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Exergy analysis and flowsheet modification of PT. PUSRI II Palembang's reformer unit for the production of synthesis gas from natural gas

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ABSTRACT: Several processes which produce synthesis gas from natural gas have been analyzed by the exergy method. To minimize the exergy losses associated to chemical reaction, it is important to manage the exergy losses through the analysis, reconsidering the chemical path. A generally applicable and schematic way of performing exergy analysis and dealing with their results are illustrated. It is integrated to the modified flowsheeting reformer. As petrochemical industry in Indonesia, PT. Pupuk Sriwijaya II Palembang uses natural gas as a raw material to produce synthesis gas through the primary and the secondary reformers in a series. In the modified flowsheeting reformer, partial oxidation process has been added before the primary reformer and the secondary reformer has been eliminated from the process pathways. The exergy method of analysis has been implemented for each process, in order to calculate the exergies of the material streams along with the energy and mass-balance calculations both in the modified flowsheeting reformer and in a series process of the primary and the secondary reformers. And, the results of the calculations of the modified flowsheeting reformer in the process proposed modification are then compared to the results of the calculations of the series process of reformers in the existing conventional process. From the analysis, the overall exergy losses in a series process of the primary and secondary reformers can be reduced until 61.33%, by applying the modified flowsheeting reformer. © 2011 Curtin University of Technology and John Wiley & Sons, Ltd.

KEYWORDS: exergy analysis; flowsheet modification; reformer unit; partial oxidation; synthesis gas; natural gas

INTRODUCTION

Indonesia, as an agricultural country, still considers the agricultural sector as a significant contributor to its economy besides the growing industrial sector. Petrochemical is one of the industries, which is still developing in this country. PT. Pupuk Sriwijaya (PUSRI) II is the largest petrochemical plant in Palembang, Indonesia that produces fertilizers for the large agricultural sector.

In the production of fertilizers, natural gas is used as a raw material to generate synthesis gas as a base for forming ammonia and urea fertilizer. Synthesis gas is produced in the primary and the secondary reformer units. The two reformers require large amount of fuel and heat to achieve a synthesis gas conversion of only around 97.8%. In addition, exergy analysis

around the reformers in PT. PUSRI II shows that the exergy losses are definitely high. In this study, modification of the process through flowsheet simulation of reformer is been explored, in which a partial oxidation process has been added before the primary reformer. The secondary reformer has been eliminated from the process pathways. The flowsheet simulation enables the optimum process condition to be determined and the process with the minimum exergy losses for the production synthesis gas production to be selected.

EXERGY ANALYSIS METHOD

The method of exergy analysis is based on the second law of thermodynamics and the concept of irreversible production of entropy.[1] The method has found early development and application in the Soviet Union and Europe, primarily Germany and Poland. The earliest use of the word exergy has been attributed to Rant in 1956 by Bosjnakovic (1960), Trepp (1961) and Baehr

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(1962). Exergy has been generally referred to as work capacity or available work. The concept was initially introduced by Gibbs and Helmholtz for thermodynamic analysis of chemical systems. A review on the use of exergy in systems analysis since its early beginning has been provided in the early millennium year.[2] Bosnjakovic (1960) demonstrated the exergy analysis method on a power plant using the enthalpy–entropy diagram to present his results. He also made reference to the benefit of using exergy analysis in other related systems. Trepp (1961) examined exergy losses in refrigeration machines and develop optimum low temperature cycle design. Beahr (1962) provided an extensive discussion on exergy and presented his analytical results by comparing flowcharts of exergy and energy.

Szargut (2005) mentioned that exergy analysis is based upon the second law of thermodynamics which stipulates that all macroscopic processes are irreversible. Every such irreversible process entails a non-recoverable exergy lost, which is expressed as the product of the environment temperature and the entropy generated. The quantity of entropy generated is the sum of the values of the entropy increase for all the bodies taking part in the process.[3] The elementary irreversible phenomena that generate entropy are mechanical or hydraulic friction, heat transfer with a finite temperature gradient, diffusion with a finite gradient of concentration, and the mixing of substances with different parameters and chemical composition.

EXISTING CONVENTIONAL PROCESS

In the conventional process at PT. PUSRI II, natural gas is converted into synthesis gas through steam reformers. The essential configuration of the primary steam reformer is first established by Badische Anilin and Soda Fabrik (BASF) at the end of 1920s and the technology was used in 1931 by Standard Oil of New Jersey to produce hydrogen from off-gases at its refineries. Since then, the process has been improved such as by M.W. Kellog at PT. PUSRI II.

