Stream As Fluid
 Set Stream = ActiveObject.DuplicateFluid
 Dim PhysicalExergy As RealVariable
 Set PhysicalExergy = ActiveVariableWrapper.Variable
 Dim T0,P0,H,S,H0,S0,F0,M0 As Double
 Dim X As InternalVariableWrapper
 Set X = activeobject.GetUserVariable("AmbTemp")
 T0 = X.Variable.GetValue()
 Set X = activeobject.GetUserVariable("AmbPres")
 P0 = X.Variable.GetValue()
 If (Stream.VapourFraction.IsKnown And Stream.Pressure.IsKnown And Stream.MolarFl
  H = Stream.MolarEnthalpy.GetValue("kJ/kgmole")
  S = Stream.MolarEntropy.GetValue("kJ/kgmole-C")
  Stream Temperature.SetValue(T0,"C")
  Stream.Pressure.SetValue(P0."kPa")
```

Fig. 4. Overview of User Variable coding environment



Amb. N2 Partial Pres.	75.78
Amb. O2 Partial Pres.	20.39
Amb. H2O Partial Pres.	2.200
Amb. CO2 Partial Pres.	3.350e-002
Amb. D2O Partial Pres.	3.420e-004
Amb. He Partial Pres.	4.850e-004
Amb. Ar Partial Pres.	0.9060
Amb. Ne Partial Pres.	1.770e-003
Amb. Xe Partial Pres.	8.700e-006
Amb. Kr Partial Pres.	9.700e-005
Ambient Temperature	25.00
Ambient Pressure	101.3
Distance from Sea Level	0.0000
Pipe Diameter	0.0000
Physical Exergy	8661
Chemical Exergy	114.7
Potential Exergy	0.0000
Kinetic Exergy	0.0000
Total Exergy	8776
Molar Chemical Exergy	236.7
Molar Physical Exergy	1.787e+004
Mass Chemical Exergy	12.87
Mass Physical Exergy	971.7

Fig. 5. Overview of User Variable results page

5. Simulation procedure

In this study, the information of industrial ethylene plant feed stream was simulated by Aspen HYSYS software under steady state condition. The component list was completed by available constituents restricted to Table 1. The thermodynamic data (Fluid package) and phase behavior predictions of the material streams were obtained using the Soave–Redlich–Kwong equation of state. The primary reformer, SMR, was simulated by a library model equilibrium reactor with the three main reactions of (Eq. 12-14). Furthermore, first, Gibbs free energy minimization concept was used for partial oxidation reaction (POX) section of ATR and similar to SMR reformer, the catalytic bed section was simulated by an equilibrium reactor. Also, operational facilities such as heat exchangers, pumps, compressors and other equipment's were included in exergy analysis.

Table 1. Feed characteristics of simulation cases

Parameter name	Value (Unit)	Composition	Mole(%)
Temperature	500 (°C)	Ethane	3.2
Pressure	20 (bar)	Propane	1.9
Mass flow	39 086.46 (kg/hr)	i-Butane	0.0
Molar flow	1 745 (kmol/hr)	n-Butane	0.6
Composition	Mole (%)	i-Pentane	0.0
Hydrogen	0.0	n-Pentane	0.1
CO	0.0	n-Hexane	0.0
CO_2	25.1	H_2O	0.0
Nitrogen	4.2	Oxygen	0.0
Methane	65.0		

6. Results and discussion

Exergical analysis of four primary and secondary reformers arrangements including single SMR, single ATR, combined SMR and ATR in series and parallel forms in order to produce synthesis gas with an H_2/CO molar ratio of 1 has been performed in the present article. All the feed streams conditions such as temperature, pressure, composition, and flow rate are kept constant for all simulated cases.

Comparison of exergy loss for different reformers arrangements is presented in Table 2. According to this table, although TFR has the highest productivity rate (86058 $kg.hr^{-1}$), it consumes higher amount of fuel (1740 $kmol.hr^{-1}$) and release large quantity of anthropogenic greenhouse carbon dioxide (1809 $kmol.hr^{-1}$) into the atmosphere. On the other hand, ATR reformer has no undesirable CO_2 emission and does not consume fuel, but it utilizes high cost O_2 as an oxidant agent which demand separate oxygen plant. These findings are in a good agreement with earlier studies (10).

Table 2. Comparison of exergy loss for different arrangement of synthesis gas production

Parameter/arrangement	TFR	ATR	Series TFR–ATR	Parallel TFR–ATR	Min. /Max.
