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The undersigned certify that they have read, and recommend to The Postgraduate Studies Programme for acceptance, a dissertation entitled "Exergy Analysis of Steam Methane Reforming" submitted by Amlaku Abie for the fulfilment of the requirements for the degree of master of science in process integration.

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UNIVERSITI TEKNOLOGI PETRONAS

Exergy Analysis of Steam Methane Reforming

By

Amlaku Abie

A DISSERTATION

SUBMITTED TO THE POSTGRADUATE STUDIES PROGRAMME

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DEGREE OF MASTER OF SCIENCE IN PROCESS INTEGRATION

BANDAR SERI ISKANDAR,

PERAK

JUNE, 2007

1) Catalytic reforming
2) Catalysts

Declaration

I hereby declare that the dissertation is based on my original work except for quotations and citations which have been duly acknowledged. I also declare that it has not been previously or concurrently submitted for any other degree at UTP or other institutions.

Signature :

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I would like to take this chance to thank my family and friends for their uninterrupted help.

Abstract

Steam methane reforming is an energy intensive process. Minimizing energy usage can reduce operating cost and emission to the environment. It is learned that energy requirement of the reformer depends on the operation parameters namely temperature, pressure, and steam to methane ratio. In this work it is intended to perform the exergy analysis of the reformer at various operating parameters. The exergy analysis will address both the quantity and quality of energy. Both chemical and physical exergy of the system are considered in the analysis. The composition of the outlet stream is crucial for exergy calculation hence the reformer is modeled as an equilibrium conversion reactor. The model can predict the composition of the outlet stream. The model can also explain the effect of hydrogen removal in improving the conversion of methane at milder conditions. Hydrogen removal of 10% has similar effect on methane conversion as 15K rise of reformer temperature at the same condition (other parameters remaining constant). Exergy losses of the reformer for different operating condition were investigated. Exergy loss per mole of hydrogen produced has the minimum value at about 1110K for steam to methane ratio of 3:1. Both the conventional exergetic efficiency and the recently proposed utilizable coefficient were calculated. Comparisons were made on the basis of their suitability as criteria of thermodynamic performance for the process. It is found that the utilizable coefficient is better criteria for describing thermodynamic performance. Microsoft Excel is used as computing tool.

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Nomenclature

C_P	Constant pressure heat capacity
$\langle C_P \rangle_H$	Mean heat capacity
D	Exergy loss
E_K	Kinetic exergy
E_x	Chemical exergy
E_P	Potential exergy
E_{Ph}	Physical exergy
f	Fugacity
G	Gibbs free energy
H	Enthalpy
I	Irreversibility (exergy loss)
k	Equilibrium constant
n	number of moles
p	Pressure
$\dot{Q}_r$	Heat transfer rate
R	Universal gas constant
T	Temperature
ΔT_R	Approach temperature to equilibrium
S	Entropy
X	Conversion
y	Mole fraction

Greek letters

η_i	Intrinsic exergy efficiency
η_e	Conventional exergy efficiency
η_u	Utilizable coefficient
ϕ	Fugacity coefficient
ν	Stoichiometric coefficient

Subscript

$\Delta_f G_i^O$	Standard Gibbs energy of formation
i	Species
o	Environment state
oo	Dead state
p,T	Thermomechanical
sr	Steam reforming
x	Chemical
wg	Water gas
m	mixture

Superscript

$''$	Outlet
$'$	Inlet
c	Consumed
ext	External
ig	Ideal gas
int	Internal
max	Maximum
min	Minimum
pu	Produced utilizable
tr	Transit

Chapter One

Introduction

1.1 Significance of exergy

Energy saving in the industry has been a goal of managers, engineers and scientists, but the problem has now become a priority. In the last decades it is learned that first level measures such as energy conservation, avoiding wastes, effective maintenance, and increased consciousness in energy saving programs can improve energy efficiency up to 15% [1]. Further saving can be achieved by applying second and third level measures which is accompanied by additional investment. The following questions should be answered for energy saving program to be successful.

1. Where and how is energy degraded in industry?
2. How to reduce energy degradation?

The first law of thermodynamics states that energy cannot be created nor destroyed. Energy can be transformed from one form to other. However in all real processes its quality decrease, i.e. energy is degraded (it is the second law of thermodynamics) and the increasing relevance of the second law is the result of two significant changes produced at the international level in energy policies.

The first change was a result of energy crisis of the early seventies. High energy cost reminded people that it is necessary to consider both quantity and quality of energy when its use is to be optimized. In short the cost of energy depends on both quantity and quality of the energy. This change brought to light the energy-economy connection and gave origin to the first energy saving programs. The second change refers to the need to conserve the environment for sustainable development. Increased fossil fuel consumption degrades the environment and makes the earth a difficult place to live. This has brought the recognition of the energy-ecology connection.

Figure1.1 shows the connection among energy, economy and ecology. The exergy concept is able to explain the interaction three E's (energy, economy and ecology).

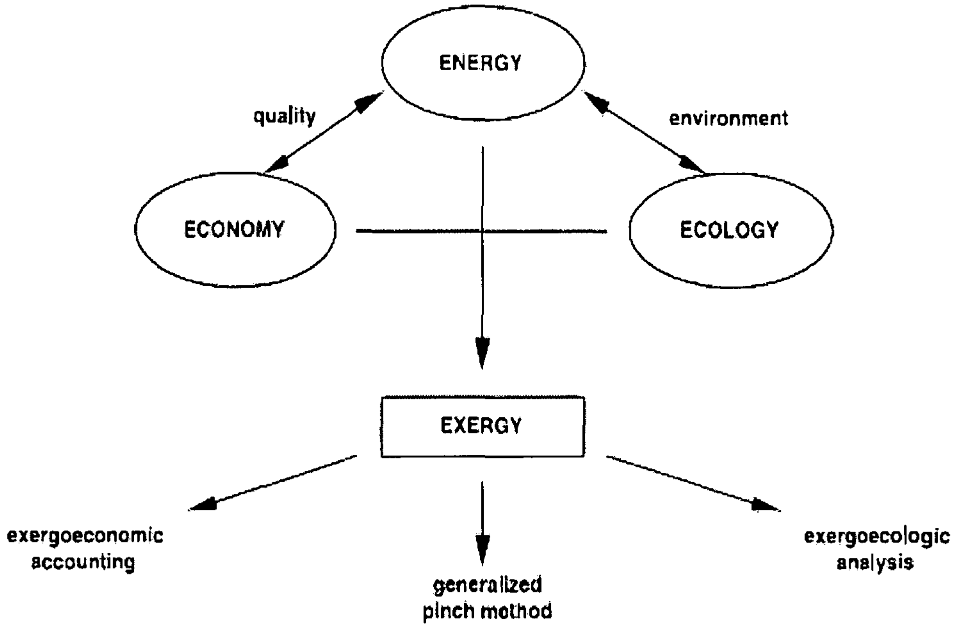

Figure 1. 1 The energy-economy-ecology connection [1]

Exergy is a measure of the quality of energy, of its ability to perform work. The quality of energy in turn tells its cost. This way exergy and economy are related. The ecological implication of exergy can be seen from the alternative definition of exergy. Exergy is a measure of the departure from the environment, of the difference in temperature, pressure, composition, etc. conditions with respect to the conditions of the environment. Hence exergy of an effluent is a measure of the effects and the work that an effluent can have on the environment.

The first law of thermodynamics deals with the quantity of energy and asserts that energy cannot be created or destroyed. This law merely serves as a necessary tool for the bookkeeping of energy during a process. The second law, however, deals with the quality of energy. More specifically, it is concerned with the degradation of energy during a process, the entropy generation, and the lost opportunities to do work; and it offers plenty of room for improvement. The energy analysis is not able to recognize different quality of energy, e.g., 1 kJ of heat equals 1 kJ of electricity. Accordingly, the energy analysis does not recognize the heat quality, which however depends on the heat source temperature, e.g., a 100 kJ of heat at 1000 ^{O}C is dramatically more valuable than the 100 kJ of heat at the 50 ^{O}C level. The energy analysis is blind for the process direction, and, e.g., will not indicate any error considering a 100 kJ of heat at 5 ^{O}C conducted through a partition to an environment at 100 ^{O}C. For these reasons the modern approach to the process analysis uses the exergy analysis, which provides a more realistic view of the process.

Exergy analysis is important to compare different technologies and to optimize processes. It has been applied to select better technology for gasification of coal and production of hydrogen. Exergy analysis can also help us to know how much and how easily a system could be improved for optimization.

1.2 The Concept of exergy

Ordered energy forms (potential and kinetic) are fully convertible to other forms of energy and their quality is invariant [2]. First law of thermodynamics is sufficient for analysis of these forms of energy. Whereas the disordered energy forms (chemical, thermal, etc) have variable quality and its quality depends on both the form of energy and on the parameters of the energy of the carrier and of the environment. To account for the variable quality of different disordered energy forms in the analysis of thermal and chemical plants, a universal standard of quality is needed. The maximum work that a given form of energy can do when it is brought in equilibrium with the environment is a convenient standard. This standard of energy quality is termed as exergy. This concept is widely applicable in the analysis of thermal and chemical processes. The exergy balance is analogous to an energy balance. The energy balance is a consequence of First law of thermodynamics while the exergy balance can be considered as a statement of the law of degradation of energy.

1.2.1 Exergy concepts for control region analysis

There are three kinds of energy transfers across a control surface that is needed to be considered in control region analysis. These are:

1. Work transfer.
2. Heat transfer.
3. Energy transfer associated with mass transfer.

In the exergy method of control region analysis an appropriate form of exergy balance shall be used with exergy transfer terms corresponding to the energy transfer forms listed above. The concept of exergy is explained by fully understanding the concept of environment and equilibrium.

1.2.1.1 Environment

The environment is a very large body of medium in the state of perfect thermodynamic equilibrium. It is to mean that this environment has uniform pressure, temperature, chemical potential, kinetic or potential energy and no driving force at all. Consequently there is no chance of doing work in the process of interaction between parts of the environment. The environment has tremendous amount of energy, but no exergy. Systems outside the environment with one or more parameters, such as pressure, temperature, or chemical potential, different from the corresponding environmental parameter has work potential with respect to the environment. It follows that the environment is a natural reference medium for the exergy of a system. The atmosphere, the seas and the oceans, and the earth's crust are components of the environment for practical terrestrial applications. Interaction of the environment with systems is possible in three different ways [2].

(a) The environment has large thermal capacity (mass × specific heat). This makes the environment a thermal reservoir at temperature T_O. The environment can exchange heat with man-made systems without significant change in its temperature.

(b) Terrestrial systems are usually surrounded by the atmosphere at pressure P_O. When these systems expand by ΔV, work with magnitude of $P_O \Delta V$ is done on the atmosphere (quasi-static is assumed). This is not useful work for the system's intended purpose. However it can be recovered when the system returns to its initial state. This is mechanical interaction as a reservoir of unusable work.

(c) When an open system with different chemical potential with the environment comes into contact, there will be rejection or withdrawal of matter. Through these types of interactions the environment determines, for the purpose of evaluating exergy, the zero reference levels for pressure, temperature and chemical potential.

1.2.1.2 Equilibrium

For a system and the environment to be in mechanical, thermal, and chemical equilibrium their pressure, temperature, and chemical potential should be the same. It is still possible to have equilibrium with the existence of chemical potential gradient by restricting exchange of matter. This is called restricted equilibrium and the state of restricted equilibrium with the environment is referred as environmental state. It is important to notice that chemical equilibrium is not achieved in restricted equilibrium.

The dead state is the state at which the environment and a system are in mechanical, thermal and chemical equilibrium. Barrier to restrict exchange of matter as in the case of environmental state is not needed. Thus, in addition to pressure and temperatures, the chemical potentials of the substances of the system and environment must be equal. The system and the environment are in full thermodynamic conditions. No state of change of the system is possible by any means of interaction with the environment. This is called dead state, i.e. no heat transfer, no mass transfer, no reaction. Below is a descriptive example of environmental state and dead state taken from [2].