In this work, process used by PT. PUSRI II Palembang would be as reference process in modification design and calculations analysis. This reference process, labeled as process A, uses a primary and a secondary reformer in series as shown in Fig. 1. Natural gas, as feed for the reforming process in the primary reformer, enters the feed preparation step where a heavy hydrocarbon and suspended particles are removed. Natural gas feed to the primary reformer consists of 81.90% CH_4 by volume and other higher hydrocarbons with 5.45% C_2H_6, 2.87% C_3H_8, 0.44% i-C_4H_{10}, 0.56% n-C_4H_{10}, 0.15% i-C_5H_{12}, 0.08% n-C_5H_{12}, 0.03% C_{6+}, 0.20% CO_2, 0.01% Ar, 1.63% N_2, and 6.68% H_2. In addition, CO_2 removal, dehydration, and desulfurization are also applied to the feed gas. Natural gas feed is then preheated to 430 °C and pressured to 33.87 atm before entering radiant section of the primary
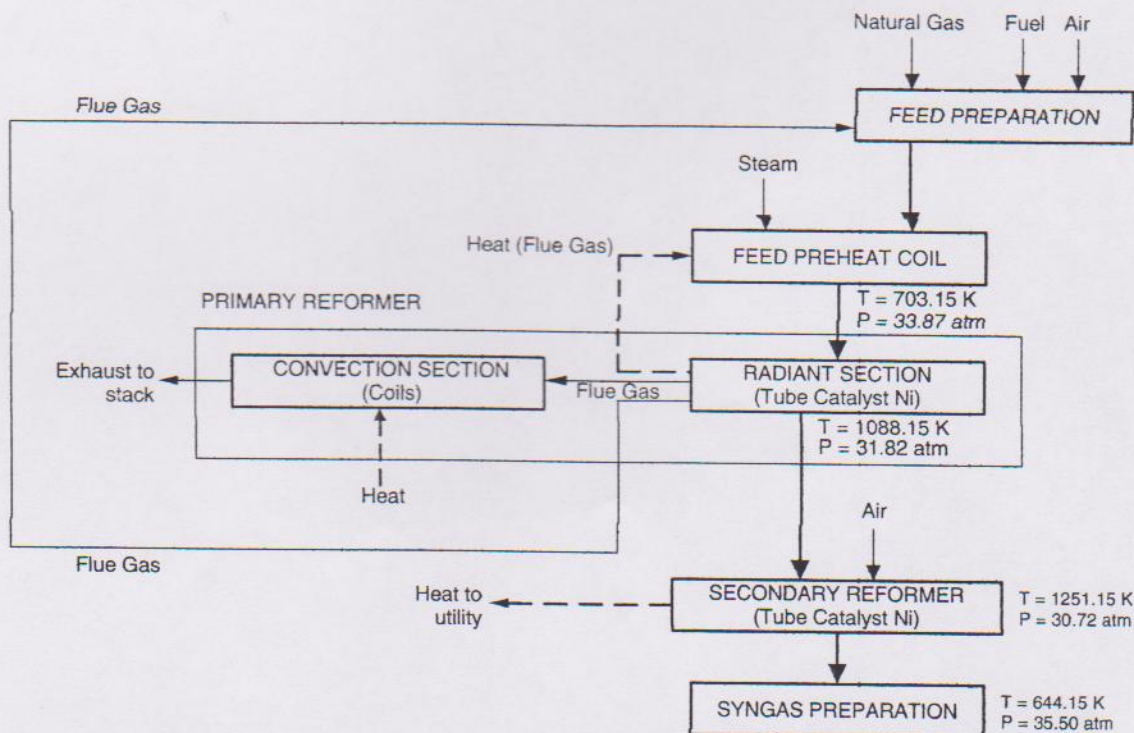

Figure 1. Block diagram of the series reformers, process (A).

reformer. Energy from the hot flue gas is recovered in the convection section to raise steam or for other uses.

In the radiant section, previously natural gas feed is mixed with saturated steam to give methane-to-steam ratio of 1 : 4.25 then reacts in endothermic reaction with Ni-catalyst in a tubular reactor of the radiant section of the primary reformer at 815 °C, 31.82 atm. To increase and enrich the synthesis gas output from the primary reformer, the secondary reformer is then applied with air supply and the operating condition is 1251.15 °K, 30.72 atm. Its synthesis gas reacts in exothermic reaction in the secondary reformer with Ni-catalyst supported in a tubular reactor then enters the synthesis gas preparation steps.

Conversion of CH_4 in the primary reformer of the natural gas feed only reaches to 51.69%, while all heavier hydrocarbons in the natural gas feed are completely converted. In the secondary reformer, conversion of CH_4 is 95.48%. Consequently, the overall conversion of CH_4 from the series reformers reaches to 97.82%.

Large amount of energy is consumed to raise the process temperature from preparation step to 815 °C in the primary reformer and to 978 °C in the secondary reformer. The overall energy consumed from both processes is 237 534.61 kJ h^{-1}.

Material streams in processes A and B of this study (based on data of January 2009), could be seen from Table 1, for our focus on a synthesis zone of each block diagram.

The calculation of the material and energy balances are given in Table 3 and are based on the previous study about natural gas conversion and will not be discussed here, and only the calculation steps and results are showed in this article. The exergy losses of process A in every step are shown in Table 4. It is shown that the exergy lost in process A is high. Clearly, although the overall conversion for the reforming could reach up to 97.82%, the consumption of energy, fuel, and the exergy losses in this process are definitely high because these parameters have not been optimized in the design.

PROPOSED PROCESS MODIFICATION

Exergy analysis with a flowsheeting simulator for synthesis gas production from natural gas to become methanol as a final product has been learned by Hinderink et al.[4,12] In their method, they have implemented a set of external subroutines that have been integrated with a flowsheeting simulator, in order to calculate exergies of material streams along with the traditional energy and mass-balance calculations. They proposed four different pathways for the process: conventional steam reforming, conventional steam reforming and pre-reformer; combined reforming with a natural gas bypass, and convective reforming parallel to non-catalytic partial oxidation.

Run from those types of pathways as reference by using the operating condition and material streams similar to process A in our work, we have calculated its conversion and exergy analysis of each process which would not be discussed and compared in this article. Material streams input in the synthesis part of those processes are similar to process A, which is shown in Table 1 for primary reformer input at temperature 703.15 K and pressure 33.87 atm.

The block diagram of each process is shown in Fig. 2 for conventional steam reforming process (a) and

Table 1. Material streams of processes A and B.

