Modelling of a Catalytic Reformer Unit

by

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Dissertion submitted in partial fulfillment of
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CERTIFICATION OF APPROVAL

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A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
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Approved by,

(DR SHUHAIMI MAHADZIR)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
January 2009

CERTIFICATION OF ORIGINALITY

This is to certify that I am responsible for the work submitted in this project, that the original work is my own except as specified in the references and acknowledgements, and that the original work contained herein have not been undertaken or done by unspecified sources or persons.

MOHD UZAIR BIN ZAKARIA

ABSTRACT

Catalytic reforming unit is practiced extensively in the petroleum refining industry to convert gasoline boiling-range low-octane hydrocarbons to high-octane gasoline compounds for use as high-performance gasoline fuel. This is accomplished by conversion of n-paraffins and naphthenes in naphtha to iso-paraffins and aromatics over bifunctional catalysts. Petronas Penapisan Terengganu Sdn Bhd employed two catalytic reformer units that are in Kerteh Refinery-1 (KR1) and Kerteh Refinery-2 (KR2) respectively. This project will focused mainly on catalytic reformer unit located at Kerteh Refinery-1 as it is more concern on the requirement of standard for research octane number, RON. The data from the unit is used to test the correlation for prediction of LPG and reformate yield. The correlation used is provided by HPI Consultant. The process correlation for catalytic reforming estimates the product yields and reformates properties for reforming full boiling range naphtha. Moreover, the correlation have some variables that can be changes such that pressure required in the unit, research octane number (RON), napthene content plus 2 times the aromatic content of feedstock (N2A) and specific gravity of the feed. This will help the study on the catalytic reformer unit in refinery such as Petronas Penapisan Terengganu Sdn Bhd to evaluate and model the unit. The correlations given are the standard or the benchmark for the typical production of LPG and reformate. By then, the actual data from the plant or the unit needed to compare both of them and analysis need to be done to extract the information. In the same time, the fundamental of the unit must be understood thoroughly as from the feedstock to the product yield. Moreover, each step of the process has different operating capabilities such as endothermic or exothermic reactions which are then why the temperature are slightly decreasing and from the process there is a burner which can counteract and maintain the temperature along the process. This fundamental of understanding the process in catalytic reformer is important as to justify of those data coming from the plant or the correlation is valid. More importantly, the other throughput of the project is to model the catalytic reforming unit in Petronas Penapisan Terengganu Sdn Bhd using the correlation from HPI Consultant so that the requirement of LPG and reformate yield are met.

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ABBREVIATIONS AND NOMENCLATURES

Nomenclature:

The symbols used in the equations for the catalytic reforming correlation are defined below.

RON = Research octane number (clear) of C_5+ reformate divided by 100

N2A = Napthene content plus 2 times the aromatic content of feedstock, volume fraction

SGF = Specific gravity of feed

REFBASE = Base reformate yield at 200psig, vol. pct.

REFORMATE = Reformate yield corrected for operating pressure, vol. pct.

C3BASE = Base propane yield at 200psig, vol. pct.

PROPANE = Propane yield corrected for operating pressure, vol. pct.

IC4BASE = Base isobutene yield at 200psig, vol. pct.

ISOBUTANE = Isobutane yield corrected for operating pressure, vol. pct.

NC4BASE = Base normal butane yield at 200psig, vol. pct.

N-BUTANE = Normal butane yield corrected for operating pressure, vol. pct.

P = Operating pressure, psig

CHAPTER I

INTRODUCTION

1.1 BACKGROUND

Catalytic reforming unit is practiced extensively in the petroleum refining industry to convert gasoline boiling-range low-octane hydrocarbons to high-octane gasoline compounds for use as high-performance gasoline fuel. The unit produce reformate as main product while LPG as byproducts. The projects will study the model of catalytic reformer unit employed at Petronas Penapisan Terengganu Sdn Bhd specifically at Kerteh Refinery 1 (KR1). This project will fully utilize the correlation provided by HPI Consultant to estimate the yield of LPG and reformate to see the trend of production of both products. As matter of fact, the correlation have variables that can be changes such that pressure required in the unit, research octane number (RON), napthene content plus 2 times the aromatic content of feedstock (N2A) and specific gravity of the feed. The throughput of the project is to model the catalytic reforming unit in Petronas Penapisan Terengganu Sdn Bhd using the correlation from HPI Consultant so that the requirement of LPG and reformate yield are met.