To illustrate these equilibrium states, consider a simple substance, CO_2. When pure CO_2 is contained in a vessel or is flowing in a pipe, and its pressure and temperature are those of the environment, P_O and T_O, it is in the environmental state. However, when CO_2 is at T_O but its pressure $(P_{OO})_{CO_2}$ i.e. the partial pressure at which it is normally found in atmospheric air, then it is in unrestricted equilibrium with the environment, the dead state. In this state the gas could also be described as being in membrane equilibrium with the environment since it could pass reversibly to the environment through a suitable semi-permeable membrane.

1.2.2 Exergy associated with a work transfer

Magnitude and direction of exergy can be determined from respective work transfer. Work is equivalent to exergy.

1.2.3 Exergy associated with a heat transfer

Thermal energy is low quality energy. Fraction of the thermal energy of a system can do useful work. Exergy of heat transfer is when that fraction is the maximum. The maximum fraction is given by the Carnot efficiency. The environment is considered as a reservoir of zero-grade thermal energy. For a heat transfer rate $\dot{Q}_r$ and a temperature at the control surface where the heat transfer is taking place T_r, the maximum rate of conversion from thermal energy to work is [2]:

$$\dot{W}_{MAX} = \dot{E}^Q = \dot{Q}_r(1 - T_O/T_r) \tag{1.1}$$

This exergy associated with heat transfer rate is termed as thermal exergy flow. As it is seen from equation (1.1), when heat transfer takes place at a higher temperature than the environment temperature, a heat transfer to the control region results in a gain of exergy by the control region. Figure 1.2(a) is a model depicting the exergy associated with heat transfer (for $T_r > T_O$). The total energy is composed of heat and work. The work is the exergy. As the magnitude of T_r get higher the exergy magnitude will also be higher.

Figure 1.2(b) shows thermal exergy of system with $T_r < T_O$.TER is thermal energy reservoir.

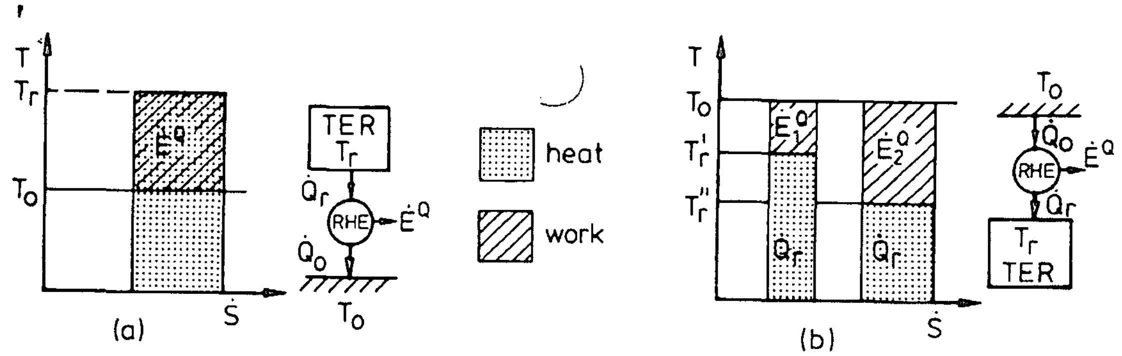

Figure 1. 2 Thermal exergy [2]

In some cases the heat transfer occurs at a temperature which varies from point to point on the control surface. The expression of the thermal exergy will take a different form for such cases. If the heat flux $\dot{Q}_A$ (heat transfer rate per area) distribution at the various, T, is know, the associated thermal exergy flux can be determined from:

$$\dot{E}^Q = \int_A \left(\frac{T - T_O}{T}\right) \dot{Q}_A \, dA \tag{1.2}$$

where A is the heat transfer area.

1.2.4 Exergy associated with a steady stream of matter

Exergy of a steady stream of matter is equal to the maximum amount of work obtainable when the stream is brought from its initial state to the dead state by processes during which the stream may interact only with the environment.

1.3 Problem statement

Efficiency is one of the most used criteria in evaluating the performance of all types of processing plants; in particular those of the energy and chemical industries. The strength of exergetic approach for thermodynamic analysis is that it permits a universally applicable definition of efficiency and is free of contradictions in its treatment of numerous and diverse systems.

The traditional exergy efficiency has been used by many researchers. It has been shown that this efficiency doesn't describe all processes well. A comprehensive definition of exergetic efficiency called intrinsic efficiency was first proposed by Brodynansky, Sorin and Goff [3]. Though its introduction, only few works uses the concepts while others insist on using the traditional definition. This work uses both exergetic definitions and compares them based on their ability to describe the process. The basic difference of the two exergy definitions is their consideration of transit exergy. The intrinsic exergetic efficiency takes transit exergy into account. Therefore, in other words this work is trying to show the importance of transit exergy in exergy analysis of a process.

1.4 Objective

The objectives of this project are:

I. To develop an equilibrium conversion model for the steam methane reactor.
II. To investigate effect of pressure, temperature, steam to methane ratio and hydrogen removal on the output composition of steam methane reforming unit.
III. To compute the exergy losses, conventional exergy efficiency, and utilizable coefficient at different operating conditions.
IV. To select the better criteria to describe the thermodynamic performance of the process.

Chapter Two

Literature Review

2.1 Steam methane reforming process

Steam reforming is a process of converting hydrocarbon feedstock to hydrogen and carbon oxides. The product gas is mainly used for the production of hydrogen and as input for the synthesis of a large variety of chemicals, such as ammonia, methanol, and oxoalcohols. Oil resources have lower H/C ratio than the ratio required in transportation fuels. The H/C (hydrogen to carbon) ratio of transportation fuels is close to 2:1. Hydrogen is needed to increase the H/C ratio of naturally formed oil to make it suitable for transportation vehicles. In refineries, hydrogen is available as a by-product from other refinery processes, primarily the catalytic reforming process (catalytic reforming produces high octane products for gasoline blending). Catalytic reformers operate at mild conditions to meet the requirement of lower content of aromatics in gasoline. This will lower hydrogen yield from catalytic reformer. Moreover hydrogen is needed for hydrotreating of diesel and heavy oil fractions. There is a gap of hydrogen supply and demand. Thus steam reforming is the obvious choice to fill this gap. In general, there is a need for more hydrogen to provide the optimum fuel products.

In the early years of the modern ammonia industry the hydrogen required was obtained mainly from by-product coke oven gas, from water (by electrolysis), and from coke (by gasification). In 1950s, exploration and exploitation of large natural gas reserves and the availability of infrastructure to transport the gas to consumer made natural gas easily available. Natural gas is ideal raw material for steam reforming for two reasons; it gives off equal amount of hydrogen and it produces fewer undesirable by-products [4].

2.1.1 Reactions of steam methane reforming

Steam methane reforming (SMR) is the most common process for hydrogen production from natural gas [5]. The reformer is a fired heater containing numerous catalyst filled tubes. Natural gas and steam are preheated to about 850K and passed through catalyst tubes. The natural gas-steam mixture is catalytically converted to hydrogen, carbon monoxide and carbon dioxide. The overall reaction is endothermic, consequently heat supplied by external burners. The following global reactions take place inside the catalyst tubes:

$$CH_4 + H_2O \leftrightarrow CO + 3H_2 \quad \Delta H = +206.28\,kJ/mol \tag{2.1}$$

$$CO + H_2O \leftrightarrow CO_2 + H_2 \quad \Delta H = -41.16\,kJ/mol \tag{2.2}$$

Equation (2.1) is the reforming reaction (endothermic) and equation (2.2) is the water-gas shift reaction (slightly exothermic). Summation of the heat of reactions reveals that the net reaction is endothermic. For this reason, additional energy has to be provided by external heating. Typical steam methane reforming is shown in figure 2.1.

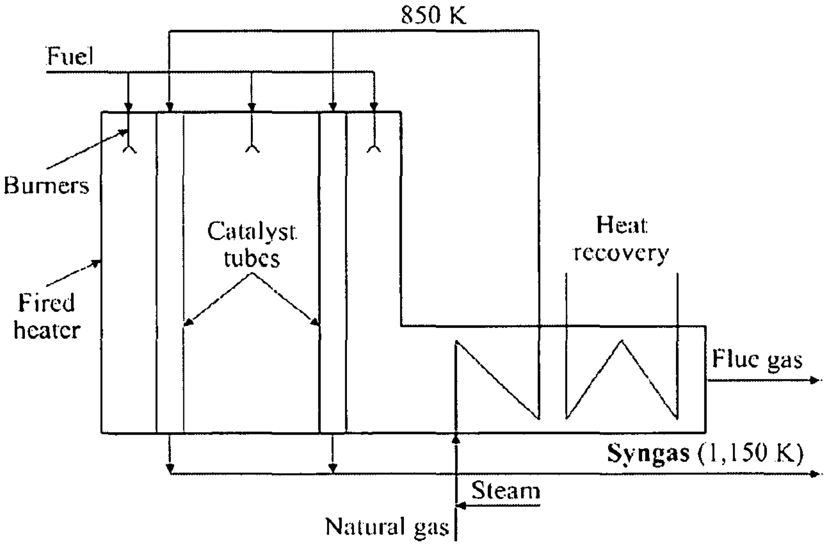

Figure 2. 1 Typical steam methane reforming scheme [5]

The product gas is close to equilibrium in most practical cases [6]. Hence thermodynamic calculations can predict the composition of the product from a reformer with small deviation. In industrial practice, the 'approach to equilibrium' at reformer outlet for the reforming reaction is expressed by a temperature difference defined as:

$$\Delta T_R = T(exit\ catalyst) - T(Q_R) \tag{2.3}$$

In which $T(Q_R)$ is the equilibrium temperature corresponding to an equilibrium constant equal to the reaction quotient Q_R, which is the product of the partial pressures of the individual components raised to the power of their stoichiometric coefficients. The rate of shift reaction (2.2) is so fast that it can be assumed to be at equilibrium in the major part of the reformer. The approach to equilibrium indicates the distance of a reaction from equilibrium: $\Delta T_R = 20^O C$ means that the composition at a given reformer operating temperature T_{RF} is that calculated at $(T_{RF} - 20)$. For a typical reformer using commercial catalysts ΔT_R is given by the following equations [7]:

$$\Delta T_R = 0 \qquad if\ T_{RF} \geq 650^o C$$

$$\Delta T_R = 43.33\left(1 - \frac{T_{RF}}{650}\right) \quad if \quad T_{RF} < 650^o C \tag{2.4}$$

Most industrial steam reformers are fixed bed reactor and their design is usually based on thermodynamic equilibrium rather than kinetics basis. It has been observed that design of steam reformers based on kinetic gives better result than thermodynamic based design [8]. Proper and reliable diffusion reaction model is important for the kinetic based design of the reformer. Predictions of effectiveness factors are very important in the efficient design and optimization of steam reformers.

2.1.2 Rate equations

Xu and Froment [8] proposed more general intrinsic rate equations for the steam reforming of methane. Integral flow reactor and a commercial catalyst were used. They used Langmuir-Hinshelwood principles with a mechanism of thirteen steps, three of which are rate determining steps and ten occur at equilibrium.

The three reactions considered for their model development are equations (2.1), (2.3) and (2.5).

$$CH_4 + 2H_2O \leftrightarrow 4H_2 + CO_2 \tag{2.5}$$

The corresponding rate equations for reactions (2.1), (2.2) and (2.5) are:

$$R_I = \frac{k_1}{p_{H_2}^{2.5}}\left(p_{CH_4}p_{H_2O} - \frac{p_{H_2}^3 p_{CO}}{K_1}\right)\Big/ DEN^2 \tag{2.6}$$

$$R_{II} = \frac{k_2}{p_{H_2}}\left(p_{CO}p_{H_2O} - \frac{p_{H_2} p_{CO_2}}{K_2}\right)\Big/ DEN^2 \tag{2.7}$$

$$R_{III} = \frac{k_3}{p_{H_2}^{3.5}}\left(p_{CH_4}p_{H_2O}^2 - \frac{p_{H_2}^4 p_{CO_2}}{K_1 K_2}\right)\Big/ DEN^2 \tag{2.8}$$

where

$$DEN = 1 + K_{CO}p_{CO} + K_{H_2}p_{H_2} + K_{CH_4}p_{CH_4} + K_{H_2O}p_{H_2O}/p_{H_2} \tag{2.9}$$

DEN represents the denominator .