Compounds	Process A		Process B	
	Primary reformer input (% kmole/h)	Secondary reformer input (% kmole/h)	Partial oxidation (% kmole/h)	Steam reformer (% kmole/h)
Natural gas				
CH_4	18.37	5.38	59.00	5.69
C_2H_6	1.29	0.00	4.15	0.00
C_3H_8	0.81	0.00	2.59	0.00
C_4H_{10}	0.25	0.00	0.82	0.00
CO	0.00	4.52	0.00	12.39
CO_2	0.06	4.92	0.20	0.21
H_2	0.86	31.42	2.77	10.24
N_2	0.30	16.21	0.96	14.61
Ar	0.00	0.19	0.01	0.00
O_2	0.00	4.31	29.50	0.00
H_2O (steam)	78.05	33.04	0.00	56.87
Methane : Steam input ratio	1 : 4.25	–	–	1 : 10
Methane : O_2 ratio	–	–	1 : 0.5	–
N_2 : H_2 output ratio	–	1 : 3	–	1 : 3
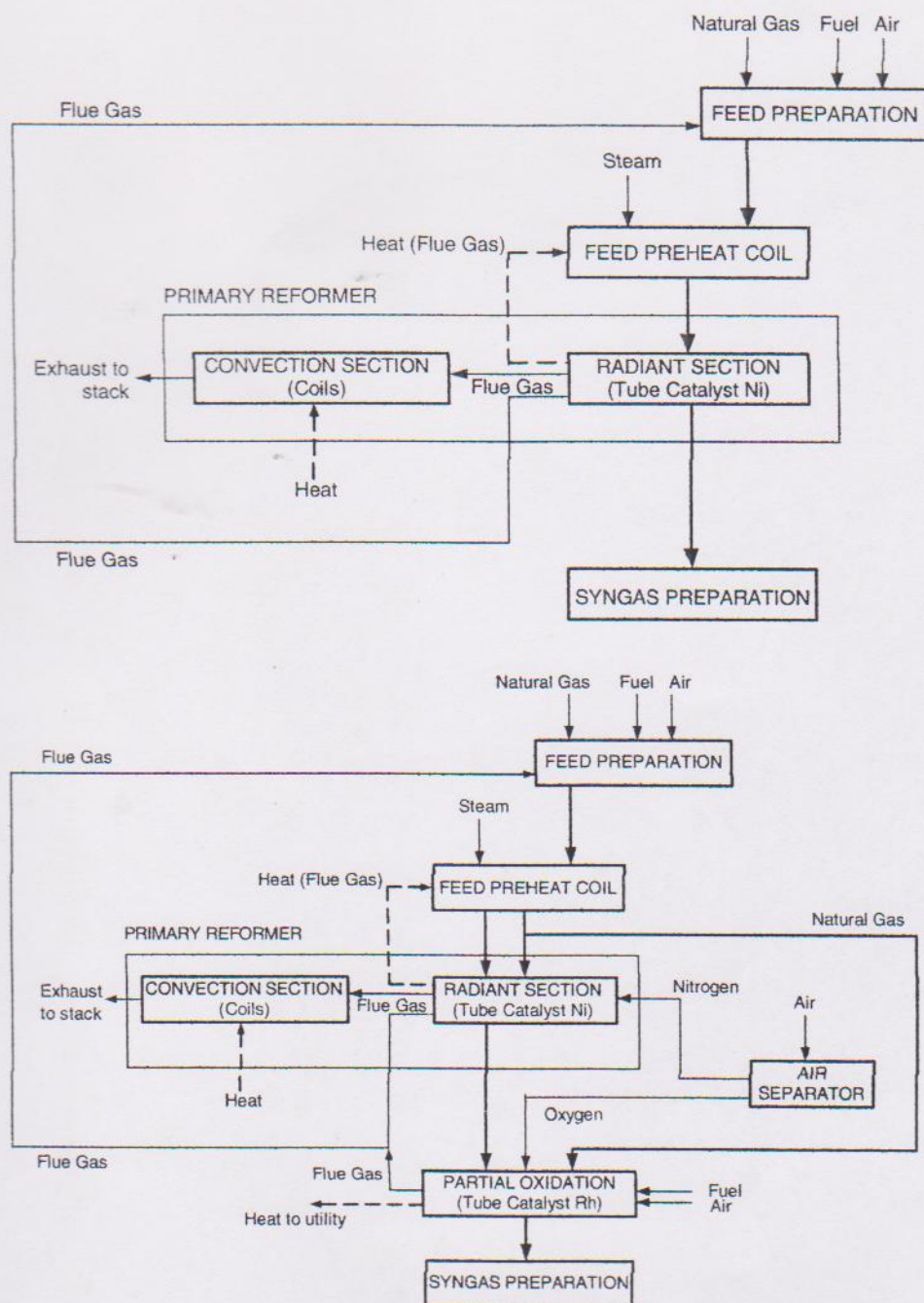
Figure 2. (a) Block diagram of the conventional steam reforming process (A). (b) Block diagram of the combined reforming with natural gas baypass process (B).

combined reforming with a natural gas bypass process (b).

From these two processes (Fig. 2(a) and (b)), it is known that both processes give no satisfied conversion of methane and yield of hydrogen and carbon dioxide gas compared to process A as reference and also high in exergy losses.