Productivity* ($kg.hr^{-1}$)	86 058	80 542	74 796	73 220	Parallel/TFR
Feed molar flow ($kmol.hr^{-1}$)	1 745	1 745	1 745	1 745	-
Consumed fuel($kmol.h^{-1}$)	1 740	0	522	820	ATR/TFR
Released CO_2($kmol.h^{-1}$)	1 809	0	148	375	ATR/TFR
H_2/CO ratio (mol/mol)	1.05	1.1	0.99	1.02	ATR/TFR
Physical exergy loss (W)	-162 113	-37 060	-54 758	-41 958	ATR/TFR
Chemical exergy loss (W)	148	93	105	86	TFR/Parallel
Total exergy loss (W)	-161 965	-36 968	-54 653	-41 872	ATR/TFR
Exergy Loss/Productivity ($W.kg^{-1}.s$)	1.88	0.46	0.73	0.57	ATR/TFR

Productivity has been reported on dry basis

The third row of Table 2 shows that parallel reformers arrangement has consumed around 57% more fuel than series arrangement. Although, physical exergy of series reformers are 31% more than parallel arrangement, however, the chemical exergy of parallel is 22% more than series ones. Investigation of total exergy loss which is the summation of physical and chemical exergies reveals that alone ATR and TFR have the minimum (-36968 W) and maximum (-161965 W) amount of total exergies respectively. The series and parallel arrangements lie between these two amounts. The last row of Table 2 represents the total exergy loss divided to dry productivity rate. Again, the ATR and TFR have assigned to the minimum (0.46) and maximum (1.88) amounts, and series (0.73) and parallel (0.57) arrangement are in the next ranks, respectively. Detailed exergy loss calculation data for studied cases have been presented in Tables 3-6. These tables have been classified into five columns. The first column shows the name of input and output of material and energy streams which have been connected to each arrangement mode. Second and third columns represent the values of physical and chemical exergies of related streams. Moreover, the fourth column corresponds to the summation of physical and chemical exergies of each stream, and finally, fifth ones are the fraction of total exergy of each stream to total input or output exergy. The exergy loss indicates the difference between input and output exergies. Table 3 present results of exergy analysis for single TFR. As it is obvious, required steam stream in TFR reformers has the highest fraction of total exergy around 76.81% (67441/87806) and air stream has the lowest existence exegy with 0.02% from input streams. Since the TFR reformer does not consume pure oxygen, the related exergy will be set to zero. Table 4 shows the exergy analysis of single ATR. No gas fuel is involved in ATR process, so the amount of gas fuel exergy will be zero. Again, input steam stream to ATR reformer has the highest value of total exergy about 56.98% and O_2 assigned to the minimum value around 3.99%. Comparison of Table 3 and 4 proves that alone ATR reformer has lower exergy loss (-36968 W) compared to TFR reformer (-161965 W). Also, it can be concluded that high consumption of steam rate in processes will increase the possibility of exergy loss. Perhaps, a sharp decrease in temperature and pressure of steam in the process is the reason for such behavior. As it was mentioned before, the advantages of ATR process compared to TFR are a lower initial investment and relatively no carbon dioxide emission, but investment on distinct air separation unit to provide expensive oxygen is accounts disadvantages. Moreover, it can be concluded that the alone TFR is preferable in accordance with high productivity object, but it has high exergy loss.