The influence of temperature on rate constants and adsorption coefficients are given by Arrhenius and Van't Hoff relations [8].

$$k_i = A_i \exp\left[\frac{-E_i}{RT}\right] \qquad i = reaction\ 1, 2$$

$$K_j = B_j \exp\left[\frac{-\Delta H_j}{RT}\right] \qquad j = CO, H_2, CH_4, H_2O$$

The kinetic parameter for Arrhenius equation is shown in table 2.1.

Table 2. 1 Kinetic parameters

Re*action*	$A_i\left(mol - MPa^{0.5}\left(g_{cat}\right)^{-1}.h^{-1}\right)$	$E_i\left(KJ.mol^{-1}\right)$
I	1.336×10^{15}	240.1
II	1.995×10^{7}	67.3
III	3.22×10^{14}	243.9

Table 2.2 lists the adsorption constantans of selected species for Van't Hoff equation.

Table 2. 2 Adsorption constant

Species	$B_j\left(MPa^{-1}\right)$	$\Delta H_j\left[KJ.mol^{-1}\right]$
CO	8.23×10^{-4}	-70.65
H_2	6.12×10^{-8}	-82.90
H_2O	1.77×10^{5}	88.68
CH_4	6.65×10^{-3}	-38.28

2.2 Problems in conventional steam reforming

Heat transfer is a major problem in the operation of the steam reformer [9]. The temperature of the reformer should be maintained high and this is done by supplying heat. Heat is supplied by burning supplemental fuel gas in the furnace chamber. It is known that gas is a poor thermal conductor and heat transfer from the gas phase to the catalyst pellets is a slow process. In the process of heat transfer from the combustion chamber to the catalyst, the outermost sections of the packed bed will turn to be a resistance of heat transfer to the inner sections. Packing the catalyst in a long narrow tubes made of super alloy will result in better heat transfer rate. Formation of carbon deposits or coking is also another problem. It may cause deactivation of catalyst, reduce conversion of methane, block the packed bed, increase pressure drop, cause overheating of tube metal due to formation of hotspots. This will badly affect the productivity of the plant. Carbon deposition may occur according to the following reactions:

$$2CO(g) \rightarrow C(s) + CO_2(g) \tag{2.10}$$

$$CO(g) + H_2(g) \leftrightarrow C(s) + H_2O(g) \tag{2.11}$$

$$CH_4 \rightarrow C(s) + 2H_2(g) \tag{2.12}$$

Selection of proper operational parameters and improvements in catalyst can reduce carbon formation. Nickel based catalyst supported on α-alumina ceramic is commonly used. The acidic property of the alumina results in cracking of hydrocarbons and formation of coke. To counteract this effect an alkali promoter, such as potash (KOH), is added to the catalyst. Steam can oxidize the carbon deposit through the following reversible reaction:

$$C(s) + H_2O \leftrightarrow CO(g) + H_2(g) \tag{2.13}$$

Operating at higher steam-to-methane ratio minimizes the chance of carbon deposit. The formation and consumption of carbon is a competitive process and the most suitable steam-to-carbon ratio is usually obtained in operation through attempts to eliminate carbon deposit while achieving the best economics.

2.3 Review of exergy analysis on steam methane reforming.

The concept of exergy analysis has been used in many processes. It has been used to evaluate performance of heat exchangers, distillation column, heat absorption pumps, fuel cells, reactors, combustion processes etc. Although exergy efficiency has been widely used, most of the works were based on the traditional efficiency of exergy.

Rosen [10] has made thermodynamic comparison of hydrogen production processes. A wide range of hydrogen production processes, including processes which are hydrocarbon based (steam methane reforming and coal gasification), non-hydrocarbon based (water and thermo chemical water decomposition) and integrated (steam methane reforming linked to the non hydrocarbon based processes) were considered. The processes were compared on the base of energy and exergy losses and efficiencies.

Hinderink et.al. [11] conducted exergy analysis of different technologies of steam reforming for synthesis gas production. In his work four process schemes were considered. Conventional steam reforming, conventional steam reforming with pre-reformer, combined reforming with a natural gas bypass and convective reforming parallel to non-catalytic partial oxidation were few of the processes analyzed. Comparison was made by the total exergy loss of each process and then the locations of major exergy loss were revealed and their potential improvements were indicated.

Sorin et al. [12] considered improvements of steam methane reforming by oxygen enrichment. The air for the combustion is enriched with oxygen using membrane separation and the flame temperature of the combustion gas will be raised. This will improve the conversion of methane but at the expense of electrical energy input for the membrane separation. The conventional exergy efficiency and the utilizable coefficient were applied as a criterion for the thermodynamic performance. The work showed that utilizable coefficient (modified intrinsic exergy efficiency) can best describe the thermodynamic performance.

Chapter Three

Methodology

This part of the project has three parts. The first part is basic thermodynamics to describe the equilibrium condition of the outlet stream of steam reformer. The second part describes components of exergy, methods to compute exergy, and exergy efficiency. Lastly exergy analysis is applied to steam methane reforming process.

3.1 Thermodynamics of steam methane reforming

The equilibrium of constant of a reaction can be defined in terms of fugacity as [13]:

$$k = \prod_i \left(\hat{f}_i / f_i^o \right)^{v_i} \tag{3.1}$$

For homogeneous gaseous reactions, the standard state fugacities can be considered to be unity, that is, $f_i^o = 1$. If the fugacity is expressed as the product of partial pressure and fugacity coefficient.

$$f_i = \phi_i p_i \tag{3.2}$$

Also by definition:

$$p_i = y_i p \tag{3.3}$$

For an ideal gas, $\phi_i = 1$, thus, for steam reforming reaction (refer to equation (2.1)),

$$k_{sr} = \frac{p_{CO} p_{H_2}^3}{p_{CH_4} p_{(H_2O)}} \tag{3.4}$$

And for water gas shift reaction (refer to equation (2.2)),

$$k_{wg} = \frac{p_{CO_2} p_{H_2}}{p_{CO} p_{(H_2O)}} \tag{3.5}$$

Substituting equation (3.3) into equations (3.4) and (3.5) yields

$$k_{sr} = \frac{y_{CO} y_{H_2}^{\ 3} p^2}{y_{CH_4} y_{(H_2O)}} \tag{3.6}$$

$$k_{wg} = \frac{y_{CO_2} y_{H_2}}{y_{CO} y_{(H_2O)}} \tag{3.7}$$

If it is assumed that ΔH^O is independent of temperature, the equilibrium constant can be expressed as :

$$\frac{\ln k_2}{\ln k_1} = -\frac{\Delta H^O}{R}\left(\frac{1}{T_2} - \frac{1}{T_1}\right) \tag{3.8}$$

Equation (3.8) implies that a plot of $(\ln k)$ against $(1/T)$ is linear with a slope of$(\Delta H^O/R)$. For an exothermic reaction, $\Delta H^O < 0$ and k decreases as temperature increases. For an endothermic reaction, $\Delta H^O > 0$ and k increases as with increasing temperature. Equation (3.8) can be written in linear form:

$$\ln k = A + \frac{B}{T} \tag{3.9}$$

The equilibrium constant for reaction (2.1) and (2.2) are given as follow [6]:

$$\ln k_{sr} = 30.4197 + \frac{-27106.2}{T} \quad , \quad k_{sr}\left[bar^2\right] \tag{3.10}$$

$$T[K]$$

$$\ln k_{wg} = -3.79762 + \frac{4159.54}{T} \quad , \quad T[K] \tag{3.11}$$

Figure 3.1 shows the plot of $\ln k \quad Vs \quad 1/T$ for steam reforming and water gas reaction.

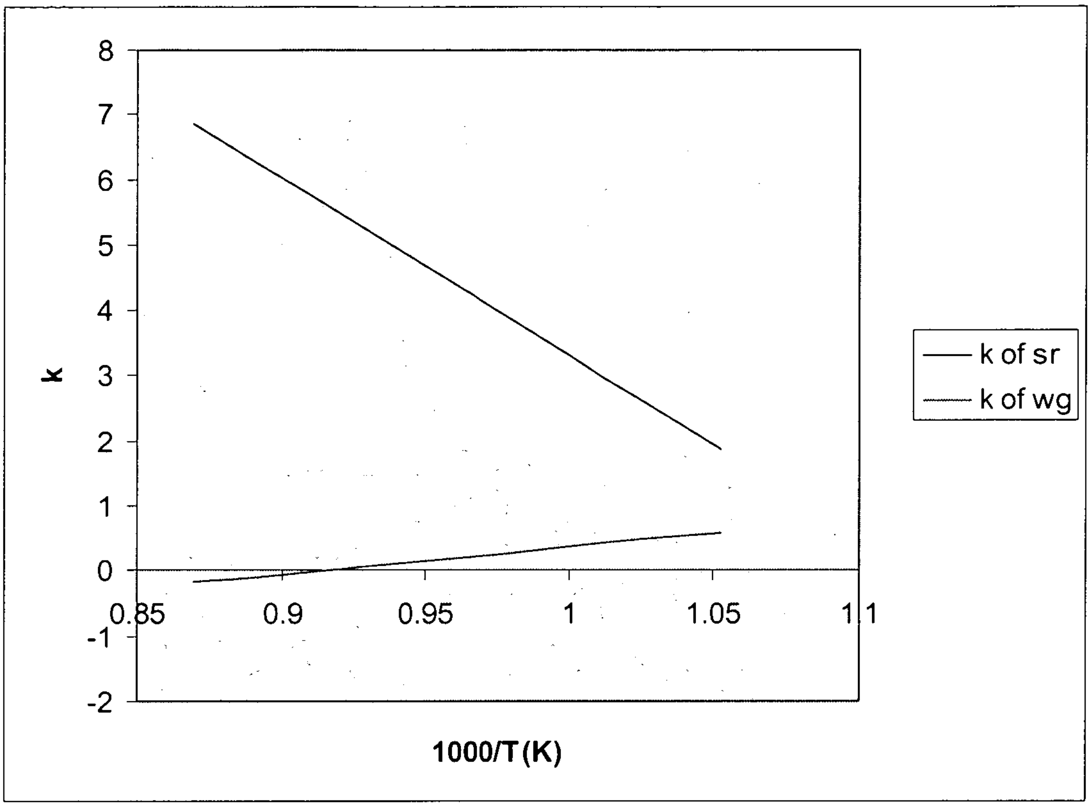

Figure 3. 1 Equilibrium constants as function of temperature

Equations (3.6) and (3.7) can be solved if the composition of each species is expressed in terms of temperature, steam to methane ratio and pressure. Let r be molar ratio of steam to methane in the feed, x_1 be the conversion of the steam reforming reaction and x_2 be the conversion of water-gas shift reaction.

$$\underset{1-X1}{CH_4} + \underset{r-X1-X2}{H_2O} \leftrightarrow \underset{3X1}{3H_2} + \underset{X1-X2}{CO}$$

$$\underset{X1-X2}{CO} + \underset{r-X1-X2}{H_2O} \leftrightarrow \underset{X2}{H_2} + \underset{X2}{CO_2}$$