On the basis of those processes results of calculations learned before and its weaknesses and also

from weaknesses of process A as our reference in this article, process modification is proposed by adding a partial oxidation process before the primary reformer and eliminating the secondary reformer. The modified process is designated as process B. Process B has been proposed to optimize the process design in the production of synthesis gas from natural gas and *the improvement in exergy losses will be compared in reference to process A. Process B is described*
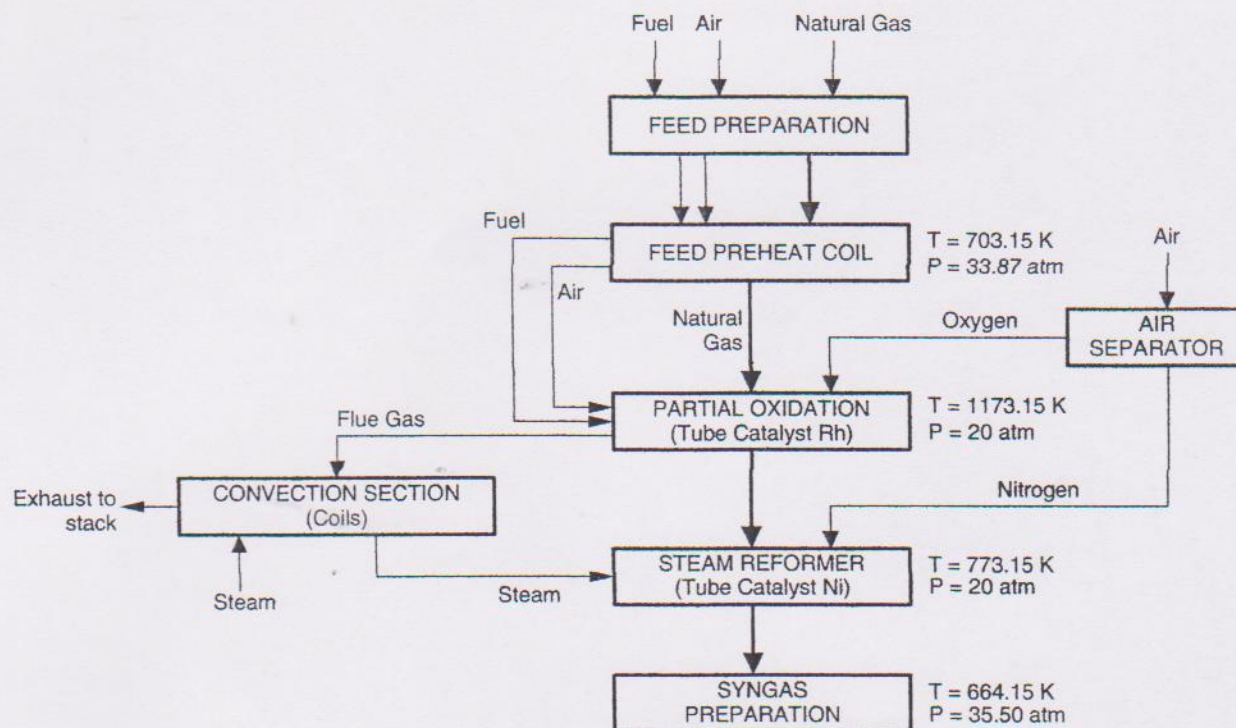
Figure 3. Block diagram of the modified flowsheeting reformer, process (B).

below, while the block diagram for calculating exergies of the material streams is shown in Fig. 3. The operating conditions are taken from the previous study.[5]

Figure 3 illustrates the major process steps of the modified flowsheeting reformer in a block diagram. The partial oxidation process has been added before the primary reformer and the secondary reformer eliminated in process B. Natural gas with the same characteristics and compositions with process A supplies as a feed for the partial oxidation process, previously it will enter the feed preparation steps. In this first step, heavy hydrocarbon and suspended particles separation, CO_2 removal and dehydration process are applied to the *natural gas feed. Similar to the process A, natural gas* feed is then preheated to the temperature of 430 °C in the feed preheat coils and pressured to 33.87 atm, to enter the partial oxidation process. Natural gas feed is then mixed with limited oxygen to give methane-to-oxygen ratio of 1 : 0.5 and reacts in exothermic reaction with Rh-catalyst in a tubular reactor of the partial oxidation,[6,7] at the operating condition 900 °C, 20 atm.

To increase and enrich the synthesis gas output from the partial oxidation, synthesis gas output is then mixed with steam in methane-to-steam ratio of 1 : 10 in the primary/steam reformer at the operating condition 500 °C, 20 atm. Its synthesis gas reacts in exothermic reaction with Ni-catalyst supported in a tubular reactor of the primary reformer. Nitrogen has been added in the primary/steam reformer in this process because in

the process A as a reference condition to the next step to produce ammonia, nitrogen is needed with ratio of N_2-to-H_2 1:3.

Material streams in this modified flowsheeting reformer (process B) could be seen from Table 1 previewed before, for focus in a synthesis zone of Figure 3 block diagram. Material streams of natural gas feed compositions in process B are same as process A.

EXERGY CALCULATIONS OF THE MATERIAL STREAMS

The overall reactions and their standard Gibbs energy of reactions presented for the conversion of natural gas to synthesis gas for each process, is determined in Table 2.[8,9]

In Table 2, the minus of standard Gibbs energy of the overall reaction is denoted as available reaction exergy. It plays an important role in understanding the exergy losses associated to chemical reactions.

In basic thermodynamics calculation of the material streams, the conversion and fraction equations were performed and adopted from Smith and Van Ness.[10] Determining the reactions that occur in catalytic partial oxidation process from natural gas with higher hydrocarbons exist would be the first step to do in thermodynamics calculation with certain pressure and range of temperature for trial the best operating condition.

Table 2. The overall reactions.