1.2 PROBLEM STATEMENT

Each year, there is a slight increased in the demand of LPG as the world now realized the advantage of using LPG in everyday life. While LPG production also come with a tradeoff of reformate production, there is still an economical potential underlying the amount of LPG that the refinery can produced. LPG is a mixture of gaseous hydrocarbon of butane and propane and has many uses such as fuel in heating appliances and vehicles, a new alternative of CFC and also generating a power plant while reformate is use in high performance gasoline fuels. So there is a need to study the yield of reformate and LPG in catalytic reformer unit. The unit under study is employed at Kerteh Refinery 1 (KR1), Petronas Penapisan Terengganu Sdn Bhd.

1.3 OBJECTIVES

The objective of the project is to do an intensive study of the typical production value of LPG and reformate produce provided by the correlation. Then, the data from refinery plant, Petronas Penapisan Terengganu Sdn Bhd are compared to the typical production from the correlation. By that, from the analysis of both actual and typical production trend, the catalytic reformer unit employed at the refinery plant can be modeled.

1.4 SCOPE OF STUDY

The scope of the project will cover on the processing site of the catalytic reforming unit from the hydrotreated naphtha feed, hydrogen recycle gas line, furnace, reforming reactors, reformate stabilizer or butanizer until LPG recovery and reformate production employed at KR-1. The operating principles of each process step need to be understood. This fundamental of understanding the process in catalytic reformer is important as to justify of those data coming from the plant or the correlation is valid. The data is taken from the refinery plant process and compared with the correlation. From that, the model of catalytic reformer unit that produced both reformates and LPG can be predicted.

CHAPTER II

LITERATURE REVIEW

2.1 CATALYTIC REFORMING UNIT AND REFORMATE

Catalytic naphtha reforming is the technology that combines catalyst, hardware, and process to produce high-octane reformate for gasoline blending or aromatics for petrochemical feedstocks. Reformers are also the source of much needed hydrogen for hydroprocessing operations. Several commercial processes are available worldwide, and the licensing of technology for semiregenerative and continuous reforming is dominated by UOP and Axens (formerly IFP) technologies (George, 2004).

The main difference between commercial reforming processes is catalyst regeneration procedure, catalyst type, and conformation of the equipment. Currently, there are more than 700 commercial installations of catalytic reforming units worldwide, with a total capacity of about 11.0 million barrels a day. About 40% of this capacity is located in North America followed by 20% each in Western Europe and the Asia–Pacific region (George, 2004).

Specifically, catalytic reformer unit is practiced extensively in the petroleum-refining industry to convert gasoline boiling-range low-octane hydrocarbons to high-octane gasoline compounds for use as high-performance gasoline fuel. This is accomplished by conversion of n-paraffins and naphthenes in naphtha to iso paraffins and aromatics over bifunctional catalysts such as Pt/Al_2O_3 or $Pt\text{-}Re/Al_2O_3$ (Jin and Yuejin, 2005).

Recent environment legislation in the United States has banned the use of lead as an additive for boosting antiknock properties of motor fuel. Coupled with these stricter environmental regulations, there has been a consistent increase in the demand for higher octane number gasoline. This can be achieved by reforming the naphtha under more severe conditions, but this will also cause an increase in the rate of coke deposition, resulting in the reduction of cycle lengths of the catalyst. A proper selection of operating conditions within plant constraints is essential to maximize the profitability of the reformer (Jin and Yuejin, 2005).

The refinery plant that is under study is Petronas Penapisan Terengganu Sdn. Bhd which is subdivided into two, Kertih Refinery-1 (KR-1) and Kertih Refinery-2A (KR-2A). KR-1 processes crude oil and condensate form Terengganu Crude Oil Terminal (TCOT) and condensate from Bintulu Crude Oil Terminal (BCOT). On the other hand, KR-2A only processes condensate, from Terengganu and Bintulu to supply Heavy Naphtha as a feedstock for KR-2B which is an Aromatic Production Department of PPTSB (PPTSBb).

KR-1 consists of three major units, Crude Distillation Unit (CDU), Naphtha Hydrotreating Unit (NHTU) and Catalytic Reforming Unit (CRU). CDU through distillation process alone separates the crude oil and condensate to its components: Liquified Petroleum Gas (LPG), Light Naphtha, Heavy Naphtha, Fuel Gas, Diesel, Low Sulfur Waxy Residue (LSWR), and kerosene. NHTU treat impurities from CDU Heavy Naphtha to protect CRU catalyst thru catalytic pre-treating reaction and distillation. CRU reform low octane number naphtha to high octane number gasoline (Reformate) using platinum-rhenium catalyst (PPTSBb).