Total number of moles at equilibrium

$$= (1 - X1) + (r - X1 - X2) + 3X1 + (X1 - X2) + X2 + X2$$

$$= r + 1 + 2X1 \qquad (3.12)$$

Table 3. 1 Compositions of species at equilibrium

species	CH_4	H_2O	H_2	CO	CO_2
Moles at equilibrium	$1-X1$	$r-X1-X2$	$3X1+X2$	$X1-X2$	$X2$
Mole fraction at equilibrium	$\frac{1-X1}{r+1+X1}$	$\frac{r-X1-X2}{r+1+X1}$	$\frac{3X1+X2}{r+1+X1}$	$\frac{X1-X2}{r+1+X1}$	$\frac{X2}{r+1+X1}$

Putting the value of mole fraction in equations (3.6) and (3.7) gives:

$$k_{sw} = \frac{\left(\frac{3X1+X2}{r+1+X1}\right)^3\left(\frac{X1-X2}{r+1+X1}\right)}{\left(\frac{1-X1}{r+1+X1}\right)\left(\frac{r-X1-X2}{r+1+X1}\right)}p^2$$

$$k_{sw} = \frac{(3X1+X2)^3(X1-X2)}{(1-X1)(r-X1-X2)(r+1+X1)^2}p^2 \qquad (3.13)$$

$$k_{wg} = \frac{\left(\frac{3X1+X2}{r+1+X1}\right)\left(\frac{X2}{r+1+X1}\right)}{\left(\frac{X1-X2}{r+1+X1}\right)\left(\frac{r-X1-X2}{r+1+X1}\right)}$$

$$k_{wg} = \frac{(3X1+X2)X2}{(X1-X2)(r-X1-X2)} \qquad (3.14)$$

Combining equations (3.10), (3.11), (3.13), and (3.14), there are seven unknown variables and four equations. This results in three degree of freedom. We need to specify three variables to be able to solve the equations. Given the operation temperature and pressure of the reformer with steam to methane ration of the feed, it is possible to determine the conversion of the reactions. However, X1 and X2 cannot be eliminated by substitution and the equations must be solved numerically.

This can be done by assuming a value for X1 and substituting this in both equations, then yielding values of X2 from both equations. X1 is then varied until the values of X2 predicted by both equations are equal. Alternatively, X1 and X2 can be varied simultaneously in a non linear optimization algorithm to minimize the errors. Equation (3.13) and (3.14) can be reduced to a form suitable for general-purpose optimization software [14].

$f_1(X1, X2) = k_{sr}$ and $f_2(X1, X2) = k_{wg}$

Three possible ways to formulate the objective for optimization are:

1. minimize$\left(\left|f_1(X1, X2) - k_{sr}\right| + \left|f_2(X1, X2) - k_{wg}\right|\right)$

2. minimize$\left(\left[f_1(X1, X2) - k_{sr}\right]^2 + \left[f_2(X1, X2) - k_{wg}\right]^2\right)$

3. minimize$\left(S_{11} + S_{12} + S_{21} + S_{22}\right)$

Subject to

$$f_1(X1, X2) - k_{sr} + S_{11} - S_{12} = 0$$

$$f_2(X1, X2) - k_{wg} + S_{21} - S_{22} = 0$$

$$S_{11}, S_{12}, S_{21}, S_{22} \geq 0$$

Where $S_{11}, S_{12}, S_{21}, S_{22}$ are slack variables.

The choice of one of these objective functions depends on the nature of the problem, the optimization algorithm being used and the initial points for the solution [14]. In objective 1, it could be difficult to find optimum values due to discontinuous gradient. However, the problem can be transformed such that the objective function for the optimization has no discontinuities in the gradient. Objective function 2 is one possible transformation. It has a continuous gradient. However, transforming from 1 to 2 has weakness; it increases the degree of non-linearity. On the other hand, objective function 3 avoids both an increase in the nonlinearity and discontinuities in the gradient. Thus objective function 3 is used in this project.

3.2 Exergy components

Like energy, exergy of stream of matter, E, can be divided into distinct components.

$$E = E_K + E_P + E_{Ph} + E_x \tag{3.14}$$

E_K and E_P are associated with high grade energy and E_{Ph} and E_O with low grade energy. Introducing specific exergy $\varepsilon = E/m$:

$$\varepsilon = \varepsilon_K + \varepsilon_P + \varepsilon_{Ph} + \varepsilon_x \tag{3.15}$$

3.2.1 Kinetic and potential exergy

The kinetic and potential energies of a stream of substance are high quality of energy. It is possible to fully convertible these energies to work. Therefore, when evaluated in relation to the environmental reference datum levels, they are equal to kinetic and potential exergy respectively. Thus:

$$E = m\frac{C_O^2}{2} \tag{3.16}$$

and:

$$E_P = m g_E Z_O \tag{3.17}$$

Where C_O and Z_O are velocity and height relative to the environment.

3.2.2 Physical exergy

Physical exergy is equal to the maximum amount of work obtainable when the stream of substance is brought from its initial state to the environmental state defined by P_O and T_O, by physical processes involving only thermal interaction with the environment.

$$\Delta\varepsilon = \Delta h - T_O \Delta s \tag{3.18}$$

The process for determining physical exergy is shown on $T - S$ diagram in figure (3.2). The system undergoes reversible processes, and adiabatic process followed by an isothermal process.

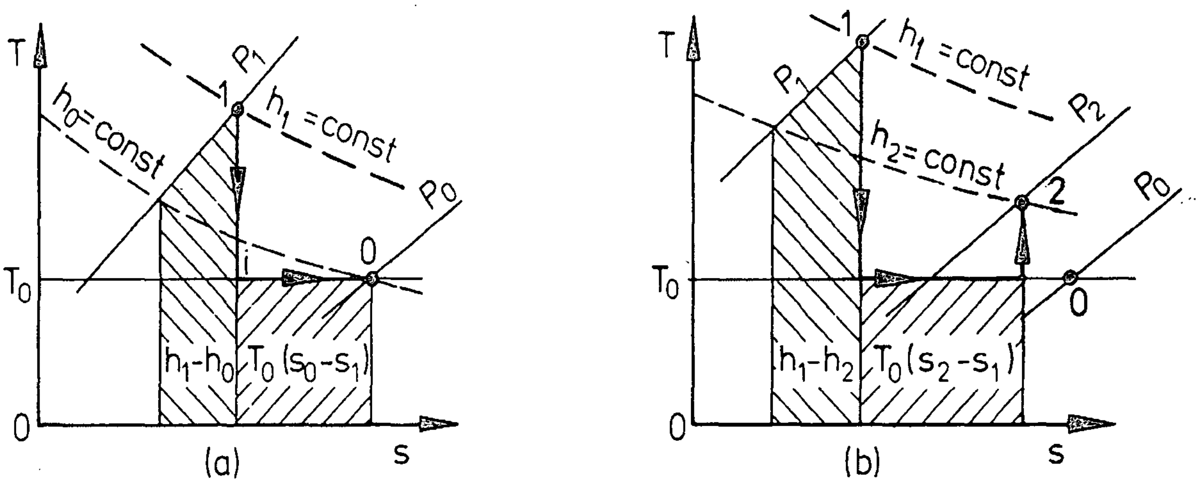

Figure 3. 2 Reversible process for determining (a) physical exergy (b) a change in physical exergy, of a homogenous simple fluid [2]

For ideal gas, the physical exergy can be written as:

$$= \langle C_P^{ig} \rangle_H (T - T_O) + \langle C_P^{ig} \rangle_S T_O \ln\frac{T}{T_O} - RT_O \ln\frac{P}{P_O} \qquad (3.19)$$

Where

$$\langle C_P^{ig} \rangle_H = \int_{T_O}^{T} C_P^{ig} dT \text{ and } \langle C_P^{ig} \rangle_S = \frac{\int_{T_O}^{T} C_P^{ig}\, dT/T}{\ln(T/T_O)}$$

C_P^{ig} can be expressed by polynomial expression as:

$$\frac{C_P^{ig}}{R} = A + BT + CT^2 + DT^{-2} \qquad (3.20)$$

A, B, C, and D are coefficients.

3.2.3 Chemical exergy

Chemical exergy is the work done when a system is brought from environment state to dead state by reversible process. In a reversible process, flow directions and interactions can be reversed. This unique characteristic of reversible process gives another definition for chemical exergy. Chemical exergy is the minimum amount of work required to synthesis and to bring to environmental state. The interaction is through heat transfer and mass transfer only with the environment.

3.2.3.4 Steps to calculate chemical exergy.

Chemical exergy is calculated in two steps [11].

1. The first step is the determination of standard chemical exergy value of the pure reference environment components. This is given in equation (3.21).

$$\varepsilon_x = RT_O \ln \frac{P_O}{P_{OO}} \tag{3.21}$$

2. The second step is to determine the chemical exergy of components which do not exist in the reference environment (non-reference species). This is done in two rounds. First, the standard chemical exergy values of the stable form of the pure elements at P_O, T_O are evaluated from a consistent set of reference species. Secondly, the non reference species will be synthesized from their elements. From the formation reaction, chemical exergy can be expressed as shown in equation (3.22).

$$\varepsilon_{xo,i} = \Delta_f G_i^O - \sum_j v_j \, \varepsilon_{xo,j} \tag{3.22}$$

In which $\varepsilon_{xo,i}$ denotes the standard chemical exergy of any species i, $\varepsilon_{xo,j}$ denotes the standard chemical exergy of the element j in species i and v_j denotes the stoichiometric coefficient of element j in species i. For calculating the standard chemical exergy values of the elements from reference species, the above expression must be used in reverse in combination with equation (3.21). It is important to remember that a gaseous reference environment will give the $\varepsilon_{xo,i}$ values of only ten elements. For the rest of the elements, additional liquid and solid phase environments should be defined. The standard chemical exergy of different species is tabulated by different researchers. In this project instead of following the two steps, exergy of species in the process is taken from reference [2].

3.2.3.3 Chemical exergy of a mixture

Chemical exergy of a mixture of ideal gas is calculated using equation (3.23).

$$\varepsilon_{x,m} = \sum_i y_i \, \varepsilon_{xo,i} + RT_O \sum_i y_i \ln y_i \tag{3.23}$$

For a real solution, the exergy of the mixture is expressed as:

$$\varepsilon_{x,m} = \sum_i y_i \, \varepsilon_{xo,i} + RT_O \sum_i y_i \ln \gamma_i y_i \tag{3.24}$$

3.3 Definition of exergetic efficiency

There are three definitions of exergetic efficiencies for steady state processes [15]. These are the conventional or simple exergetic efficiency, the rational exergetic efficiency and the intrinsic exergetic efficiency.

3.3.1 Conventional exergetic efficiency

This is most commonly used exergetic efficiency. The exergy balance for the incoming and outgoing flows can be rewritten as.

$$E_{in} = E_{out} + I \tag{3.25}$$

The conventional (traditional) exergetic efficiency is the ratio of the total outgoing exergy flow to the total incoming exergy flow:

$$\eta = \frac{E_{out}}{E_{in}} \tag{3.26}$$

This definition has both advantage and disadvantage. The advantage is that it is not ambiguous. It is good performance indicator for systems in which all components of the incoming exergy flow are transformed to other components, examples, power plant stations and building heating and cooling system. The downside of using this definition comes into picture when all the components of the incoming exergy flow are not transformed to other components. In this case, the untransformed components give a false impression of the performance of the process plant or unit. In a chemical reactor with a zero conversion factor, the input exergy rate will equal the output exergy rate and the traditional exergetic efficiency will be 100%. The reactor does not produce anything. In this case, the traditional exergetic effiency gives a false impression of the thermodynamic performance of the reactor. Other exergetic efficiencies have been proposed to adequately explain the performance of such systems.

3.3.2 Rational exergetic efficiency

The rational exergetic efficiency is defined as a ratio of the desired exergy output to the exergy used or consumed.

$$\psi = \frac{E_{desired\ \ output}}{E_{used}} = 1 - \frac{I}{E_{used}} \qquad (3.27)$$

$E_{desired\ \ output}$ is the sum of all exergy transfers from the system. E_{used} is the required exergy consumed for the process to be performed. The rational efficiency can be applied to any system, except to purely dissipative systems, because no desired product can be defined in this case.