Process	Reactions	$\Delta G^0 \, r_{298K}$ (kJ kmole^{-1})
A	1. In the primary reformer, from natural gas to synthesis gas	
	$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	141 863
	$C_2H_6 + 2H_2O \Leftrightarrow 2CO + 5H_2$	214 661
	$C_3H_8 + 3H_2O \Leftrightarrow 3CO + 7H_2$	298 499
	$C_4H_{10} + 4H_2O \Leftrightarrow 4CO + 9H_2$	349 042
	$CO + H_2O \Leftrightarrow CO_2 + H_2$	$-28\,618$
	2. In the secondary reformer, from synthesis gas to enriched synthesis gas	
	$CH_4 + H_2O \Leftrightarrow 3H_2 + CO$	141 863
	$2H_2 + O_2 \Leftrightarrow 2H_2O$	$-457\,144$
	$CO + O_2 \Leftrightarrow 2CO_2$	$-651\,549$
B	1. In the catalytic partial oxidation, from natural gas to synthesis gas	
	$2CH_4 + O_2 \Leftrightarrow 2CO + 4H_2$	$-86\,709$
	$C_2H_6 + O_2 \Leftrightarrow 2CO + 3H_2$	$-242\,483$
	$2C_3H_8 + 3O_2 \Leftrightarrow 6CO + 8H_2$	$-387\,217$
	$C_4H_{10} + 2O_2 \Leftrightarrow 4CO + 5H_2$	$-565\,246$
	$2CO + O_2 \Leftrightarrow 2CO_2$	$-257\,190$
	2. In the steam reformer, from synthesis gas to enriched synthesis gas	
	$CH_4 + H_2O \Leftrightarrow CO + 3H_2$	141 863
	$CO + H_2O \Leftrightarrow CO_2 + H_2$	$-28\,618$

To calculate the equilibrium mixture for multi-reaction equilibria, we need the equilibrium constant K for the reaction, and is shown in Eqn (1).

$$-RT \ln K = \sum_i \upsilon_i G_i^0 \equiv \Delta G^0 \qquad (1)$$

The final term ΔG^0 is the conventional way of representing the quantity $\sum_i \upsilon_i G_i^0$. It is called the standard Gibbs energy change of reaction. The function of ΔG^0 is the difference between the Gibbs energies of the products and reactants (weighted by their stoichiometric coefficients) when each species in its standard state as a pure substance at the system temperature and at a fixed pressure. Thus, the value of ΔG^0 is fixed for a given reaction once the temperature is established and is independent of equilibrium pressure and composition. And, $\Delta G^0/RT$ could be explained by Eqn (2).

$$\frac{\Delta G^0}{RT} = \frac{\Delta G_0^0 - \Delta H_0^0}{RT_0} + \frac{\Delta H_0^0}{RT} + \frac{1}{T}\text{ICPH} - \text{ICPS} \qquad (2)$$

Integral Differential Heat Capacity for Enthalpy Calculations (ICPH) and Integral Differential Heat Capacity for Entropy Calculations (ICPS) are symbols for computational purposes as described in Eqns (3) and (4).

$$\text{ICPH} = \int_{T_0}^{T} \frac{\Delta C_P^0}{R} dT = (\Delta A)T_0(\tau - 1)$$
$$+ \frac{\Delta B}{2}T_0^2(\tau^2 - 1) + \frac{\Delta C}{3}T_0^3(\tau^3 - 1)$$
$$+ \frac{\Delta D}{T_0}\left(\frac{\tau - 1}{\tau}\right) \qquad (3)$$

$$\text{ICPS} = \int_{T_0}^{T} \frac{\Delta C_P^0}{R}\frac{dT}{T} = \Delta A \ln \tau$$
$$+ \left[\Delta BT_0 + \left(\Delta CT_0^2 + \frac{\Delta D}{\tau^2 T_0^2}\right)\left(\frac{\tau + 1}{2}\right)\right](\tau - 1) \qquad (4)$$

The evaluation of the integral $\int C_p dT$ is accomplished by substitution for C_p, followed by formal integration, for temperature limits of T_0 and T, where

$$\tau = \frac{T}{T_0} \qquad (5)$$

Thus, $\Delta G^0/RT$ ($= -\ln K$) as given by Eqn (2) is readily calculated at any temperature from standard heat of reaction and the standard Gibbs energy change of reaction at a reference temperature, T_0 (usually 298.15 °K) and from two functions which can be calculated by standard computational procedures.

When two or more reactions proceed simultaneously, mole fractions y_i of the species are related to ε or called reaction coordinate, characterized the extent or degree to which a reaction has taken place, shown by Eqn (6).

$$y_i = \frac{n_{i0} + \sum_j v_{i,j}\varepsilon_j}{n_0 + \sum_j v_j \varepsilon_j} \qquad (i = 1, 2, \ldots N) \qquad (6)$$

where j is the reaction index, and associates a separate reaction coordinate ε_j with each reaction. The stoichiometric numbers are doubly subscripted to identify their

association with both a species and a reaction. Thus, $\upsilon_{i,j}$ designates the stoichiometric number of species i in reaction j.

And, when the equilibrium state in a reacting system depends on two or more independent chemical reactions, the equilibrium composition can be found by a direct extension of the methods developed for single reactions. If the equilibrium mixture is an ideal gas, it may be written as Eqn (7), where $P^0 = 1$ atm.

$$\prod_i (y_i)^{\upsilon_{i,j}} = \left(\frac{P}{P^0}\right)^{-\upsilon_j} K_j \qquad (7)$$

The mole fractions in Eqn (7) may be solved by using the mathematical program for the multireaction equilibria such Maple 11.