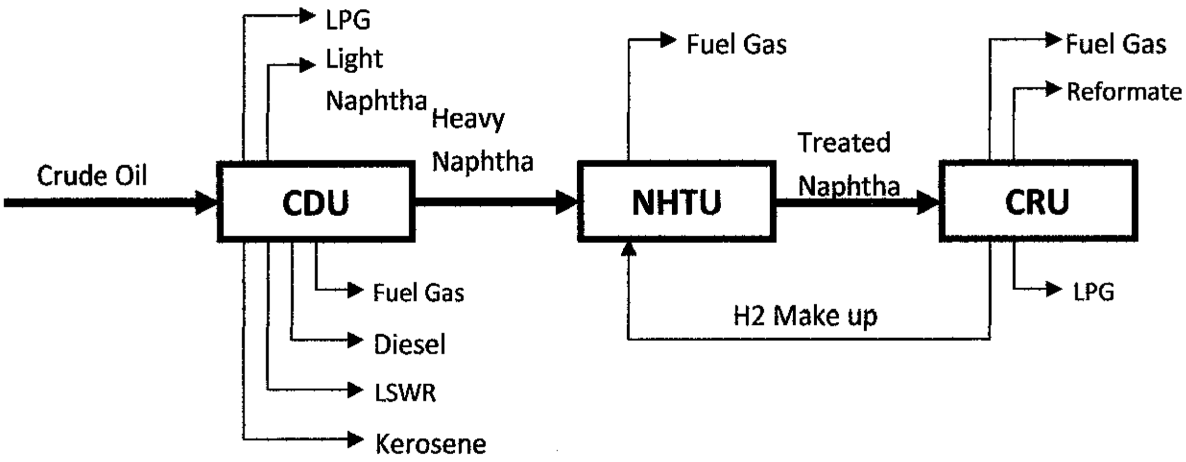

Figure 1: Block Diagram for KR1 (PPTSBb)

"Octane" or more precisely the octane number is the measure or rating of the gasoline fuels antiknock properties. "Knocking" occurs in an engine when the fuel self detonates due to high pressure and temperature before it is ignited by the engine spark. Permanent damage of the cylinder and piston parts is likely result of persistent "knocking". The octane number can be measure by research octane number (RON). For example if the RON of 95 is given, is it equal to anti knock properties to a mixture of 95% of iso-octane and 5% n-heptane (Tore and Sigurd, 2007).

The feed naphtha is typically consists of C5 - C11 paraffins, naphthenes & aromatics as the function of catalytic reforming unit is to produce aromatics from the naphthenes and paraffins. The paraffins and napthenes have relatively low octane number usually around 28 for paraffins and 60 for napthenes, whereas aromatics have high values of 100+. Unfortunately, the concentration of aromatics is usually so low that a typical reformer feedstock has an octane number around 55. The reforming process transforms this low octane feedstock into high octane gasoline by (1) converting naphthenes to aromatics, (2) converting the paraffins to high octane isomers and aromatics, and (3) removing the paraffins from the liquid product via cracking reactions (Baird, 1983).

So, in this process the following reactions take place and to an extent they are dependent on the quality of the feed, severity of the operation and the catalyst type. The most significant reactions which take place during the catalytic reforming are (Baird, 1983):

1. Dehydrogenation reactions
    a. Dehydrogenation of alkyl cyclohexanes to aromatics
    b. Dehydroisomerization of alkyl cyclopentanes to aromatics
    c. Dehydrocyclization of paraffins to aromatics

2. Isomerization reactions
    a. Isomerization of normal paraffins to isoparaffins
    b. Isomerization of alkyl cyclopentanes to cyclohexanes