3.3.3 Intrinsic exergy efficiency

This form of efficiency removes the shortcoming of traditional exergetic efficiency. It excludes the untransformed components of exergy from the incoming and outgoing streams. Any material, heat and work stream has exergy, which is completely defined by temperature, pressure and composition of the stream itself and of a reference state. Overall exergy balance of a system is shown below in figure 3.3 .

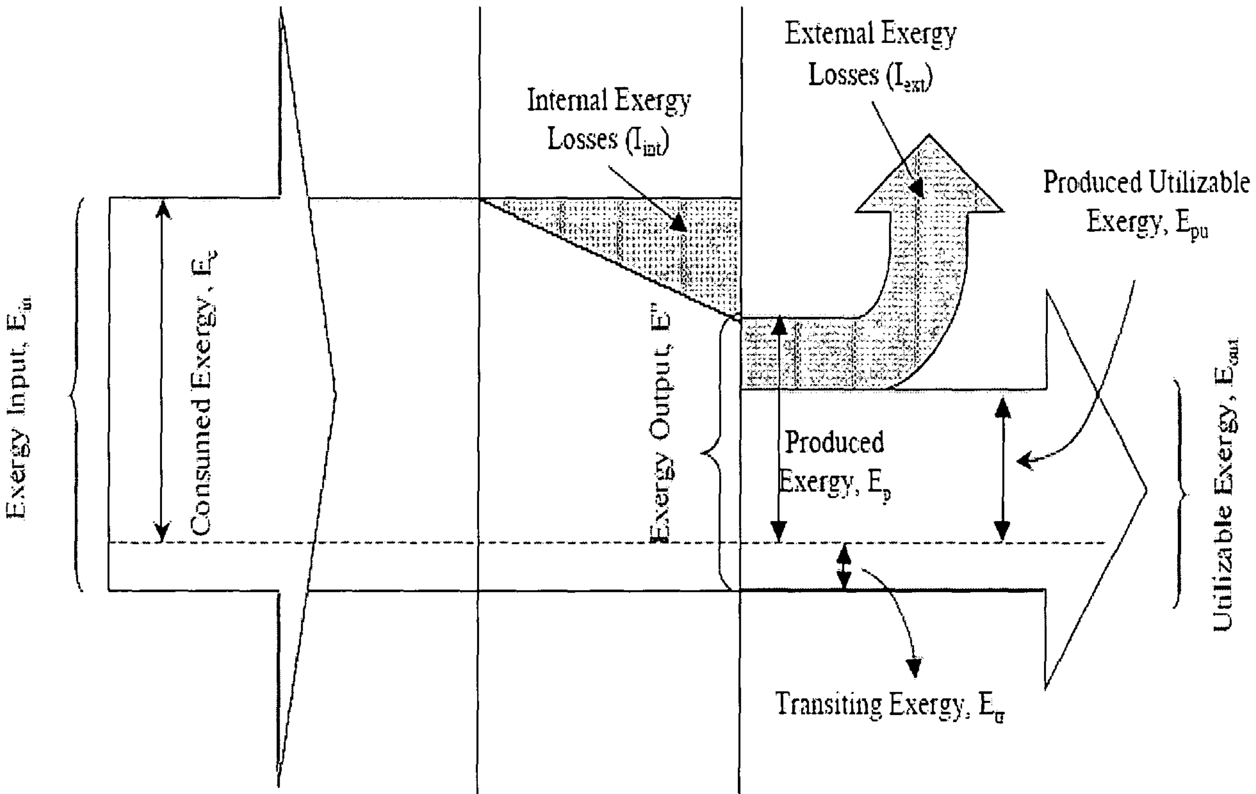

Figure 3. 3 Graphical representation of overall exergy balance [15]

The intrinsic exergy efficiency can be defined as:

$$\eta_i = \frac{E'' - E_{tr}}{E' - E_{tr}} \tag{3.28}$$

In most cases, part of the exergy output from the system may dissipate into the environment as heat losses, sewage waste or smokestack effluents. This wasted exergy (I_{ext}) will no longer be used by the subsequent processes. It is more appropriate, from the standpoint of downstream operations, to consider the exergy that remains utilizable,

E_u, rather that the total output, E''. On the basis of these observations a new coefficient of thermodynamic efficiency, the utilizable exergy coefficient, η_u, has been defined.

$$\eta_u = \frac{E' - I_{\text{int}} - I_{ext} - E_{tr}}{E' - E_{tr}} \tag{3.29}$$

$$= \frac{E_{pu}}{E_c} \tag{3.30}$$

3.4 Calculation of transit exergy

Methods of calculating transit exergy has been studied by Brodyansky et al [3]. They formulated algorithms to calculate transit exergy for different cases. Below is excerpt from their work.

$$\sum E_x^{tr} = \min\left[\sum_b E_x'; \sum_b E_x''\right] \tag{3.31}$$

$$\sum E_{p,T}^{tr} = \min\left[\sum_b E_{p,T}'; \sum_b E_{p,T}''\right] \tag{3.32}$$

The algorithm for calculating transit thermomechanical exergy for each subflow of a substance at a system's input and output are as follows:

Case 1. $T' \geq T_O; T'' \geq T_O$

$$E_{p,T}^{tr} = \min\left\lfloor E'(p', T^{\min}); E'(p'', T^{\min}); E'''(p', T^{\min}); E''(p'', T^{\min})\right\rfloor \tag{3.33}$$

Case 2. $T' \leq T_O; T'' \leq T_O$

$$E_{p,T}^{tr} = \min\left[E'(p', T^{\max}); E'(p'', T^{\max}); E''(p'', T^{\max}); E''(p'', T^{\max})\right] \tag{3.34}$$

Case 3. $T' < T_O; T'' > T_O$ Or $T' > T_O; T'' < T_O$

$$E^{''r}_{p,T} = \min \left\lfloor E'\left(p',T_O\right); E'\left(p'',T_O\right); E'''\left(p',T_O\right); E''\left(p'',T_O\right)\right\rfloor \quad (3.35)$$

The above equations (3.33) to (3.35) can be simplified when it is known beforehand that flow exergy changes monotonically with the change of pressure, as for example, in the case of an ideal gas. The above equations may be written respectively as:

$$E^{''r}_{p,T} = \min \left\lfloor E'\left(p^{\min},T^{\min}\right); E''\left(p^{\min},T^{\min}\right)\right\rfloor \quad (3.36)$$

$$E^{''r}_{p,T} = \min \left\lfloor E'\left(p^{\min},T^{\max}\right); E''\left(p^{\min},T^{\max}\right)\right\rfloor \quad (3.37)$$

$$E^{''r}_{p,T} = \min \left\lfloor E'\left(p^{\min},T_O\right); E''\left(p^{\min},T_O\right)\right\rfloor \quad (3.38)$$

3.5 Exergy balance around steam methane reformer

The input-output streams of steam methane reforming process can be represented by figure 3.4, below.

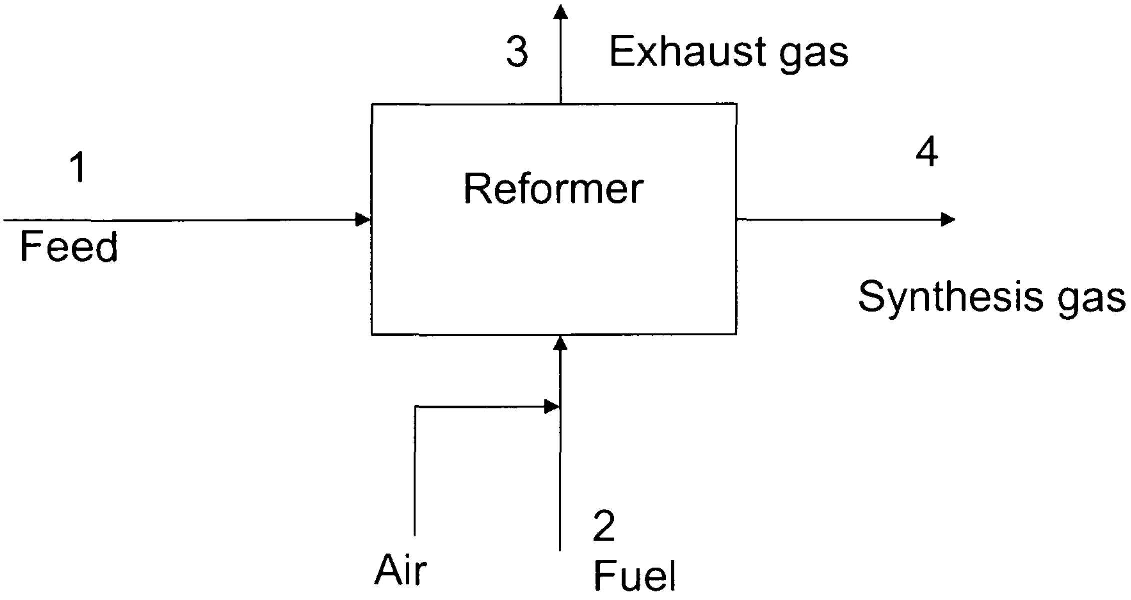

Figure 3. 4 Representation of steam methane reforming process

The overall exergy balance of the process is:

$$E_1 + E_2 + E_{air} = E_4 + E_3 + I_{\text{int}} \tag{3.39}$$

It is assumed that the exergy of the flue gas, E_3, is rejected and constitutes the external losses I_{ext}. The air is at the reference condition and its exergy is taken as zero. Equation (3.39) becomes:

$$E_1 + E_2 = E_4 + I_{\text{int}} + I_{ext} \tag{3.40}$$

This can be rewritten as:

$$\left(E_x'\right)_1 + \left(E_{p,T}'\right)_1 + E_2 = \left(E_x''\right)_4 + \left(E_{p,T}''\right)_4 + I_{\text{int}} + I_{ext} \tag{3.41}$$

Then according to equation (3.26) the conventional exergy efficiency for the reactor is:

$$\eta_e = \frac{E_4}{E_1 + E_2} \tag{3.42}$$

It is important to notice that instead of total outgoing exergy, the utilizable outgoing exergy is considered. The transiting chemical exergy in the process streams 1 and 4 can be written as:

$$E_x^{tr} = \left(n_{CH_4}\right)_4 \left(\varepsilon_{CH_4}\right)_4 + \left(n_{H_2O}\right)_4 \left(\varepsilon_{H_2O}\right)_4 \tag{3.43}$$

And the transiting thermomechanical exergy is:

$$E_{p,T}^{tr} = \min\left(E_{p,T}^1,\ E_{p,T}^4\right) \tag{3.44}$$

By subtraction of equation E_x^{tr} from $\left(E_x'\right)_1$ at the left side of equation (3.41) gives:

$$\left(E_x'\right)_1 - E_x^{tr} = E_{\Delta CH_4} + E_{\Delta H_2O} \tag{3.45}$$

Where

$$E_{\Delta i} = \left(n_i' - n_i''\right)\varepsilon_i' + n_i''\left(\varepsilon_i' - \varepsilon_i''\right) \tag{3.46}$$

The term $E_{\Delta CH_4}$ is made up of two parts, the chemical exergy of the reacted methane, $\left(n'_{CH_4} - n''_{CH_4}\right)\varepsilon'_{CH_4}$, and the reduction of chemical exergy of the non reacted methane due to dilution by the products of reaction, $n''_{CH_4}\left(\varepsilon'_{CH_4} - \varepsilon''_{CH_4}\right)$. Similarly, the subtraction of E_x^{tr} from the right side of equation (3.41) removes from this term the exergy of the non reacted methane and water and enables computation of the chemical exergies of H_2 , CO and CO_2 produced as:

$$\bar{E}''_{H_2} = n''_{H_2}\,\bar{\varepsilon}''_{H_2} \tag{3.47}$$

$$\bar{E}''_{CO} = n''_{CO}\,\bar{\varepsilon}''_{CO} \tag{3.48}$$

$$\bar{E}''_{CO_2} = n''_{CO_2}\,\bar{\varepsilon}''_{CO_2} \tag{3.49}$$

The utilizable exergy coefficient, η_u, becomes:

$$\eta_u = \frac{\bar{E}''_{H_2} + \bar{E}''_{CO} + \bar{E}''_{CO_2} + \left(E'_{p,T}\right)_1 - E^{tr}_{p,T}}{E_{\Delta CH_4} + E_{\Delta H_2O} + E_2 + \left(E''_{p,T}\right)_4 - E^{tr}_{p,T}} \tag{3.50}$$

Figure 3.5 shows steps used in the calculation.