Table 3. Exergy analysis results for top fired reformer

	Physical Exergy	Chemical Exergy	Total Exergy	% of Total
Total Feed	8 775	115	8 890	10.12%
Refinery-CO_2	11 330	4	11 334	12.91%
Air	11	10	20	0.02%
Gas Fuel	4	116	120	0.14%
Steam	0	0	0	0.00%
Required Steam	67 424	17	67 441	76.81%
O_2	0	0	0	0.00%
Input Exergy	87 544	262	87 806	100%
Total Product	136 517	51	136 568	54.68%
Fuel gas	113 140	62	113 202	45.32%
Output Exergy	249 657	114	249 771	100%
Exergy loss	-162 113	148	-161 965	

Table 4. Exergy analysis results for autothermal reactor

	Physical Exergy	Chemical Exergy	Total Exergy	% of Total
Total Feed	8 661	115	8 776	15.82%
Refinery-CO_2	11 290	4	11 295	20.36%
Air	2	2	4	0.01%
Gas Fuel	1	23	24	0.04%
Steam	0	0	0	0.00%
Required Steam	33 712	8	33 721	60.77%
O_2	1 667	1	1 667	3.00%
Input Exergy	**55 333**	**153**	**55 486**	**100%**
Total Product	85 805	34	85 839	77.94%
Fuel gas	24 287	13	24 300	22.06%
Output Exergy	**110 092**	**47**	**110 139**	**100%**
Exergy loss	**-54 758**	**105**	**-54 653**	

Table 5 and 6 represent the detailed exergy analysis of series and parallel reformers arrangement respectively. Similar to previous single reformers, the highest fraction of total exergies attributed to the steam (and required steam) stream in both series and parallel arrangements with a percentage more than 60%. The values of total exergies for series and parallel reformers are between two single reformers. Additionally, comparison of Table 3, 5 and 6 shows that the total exergy of exit streams such as total product and gas fuel in TFR reformer are close to each other, but in series and the parallel arrangement has reverse behavior. Comparison of four key parameters for single TFR, single ATR, combined TFR and ATR in series and parallel arrangements depicts in figure 8. It is clear that all the parameters should be minimized except dry productivity. It can be inferred that TFR has highest productivity rate which is considered as a pros. However, exergy loss to dry productivity ratio consumed fuel and release CO_2 parameters are also in maximum values which are considered as cons. Overall view of figure 6 reveals that single ATR has a better position from series and parallel arrangements in all four key parameters. Although exergy loss to dry productivity ratio is slightly in favor of parallel arrangement, but series mode has higher productivity rate and lowers consumed fuel and released CO_2. So it seems that series arrangement which feeds of ATR is supplied by a mixture of both SMR product and the fresh, natural gas is a better choice than the parallel mode.

Table 5. Exergy analysis results for top fired with autothermal reactor in series arrangement

	Physical Exergy	Chemical Exergy	Total Exergy	% of Total
Total Feed	8 661	115	8 776	12.73%
Refinery-CO_2	11 290	4	11 295	16.38%
Air	2	2	4	0.01%
Gas Fuel	1	23	24	0.03%
Steam	14 047	4	14 050	20.37%
Required Steam	33 712	8	33 721	48.90%
O_2	1 092	0	1 092	1.58%
Input Exergy	**68 805**	**156**	**68 961**	**100%**
Total Product	87 222	57	87 279	78.75%
Fuel gas	23 541	13	23 554	21.25%
Output Exergy	**110 763**	**70**	**110 833**	**100%**
Exergy loss	**-41 958**	**86**	**-41 872**	

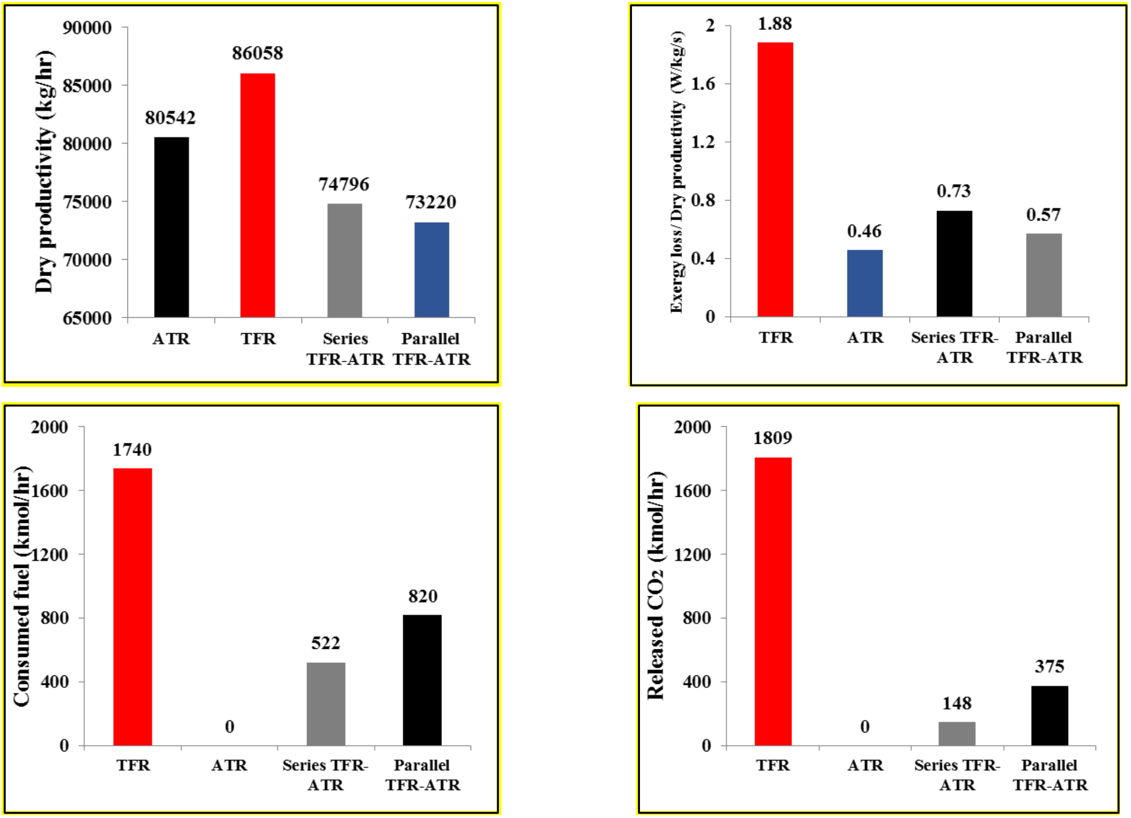