Heat requirements of the process (Q) are expressed by the summation of heat input to the reaction process and the heat of reactions itself as shown in Eqns (8) and (9), respectively.

$$Q = Q_{\text{input}} + Q_{\text{reactions}} \qquad (8)$$

$$Q = \left(nR \int_{T_0}^{T} \frac{\Delta C_p^0}{R} dT\right) + \left(\Delta Hr_o^0 + R \int_{T_0}^{T} \frac{\Delta C_p^0}{R} dT\right) \qquad (9)$$

In Eqn (9), ΔHr_0^0 is heat of reaction at reference temperature T_0.

In calculating exergies of the material streams, the following steps of calculating were performed and adopted from Ahern.[3] A primary use of the exergy analysis is to show the location, type, and magnitude of the exergy losses, in a system.[11] As a result, the system efficiency can be effectively increased by reducing these losses. The exergy losses are generated throughout the system by irreversible production of entropy caused by the non-ideal performance inherent in all real systems and components.

The exergy lost results from heat loss during combustion could be calculated by using Eqn (10). This was assumed to be (1 - overall efficiency) and considered as a direct exergy loss as it reduced the available work in the fuel by that amount.

$$Ex_a = Q_{\text{release of fuel}} \times (1 - \text{overall efficiency})$$
$$\times \text{mole of fuel} \qquad (10)$$

The exergy of fuel is $Ex_{1,7}$ the heat release from natural gas fuel to the furnace.

Exergy lost resulting from transfer of chemical energy to heat energy is calculated using Eqn (11). During the

combustion of the fuel, the remainder of the chemical energy is transferred into thermal energy,

$$Ex_{2,8} = (Q_{\text{release of fuel}} \times \text{mole of fuel}) - Ex_a \qquad (11)$$

A transfer of useful chemical energy into thermal energy is an irreversible process expressed by Eqn (12),

$$Ex_b = m_{9,4}(\Delta H_{\text{out}} - \Delta H_{\text{in}})\frac{T_0}{T_g} \qquad (12)$$

The exergy loss resulting from a heat transfer between natural gas fuel and feed of process shows in Eqn (13).

$$Ex_c = T_0(m_{9,4})\left[(\Delta S_{\text{out}} - \Delta S_{\text{in}}) - \frac{(\Delta H_{\text{out}} - \Delta H_{\text{in}})}{T_g}\right] \qquad (13)$$

The total exergy loss of fuel natural gas to natural gas feed/synthesis gas in the process is $Ex_b + Ex_c$.

Furthermore, the exergy loss during the outflow of synthesis gas of certain process in piping from one step process to the other is expressed in Eqn (14).

$$Ex_{3,5} = (\Delta H_{\text{out}} - \Delta H_{\text{in}}) - T_0(\Delta S_{\text{out}} - \Delta S_{\text{in}}) \qquad (14)$$

In Figs 4 and 5, a synthesis gas in conditions 4 and 6 has a work capacity, so

$$Ex_{4,6} = (\Delta H_{4,6} - \Delta H_{9,4}) - T_0(\Delta S_{4,6} - \Delta S_{9,4}) \qquad (15)$$

Moreover, the exergy lost in process is expressed by Eqn (16) below.

$$Ex_d = Ex_{3,5} - Ex_{4,6} \qquad (16)$$

The exergy loss of friction from the partial oxidation to the steam reformer or from the primary reformer to the secondary reformer or from the steam reformer/secondary reformer to the synthesis gas preparation is

$$Ex_e = m_{3,5}\left(\frac{P_2}{\rho_2} - \frac{P_1}{\rho_1}\right) \qquad (17)$$

A heat transfer in piping is $m(\Delta H_{3,5} - \Delta H_{4,6})$.

Figure 4 describes the material and energy calculations steps in the proposed process modification. The composition moles input used is similar to the existing conventional process A. It is divided into two big blocks, named 1 and 2.

Block 1 is the step for calculating material conversion and moles fraction of natural gas that reacts in a process. Furthermore, block 2 is the step for calculating the energy streams in a process that is continuing from steps in block 1.

Mass and heat input of the material streams from the series reformers of process A and modified reformer
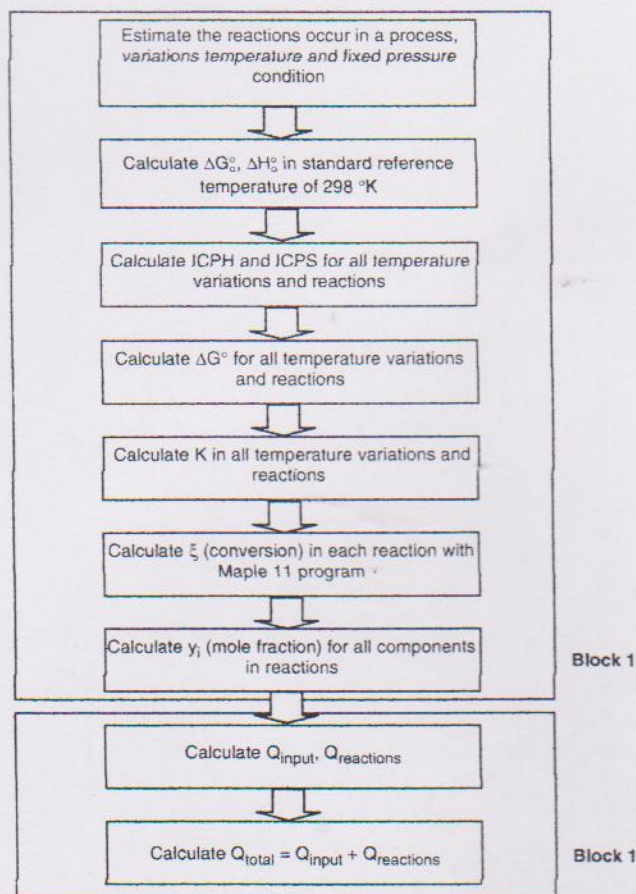
Figure 4. Block flow of calculation of material and energy streams.

condition at PT. PUSRI II reformer furnace. Natural gas fuel compositions consist of CH_4 64.61%, C_2H_6 7.97%, C_3H_8 7.08%, i-C_4H_{10} 1.25%, n-C_4H_{10} 1.76%, i-C_5H_{12} 1.01%, n-C_5H_{12} 0.56%, and CO_2 15.76% moles.