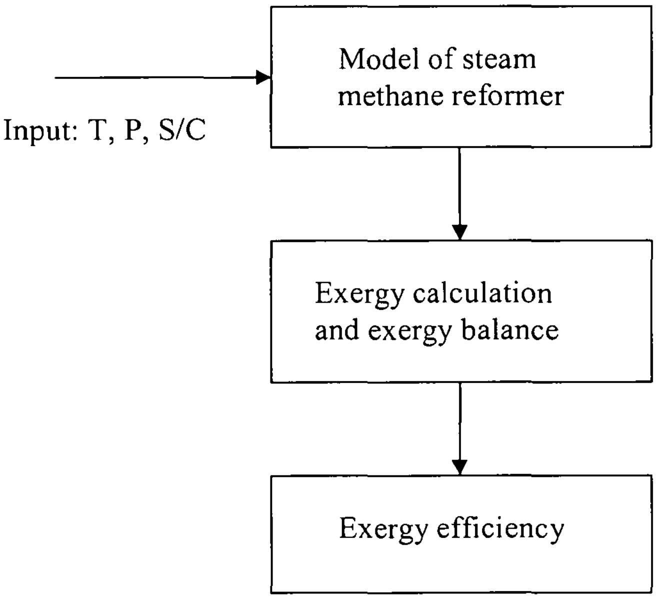

Figure 3. 5 Flow diagram of calculation procedures

Chapter Four

Results and Discussions

4.1 Effect of temperature and steam to methane ratio on conversion of methane.

The effect of temperature on the conversion of methane was investigated by varying the operating condition of the reformer from 973K to 1213K at a constant pressure and steam to methane ratio. It is observed that as the temperature increases the conversion of methane increases. Methane involves only in the steam reforming reaction which is endothermic. The result agrees with the Le Chatelier's principle, increasing the temperature of endothermic reaction will shift the reaction towards the product. As shown in figure 4.1 the conversion increases by 5% for every 20 ^{0}C rise in temperature of the reformer until the conversion reaches to 80%. For conversion of methane between 80% and 90%, it will increase by 4%. The conversion of methane from this model was compared with the HYSYS output and it was found that the model prediction is approximately 2% higher than the HYSYS result. The error gets as low as 0.8% for higher temperatures.

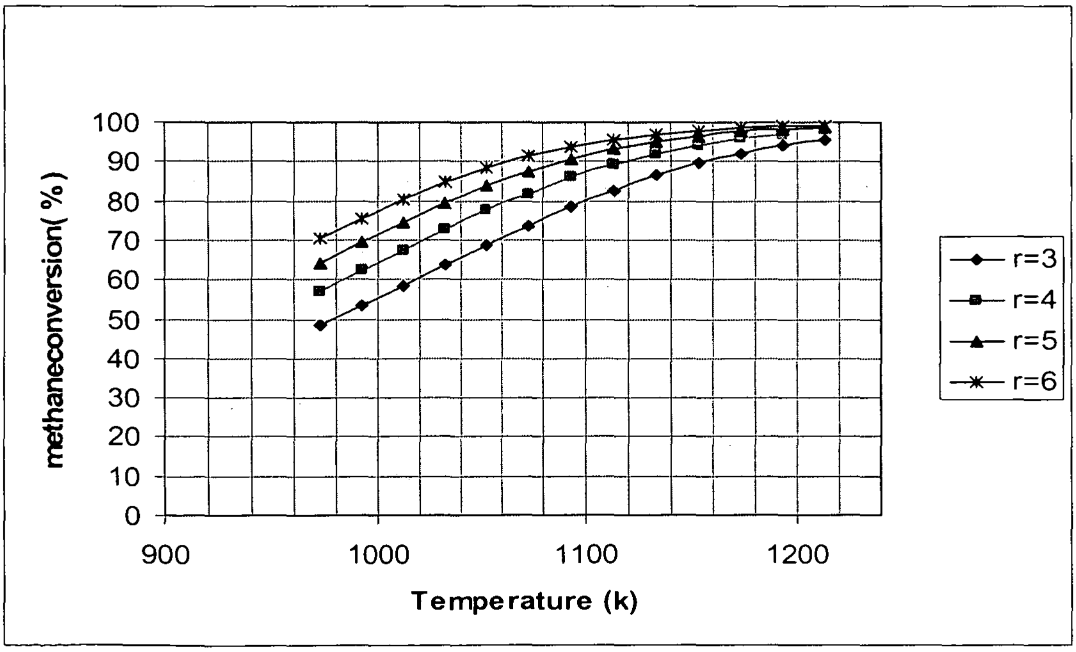

Figure 4. 1 conversion of methane as function of temperature at p=20bar for different steam to methane ratio

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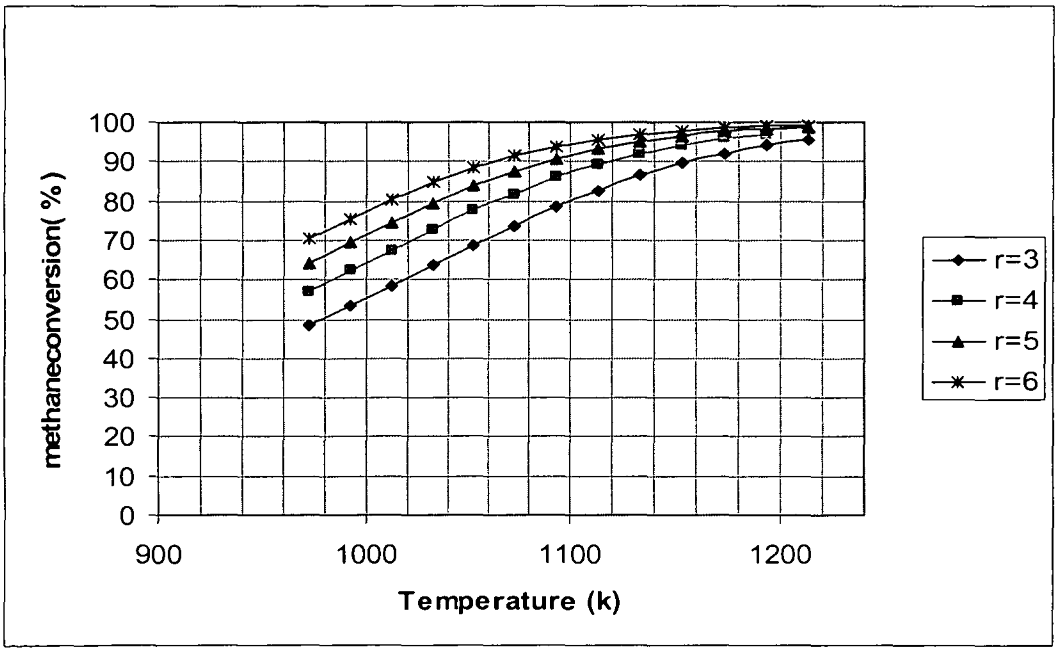

Figure 4. 1 conversion of methane as function of temperature at p=20bar for different steam to methane ratio

4.2 Effect of pressure on conversion of methane.

According to Le Chatelier's principle, pressure affects only the steam reforming reaction. The water-gas shift reaction is not affected by pressure. The number of moles of the reactant is the same as the number of moles of the products for this reaction. The steam reforming reaction produces additional moles in the product and product formation is favored by low pressure. A 5 bar reduction has approximately similar effect as a $20^{O}C$ increment on the conversion of methane at constant steam to methane ratio. Effect of pressure on methane conversion can be seen in figure 4.2 below.

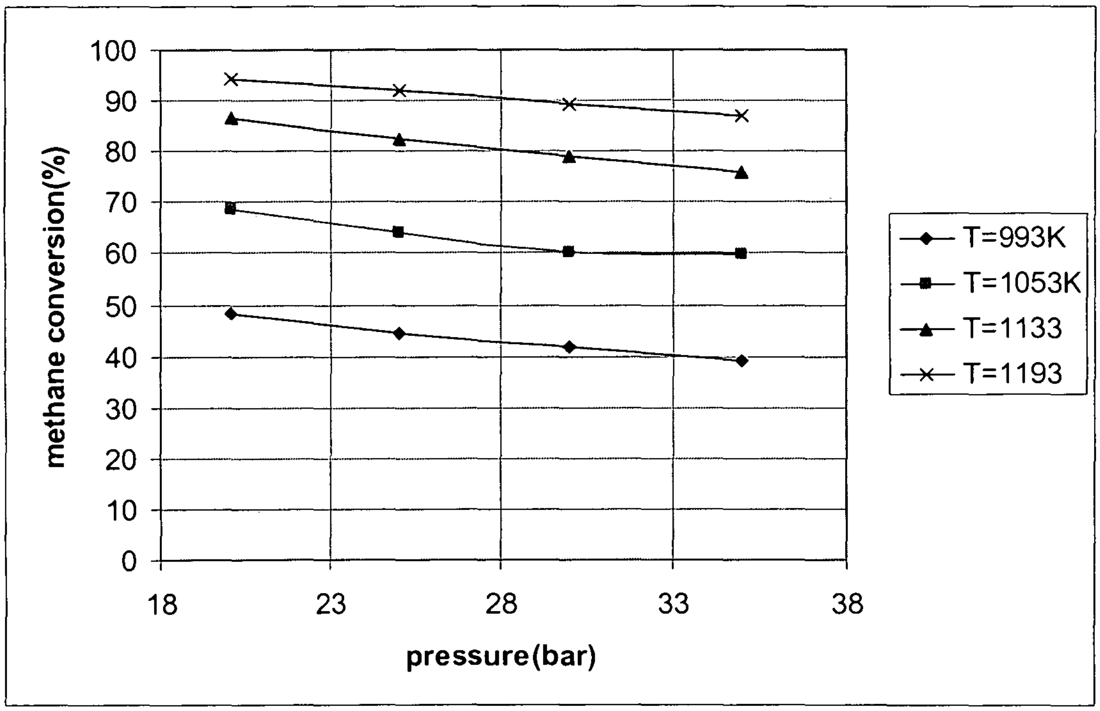

Figure 4. 2 conversion of methane as a function of pressure at S/C=3 for different temperatures

The output stream of the reformer is composed of H_2, CO, CO_2, and unreacted CH_4 *and* H_2O. The composition of the stream is dependent on the operation conditions. As it is obvious from the Le Chatelier's principle, the simulation yields an increase in H_2 and CO compositions with increase in temperature. The composition of unreacted methane and water is underestimated compared to the simulation (HYSYS) output. Where as it overestimates for the composition of H_2 and CO. Figure 4.3 depicts the effect of temperature on the composition of outlet stream species.