Fig. 6. Comparison of four key parameters in different studied cases: (a) Dry productivity; (b) Ratio of exergy loss to dry productivity; (c) Consumed fuel; (d). Released CO_2

Table 6. Exergy analysis results for top fired with autothermal reactor in parallel arrangement

	Physical Exergy	Chemical Exergy	Total Exergy	% of Total
Total Feed	8 661	115	8 776	12.73%
Refinery-CO_2	11 290	4	11 295	16.38%
Air	2	2	4	0.01%
Gas Fuel	1	23	24	0.03%
Steam	14 047	4	14 050	20.37%
Required Steam	33 712	8	33 721	48.90%
O_2	1 092	0	1 092	1.58%
Input Exergy	**68 805**	**156**	**68 961**	**100%**
Total Product	87 222	57	87 279	78.75%
Fuel gas	23 541	13	23 554	21.25%
Output Exergy	**110 763**	**70**	**110 833**	**100%**
Exergy loss	**-41 958**	**86**	**-41 872**	

7. Conclusion

In the present article, industrial synthesis gas production by some commercialized reformers such as SMR, as a primary reformer, ATR, as a secondary and their combination form in series and parallel arrangements were investigated. Several parameters such as productivity rate, fuel consumption, oxygen consumption, CO_2 released to atmosphere and exergy loss has been considered for selecting best case of syngas production. The exergy analysis regards as a powerful tool for analysis, evaluation, and improvement of thermal processes was applied to identify the magnitude and sources of thermodynamic inefficiencies of reformers arrangements which are not received proper attentions in previous studies. The mathematical code provided in the Visual Basic environment and linked to the Aspen-HYSYS as a user variable subroutine in order to calculate physical and chemical exergies of single TFR, a single ATR, combined series and parallel arrangements. Obtained conclusions revealed that single TFR is a preferable choice in accordance with productivity rate. Also, TFR has a maximum exergy loss per dry productivity ratio, fuel consumption and CO_2 emission to atmosphere among all other reformer arrangements which are not preferable to the point of process irreversibility and environmental conditions. No fuel consumption and CO_2 emission to the atmosphere in addition to minimum exergy loss to dry productivity ratio lead single ATR reformer seems to be the best choice for syngas production. From an economical point of view, ATR reformer requires expensive pure oxygen supplied from air separation unit. The dry productivity of series and parallel arrangements are lower that single reformers. In addition, the exergy loss to dry productivity ratio, fuel consumption, and CO_2 emission is between single TFR and single ATR. Finally, it was concluded that high consumption of steam in the processes would increase the possibility of exergy loss. It should be noted that among these reformers arrangements, single ATR uses the lowest amount of steam.

Nomenclature

ATR	*Autothermal*	*W*	*Work*
SMR	*Steam methane reforming*	*B*	*Energy Flow*
TFR	*Top fired reformer*	*E*	*Energy*
GTL	*Gas to Liquid*	*Ph*	*Physical*
S/C	*Steam to carbon ratio*	*Sys*	*System*
F-T	*Fisher-Tropsch*	*Kn*	*Kinetic*
In	*Input*	*Pt*	*Potential*
Out	*Output*	*E*	*Standard chemical exergy*
H	*Enthalpy*	*X*	*Mole fraction*
Q	*Heat*	*WGS*	*Water gas shift*

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