The exergy calculation of the material streams at each point of flows, based on the block diagram in the process descriptions, is described in Figs 5 and 6 for the related processes.

RESULTS AND DISCUSSION

The calculation of exergy at discrete points in a system will indicate the total exergy change, reversible and irreversible in the process and in the equipment between any two points. These exergy values are explicit values relative to the reference condition of the surrounding environment. On the basis of the calculation of exergy performed, the results of the exergy analysis are shown in Tables 4 and 5.

The overall reactions of natural gas feed occurs in the primary reformer is endothermic reaction, that consists of higher hydrocarbons reactions. From Table 4, it can be seen that the largest amount of the exergy lost is in the primary reformer that accounts for 95.17% of the total exergy lost in process A. The presence of high exergy lost in the primary reformer may indicate a poor match between the quality of the energy supplied to the process and the quality required by the process to perform a given task. This mismatch results in large irreversibility. Heat released by fuel of natural gas can reach temperature to 1927 °C through the conventional combustion furnace, while the maximum temperature required by the process only reaches 815 °C.

In the secondary reformer, the exergy loss is in the minimum percentage in which the temperature operation needed reaches 978 °C for the exothermic reaction occurred with large amounts of moles input and heat used. Although the exergy values always

process B for the same initial feed of a raw natural gas is shown in Table 3

Assumption has been taken for the conventional combustion temperature, which is 1927 °C and the ambient temperature is 25 °C. The overall efficiency of the furnace is 88% with heat release of the natural gas fuel is 15 189 Btu lb^{-1} based on the actual operating
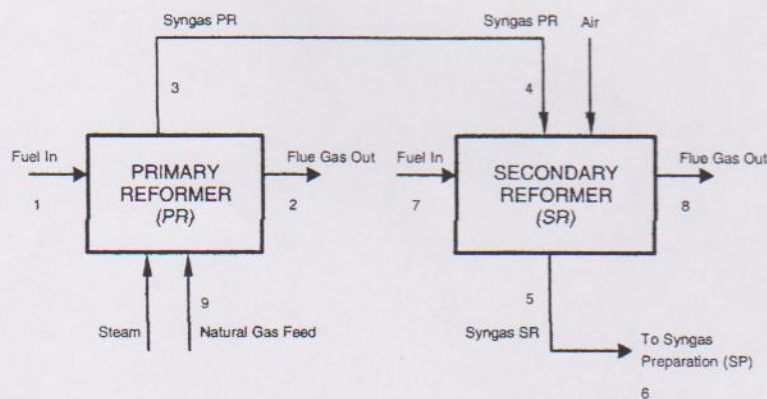

Figure 5. Exergy analysis diagram of the series reformers, process (A).

Table 3. Mass and heat input of the material streams.

|	Process	Total moles input (kmole h^{-1})	Total heat input (kJ h^{-1})
A	1. In the primary reformer, from natural gas to synthesis gas	5857.06	99 392 276.41
	2. In the secondary reformer, from synthesis gas to enriched synthesis gas	9657.16	265 845 258.21
B	1. In the catalytic partial oxidation, from natural gas to synthesis gas	1823.88	34 765 753.39
	2. In the steam reformer, from synthesis gas to enriched synthesis gas	7628.99	158 957 291.79
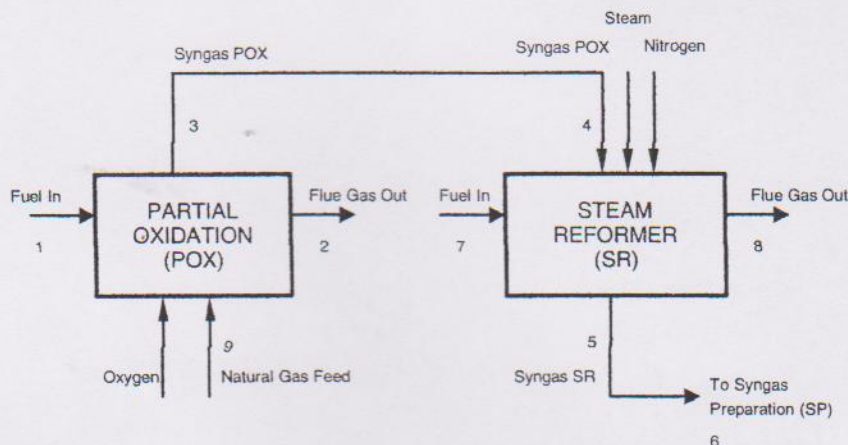
Figure 6. Exergy analysis diagram of the modified flowsheeting reformer, process (B).

show positive to the reference surrounding environment, in the secondary reformer it shows negative value. The zero reference for enthalpy and entropy values in the literature often results in positive and negative values of exergy calculation for the system. Total exergy losses of the entire processes in process A are 2 821 615.23 MJ h^{-1}, *its amounts will reduce through* the modified flowsheeting reformer which is shown in Table 5.