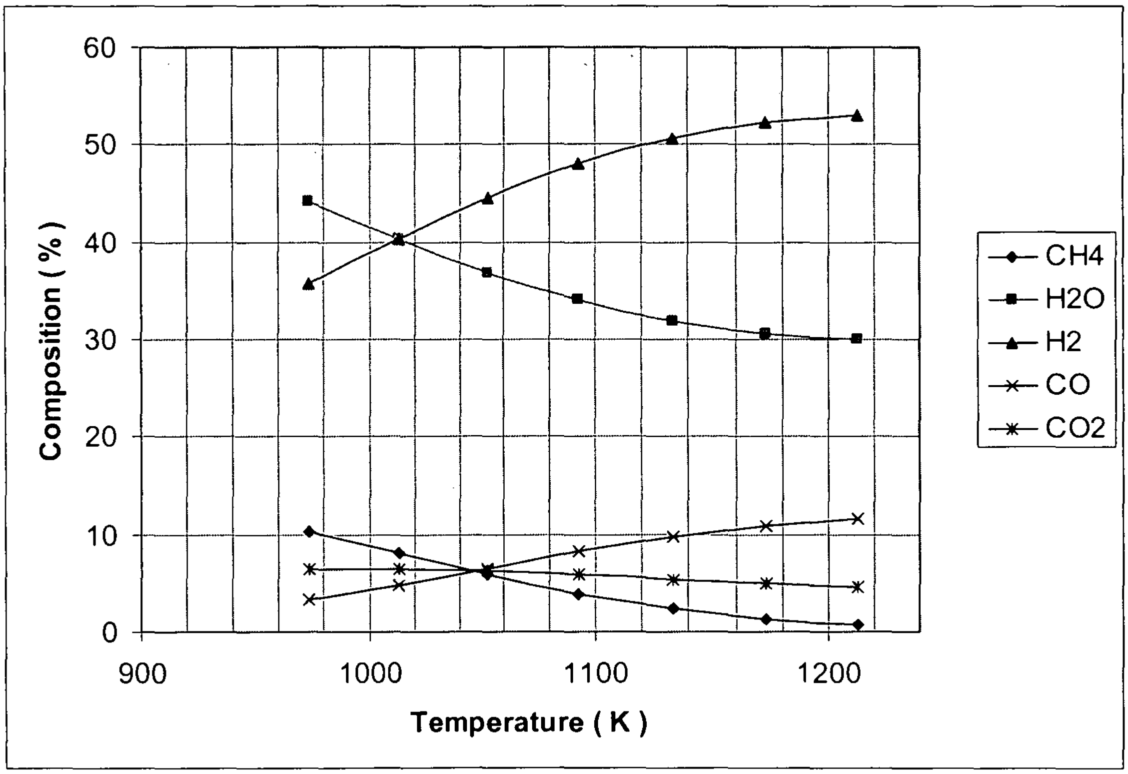

Figure 4. 3 Effect of temperature on the composition of outlet streams at p=20bar and S/C=3

4.3 Effect of hydrogen removal on methane conversion

It is well understood that removing reactants will shift the reaction towards product. This will improve the conversion of methane. The effect of removal of hydrogen from product stream on the conversion of methane was analyzed and it was observed that for every 10% removal of hydrogen, the effect is the same as increasing the operating temperature by 15K. For example conversion of methane at 1073K with 10% hydrogen removal is the same as methane conversion at 1088K without hydrogen removal at constant pressure and steam to methane ratio. Removal of hydrogen will avoid the fuel need to raise the temperature of the reformer for higher conversion. It will also make the construction of the tube easier and cheaper. However the technical and the economic feasibility should be studied further and a trade off should be made. In most cases membrane separation is used to remove hydrogen. Its economic and technical feasibility should be assessed. Effect of hydrogen removal on conversion of methane is shown in figure 4.4.

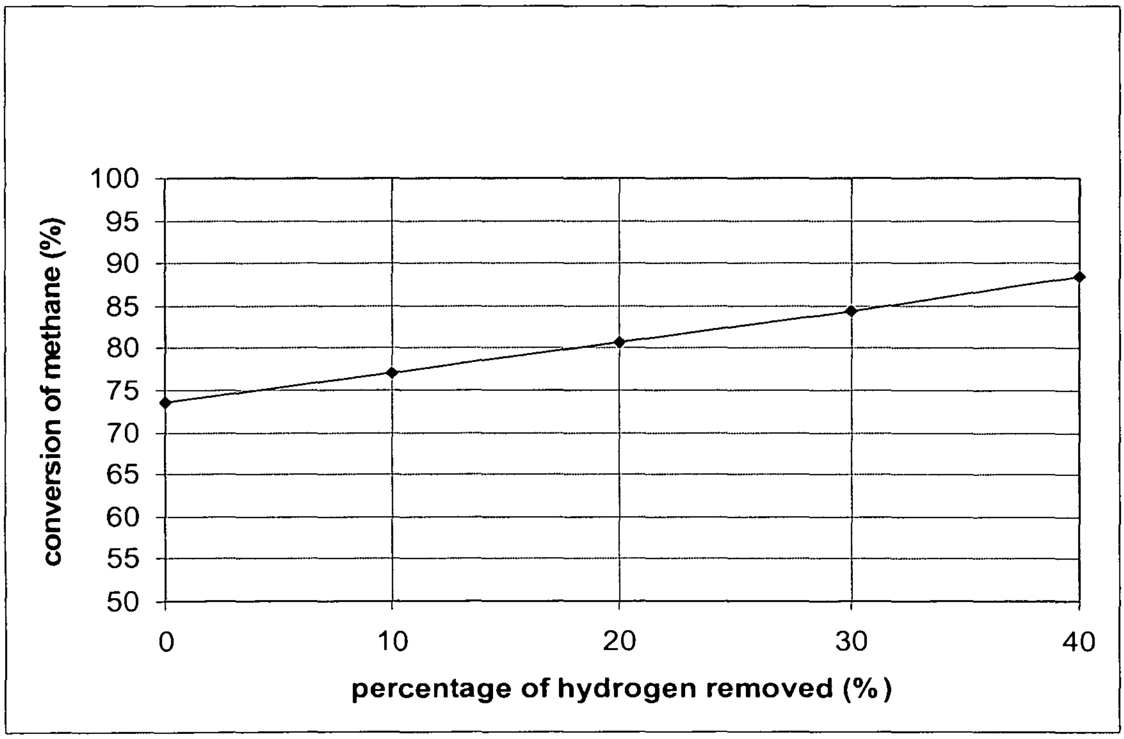

Figure 4. 4 Effect of hydrogen removal on methane conversion at T=1073K, p=20bar and S/C=3

4.4 Exergy losses

Exergy losses considered here are both internal and external losses. It is the sum of I_{int} and I_{ext}. Exergy losses indicates where and how to improve a process. The effects of parameters on internal and external exergy losses have been studied and exergy loss versus temperature is plotted as shown in figure 4.5. Temperature and pressure are the selected parameters. The total exergy loss increases with temperature. The variation due to temperature (between 1000K and 1170K) is 54.30% at 20bar, 61% at 25bar, and 66% at 30bar. The exergy loss is strongly dependent on temperature.

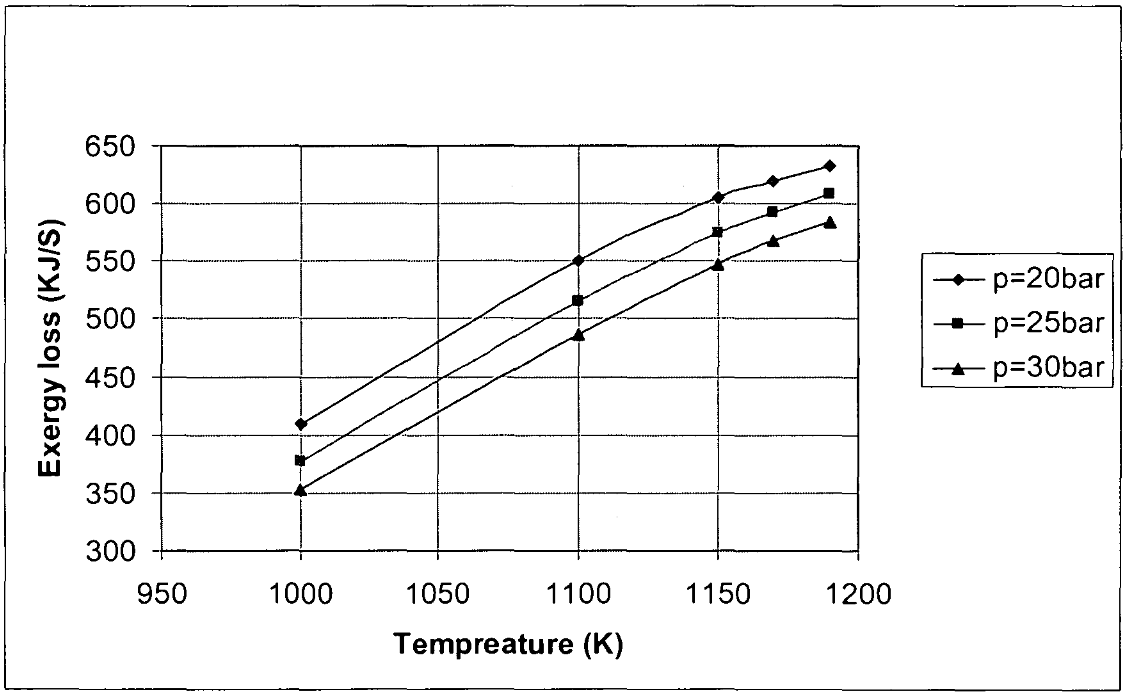

Figure 4. 5 Exergy loss as a function temperature at S/C=3

The exergy loss is lower for higher pressure. The loss at 1000K and 15bar is 1.37times the loss at the same temperature but 35bar. The variation gets narrower at higher temperature (constant) and varying pressure, i.e. the loss at 1170K and 15bar is only1.19 times the loss at the same temperature and 35bar. This shows that the exergy loss is slightly dependent on pressure

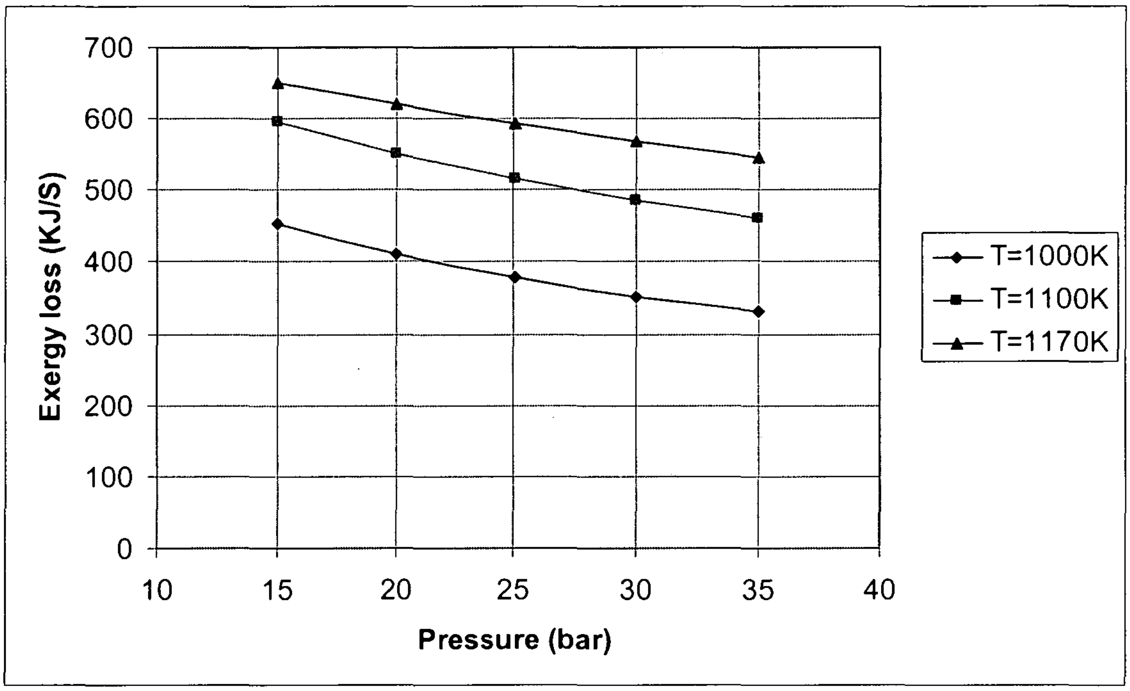

Figure 4. 6 Exergy loss as function pressure at S/C=3

The exergy losses considered previously was total losses. Additional information can be obtained by considering exergy losses per moles of hydrogen. It is the amount of exergy lost to produce unit mole of hydrogen. It can be seen in figure 4.7 that there is a temperature at which the exergy loss per moles of hydrogen produced is the minimum for the temperature ranges considered. The minimum exergy loss per moles of hydrogen produced is obtained in the temperature range of 1105 K to 1120 K.