As shown in Table 5, the total exergy lost for the entire process B is 1 091 015.74 MJ h^{-1}. The flowsheet modification of process A is done through replacement of the secondary reformer with a partial oxidation process upstream of the primary reformer. Process B shows a significant potential reduction in the total exergy lost in primary reformer (steam reformer) by up to 78.11% relative to the conventional process A. Furthermore, the operating conditions in the primary reformer of process B is reduced to 500 °C, 20 atm thereby reducing the consumption of natural gas fuel in the reformer. Heat released from the exothermic partial oxidation process may be recovered to provide heating for the endothermic reaction in steam reformer of process B.

So, the overall exergy losses in process A can be reduced through applying a modification such in process B, as much as

% exergy savings

$$= \left(\frac{\text{exergy losses in process A} - \text{exergy losses in process B}}{\text{exergy losses in process A}} \right)$$
$$\times 100\%$$

$$= \left(\frac{2821615.23 \text{ MJ/h} - 1091015.74 \text{ MJ/h}}{2821615.23 \text{ MJ/h}} \right) \times 100\%$$

% exergy savings = 61.33%

CONCLUSIONS

This article presents a path for calculating exergy losses for each step in the main parts of synthesis gas production from natural gas. The path is integrated with the modified flowsheeting reformer of process B and compared to the series reformers of process A. Exergy analysis is found to be useful for the process analysis. It provides an objective measurement for selecting and judging processes regard to their energy (or exergy) utilization. The overall exergy losses (%) in process A can be reduced until 61.33% through modification to process B. The result is achieved for the same initial feed of a raw natural gas. Furthermore, the exergy loss

Table 4. The exergy analysis of the series reformers (process A).

Station or component	Exergy (MJ h^{-1})	Change in exergy (MJ h^{-1})	Heat transfer (MJ h^{-1})	Exergy losses					Total (MJ h^{-1})	Total exergy loss (%)
				Chemical change (MJ h^{-1})	Heat transfer (MJ h^{-1})	Friction (MJ h^{-1})	Heat rejection (MJ h^{-1})			
1 Furnace primary	49.94	5.99 (Ex_a)					5.99	5.99	−0.00
2 Primary reformer	43.95	−2685 274.29 ($Ex_b + Ex_c$)	43.95	−1306 860.27 (Ex_b)	−1378 414.01 (Ex_c)			−2685 274.29	95.17
3 Piping (PR to SR)	−1187.94	898.13 (Ex_d)	−156 418.00		−156 418.00			−156 417.99	5.54
4 Secondary reformer	−2086.07	22 955.61 ($Ex_b + Ex_c$)	117.55	1 222 160.24 (Ex_b)	−1 199 204.63 (Ex_c)			22 955.61	−0.00
5 Piping (SR to SP)	931.45	−0.30 (Ex_d)	−2900.54		−2900.54	−0.05		−2900.59	0.10
6	931.75								
7	133.58								
8 Furnace secondary	117.55	16.03(Ex_a)					16.03	16.03	−0.00
								−2821 615.23	100.00

Table 5. The exergy analysis of modified flowsheeting reformer (process B).

Station or component	Exergy (MJ h⁻¹)	Change in exergy (MJ h⁻¹)	Heat transfer (MJ h⁻¹)	Exergy Losses					Total exergy loss (%)
				Chemical change (MJ h⁻¹)	Heat transfer (MJ h⁻¹)	Friction (MJ h⁻¹)	Heat rejection (MJ h⁻¹)	Total (MJ h⁻¹)	
1	17.47								
Furnace POX		2.10 (Ex_a)					2.10	2.10	−0.00
2	15.37								
Partial oxidation		−500 907.94 ($Ex_b + Ex_c$)	15.37	270 586.09 (Ex_b)	−771 494.03 (Ex_c)			−500 907.94	45.91
3	1369.34								
Piping (POX to SR)		−137.05 (Ex_d)	−2504.92		−2504.92	−0.01		−2504.92	0.23
4	1506.40								
Steam reformer		−587 614.55 ($Ex_b + Ex_c$)	70.29	−295 897.19 (Ex_b)	−291 717.36 (Ex_c)			−587 614.55	53.86
5	−209.17								
Piping (SR to SP)		0.00 (Ex_d)	0.00		0.00	−0.01		−0.01	0.00
6	−209.17								
7	79.87								
Furnace SR		9.58 (Ex_a)					9.58	9.58	−0.00
8	70.29								
								−1 091 015.74	100.00

in the primary reformer itself can be reduced to 78.11% relative to process A.

NOMENCLATURE

υ	Stoichiometric number
ε	Reaction coordinate
ρ_2, ρ_1	Density of components in the material streams at point 2 and 1, kg cm⁻³
ΔH	Total enthalpy of material streams, kJ kmole⁻¹
ΔS	Total entropy of material streams, kJ kmole⁻¹
$\Delta G^0, \Delta G^0_0$	Gibbs energy, standard Gibbs energy of pure component at 298.15 °K, J mole⁻¹
$\Delta H^0, \Delta H^0_0$	Enthalpy, standard enthalpy of pure component at 298.15 °K, J mole⁻¹
ΔC_p^0	Heat capacity
$Ex_{1,2,...,9}$	The exergy in point 1 or 2 or ... to 9, kJ h⁻¹
K	Equilibrium constant
m	Mole input to the process, mole
$n_{i,0}$	Mole of pure component; Mole total, mole
P_2, P_1	Pressure of process at point 2 and 1, atm
P_0, P	Reference pressure; Process pressure, atm
Q	Heat, kJ h⁻¹
R	Universal gas constant, J mol⁻¹ K⁻¹
T_g	The conventional combustion furnace temperature, °K
T_0	The ambient temperature, °K
T_0, T	Reference temperature; Process temperature, °K
y	Mole fraction

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