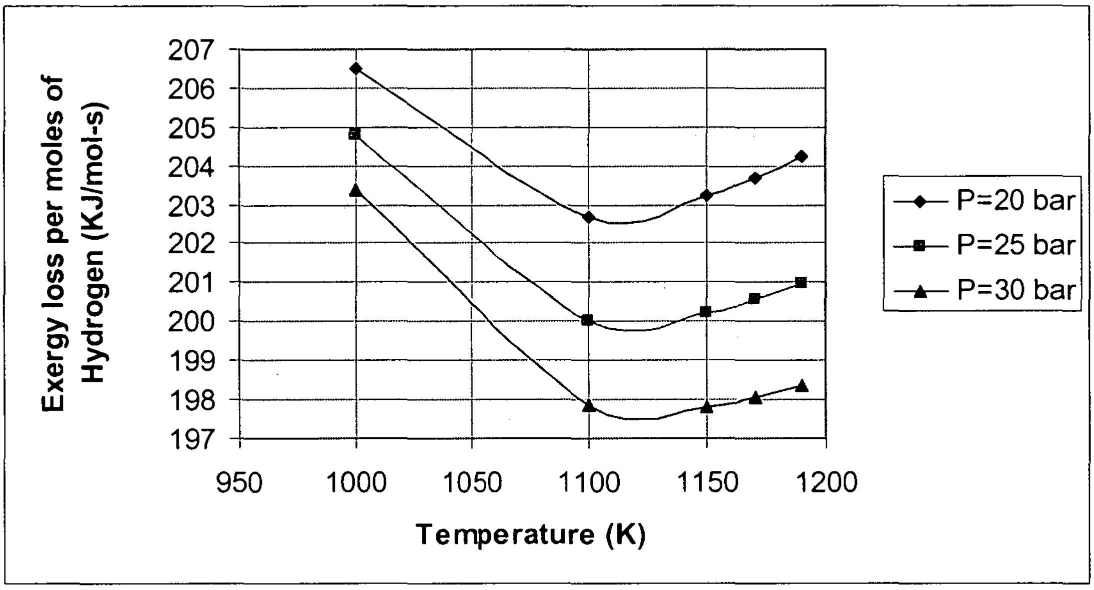

Figure 4. 7 Exergy loss per moles of hydrogne produced at different temperature for S/C=3

The effect of temperature, pressure and steam to methane ratio on the exergy efficiency, η_e, and utilizable coefficient, η_u was studied. The operating parameters were allowed to vary and the efficiency of the reformer was computed. The simultaneous computations of the two efficiencies give us the opportunity to select the appropriate efficiency definition for such kind of systems. Table 4.1 shows the exergy terms as function of temperature.

Table 4. 1 Exergy terms as function of temperature

Temperature(K)	1000	1100	1150	1170	1190
Conversion of methane	0.550	0.799	0.891	0.918	0.939
Exergy in, J/s	1640467.170	1866458.080	1956068.450	1984063.640	2007693.620
Exergy out,J/s	1230594.810	1315301.420	1351809.420	1364170.220	1375255.560
Exergy transit,J/s	306172.540	161041.310	134436.560	129527.590	126569.400
Exergy consumed,J/s	1334294.630	1705416.770	1821631.890	1854536.050	1881124.220
Exergy produced,J/s	924422.270	1154260.110	1217372.860	1234642.630	1248686.160
$I_{int}+I_{ext}$, J/s	409872.360	551156.660	604259.030	619893.420	632438.060
$(I_{int}+I_{ex}t)$/Ein	0.250	0.295	0.309	0.312	0.315
$(I_{int}+I_{ex})$/Eout	0.333	0.419	0.447	0.454	0.460
$(I_{int}+I_{ex})$/Eproduced	0.443	0.477	0.496	0.502	0.506

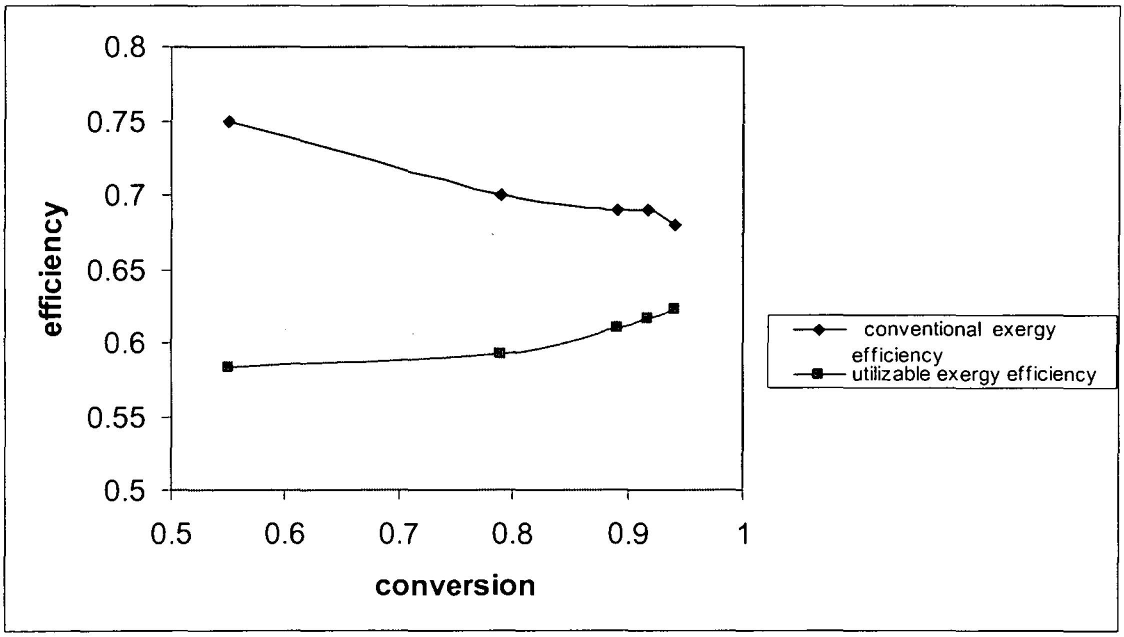

Figure 4. 8 Conventional exergetic efficiency and utilizable coefficient as function conversion (temperature)

As it is seen from the figure 4.8, the conventional exergy efficiency decreases as the temperature of the reformer increases (the conversion will increase). The temperature rise in the reformer is accomplished by burning more fuel. According to the conventional exergy efficiency, it seems wise to let the whole feedstock flow through the reformer. In this case there will be no exergy losses because there is neither chemical transformation nor fuel combustion. A different situation is observed when applying criteria η_u. As the temperature of the reformer is increased the conversion will increase and it results in decrease of transit exergy and a significant rise in exergy of production due to increase in the terms $\bar{E}''_{H_2}$, $\bar{E}''_{CO}$, $\bar{E}''_{CO_2}$. Higher temperature gives higher conversion and higher utilizable coefficient. The difference arises from the definitions treatment of transit exergy. The conventional exergy efficiency doesn't exclude transit exergy. It considers the transit exergy as part of exergy produced by the process. The utilizable coefficient excludes transit exergy. It considers the transit exergy as unaltered exergy by the process.

Chapter Five

Conclusion

The model prediction of the outlet stream of the reformer is in agreement with the famous Le Chatelier's principle. The exergy losses which shows the thermodynamic imperfection of the system was calculated. The minimum exergy loss per moles of hydrogen produced is found when the reformer operates at about 1110k.From this work it is found that the utilizable coefficient (modified intrinsic exergy efficiency), which accounts the transit exergy, is more suitable criteria of the thermodynamics performance of the process. Most of the previous analysis of exergy for different process and operations didn't address the effect of transit exergy. The works can be redone taking the transit exergy into account. It is important to revise the previous works with the new exergy definition, utilizable coefficient. Results of flow sheet simulator can be used to calculate the enthalpy, entropy and composition of stream needed for computing the exergy. This will save time and improve accuracy. It is worth mentioning that operational parameter change made in the steam methane reforming unit will have effect on the downstream and upstream operations and therefore it is more practical to analysis the effect in the whole process flow sheet.

Future works

There is potential of improving steam methane reforming using membrane and sorption of carbon dioxide. These improvements can be analyzed using utilizable coefficient. Membrane enhanced steam methane reforming requires electrical energy to run the membrane. Heat and electrical energy will involve in membrane enhanced reforming process.This makes membrane enhanced steam methane reforming a good candidate for future work. Exergy analysis can be made for the whole process (containing steam methane reforming) of hydrogen production.

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Appendix A:

Chemical element with gaseous reference substances ($T^O = 298.15\,K$, $P^O = 1.01325\,bar$) taken from Ref [2].

Chemical element	Chemica l symbol	Mole fraction in dry air	Standard partial pressure in the environment p_i^{oo} bar	$\frac{-RT^o \ln p_i^{oo}/p^o}{kJ/Kmol}$	Reference reaction
H_2	Ar	0.00933	0.00907	11690	$Ar \rightarrow Ar$
N_2	CO_2	0.0003	0.000294	20170	$C + O_2 \rightarrow CO_2$
D	$D_2O\ g$	......	0.00000137	33500	$D + \frac{1}{2}O_2 \rightarrow \frac{1}{2}D_2O$
H	$H_2O\ g$	......	0.0088	11760	$H + \frac{1}{4}O_2 \rightarrow \frac{1}{2}H_2O$
He	He	0.000005	.0000049	30360	$He \rightarrow He$
Kr	Kr	0.000001	0.00000098	34320	$Kr \rightarrow Kr$
N	N_2	0.7803	0.7583	720	$N \rightarrow N_2$
Ne	Ne	0.000018	0.0000177	27150	$Ne \rightarrow Ne$
O	O_2	0.2099	0.2040	3970	$O \rightarrow \frac{1}{2}O_2$
Xe	Xe	0.00000009	0.000000088	40300	$Xe \rightarrow Xe$

Appendix B:

Standard chemical exergy of substances.

($T^O = 298.15\ K$, $P^O = 1.01325\ bar$) taken from Ref [2]

Substance	State	Relative molecular mass	Standard Chemical Exergy [$kJ/Kmol$]
H_2	g	2.01594	238490
N_2	g	28.0134	720
$N_2(Air)$	g	28.9534	690
O_2	g	31.9988	3970
CH_4	g	16.042	836510
CO	g	28.0105	275430
CO_2	g	44.0095	20140
H_2O	l	18.01534	3120
H_2O	g	18.01534	11710

Appendix C:

Heat capacities of gases in ideal gas state

Constants in equation $C_P^{ig}/R = A + BT + CT^2 + DT^{-2}$ $T(kelvins)$ *from* 298 *to* $T_{\max}$

Chemical species	$T_{\max}$	$C_{P\ 298}^{ig}/R$	A	$10^3\,B$	$10^6\,C$	$10^{-6}\,D$
CH_4	1500	4.217	1.702	9.081	-2.164	……
CO	2500	3.507	3.376	0.557	……	-0.031
CO_2	2000	4.467	5.457	1.045	……	-1.157
H_2	3000	3.468	3.249	0.422	……	0.083
N_2	2000	3.502	3.280	0.593	……	0.040
O_2	2000	3.535	3.639	0.506	……	-0.227
H_2O	2000	4.038	3.470	1.450	……	0.121

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