3. Hydrocracking reactions
    a. Cracking and saturation of paraffins
    b. Cracking and saturation of napthenes

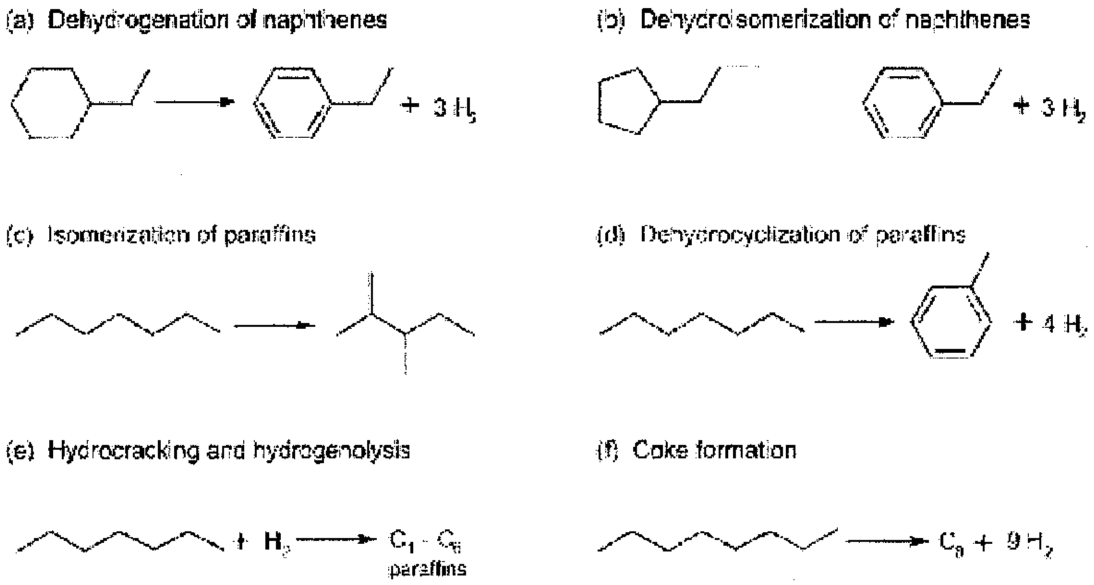

Figure 2: Reforming reactions (George, 2004)

The dehydrogenation reactions are the most desirable reactions since they contribute directly to the improvement in octane number. The isomerization reactions which occur rather easily at commercial reforming conditions improve the octane number only to a limited extent. The hydrocracking reactions contribute substantially to octane improvement by cracking out heavy, low octane components. However, hydrocracking results in a yield loss and therefore operating conditions are usually selected to minimize cracking (Baird, 1983).

The dehydrogenation of napthenes occurs rapidly over a platinum alumina catalyst. The dehydrocyclization of paraffins is also catalyzed but these reactions proceed slowly. Over the years octane requirements have been steadily advanced so that now napthenes in reformer feeds are essentially fully converted. In order to further increase the octane of reformed naptha, it has become of fundamental importance to convert the paraffin into aromatics as efficiently as possible (Baird, 1983). Catalytic reformer unit processes are generally classified into three types (George, 2004):

1. Semiregenerative
2. Cyclic (fully regenerative)
3. Continuous regenerative (moving bed)

Table 1: Regional Distribution of Catalytic Naptha Reforming by Capacity (George, 2004)

Region	Crude capacity (1000 b/d)	Reforming capacity (1000 b/d)	Reforming as % of crude capacity
N. America	20,030	4075	20.3
W. Europe	14,505	2135	14.7
Asia Pacific	20,185	2000	10.0
E. Europe	10,680	1430	13.4
Middle East	6075	570	904
S. America	6490	400	601
Africa	3200	390	12.1
Total	**81,165**	**11,000**	**13.6**

This classification is based on the frequency and mode of regeneration. The semiregenerative requires unit shutdown for catalyst regeneration, whereas the cyclic process utilizes a swing reactor for regeneration in addition to regular in process reactors. The continuous process permits catalyst replacement during normal operation. Worldwide, the semiregenerative scheme dominates reforming capacity at about 57% of total capacity followed by continuous regenerative at 27% and cyclic at 11%. Most grassroots reformers are currently designed with continuous catalyst regeneration. In addition, many units that were originally built as semiregenerative units have been revamped to continuous regeneration units. (George, 2004)

Table 2: Regional Distribution of Catalytic Reforming Capacity by Type (George, 2004)

Region	Total reforming (1000 b/d)	Percentage share of total reforming (%)			
		Semi regenerative	Continuous	Cyclic	Other
N. America	4075	46.4	26.8	22.2	4.6
W. Europe	2135	54.0	31.5	11.0	3.5
Asia Pacific	2000	42.4	44.8	1.6	11.2
E. Europe	1430	86.4	11.0	1.1	1.5
Middle East	570	63.0	23.1	7.2	6.7
S. America	400	80.4	9.3	0.6	3.5
Africa	390	81.9	0.0	1.8	16.3
Total	11,000	56.8	26.9	11.1	5.2

Table 3: Summary of Naptha Reforming Process (George, 2004)

Process Name	Licensor	Process types and key features	Installations
Platforming	UOP	Semiregenerative and continuous reforming; CycleMax regenerator; product recovery system	Over 800 units with 8 million b/d
Octanizing, Aromizing	Axens	Semiregenerative and continuous reforming; dualforming for conventional process revamp	Over 100 licensed units
Houdriforming	Houdry Div. Air Products	Semiregenerative; high-octane gasoline and aromatics	0.3 million b/d
Magnaforming	Engelhard	Semiregenerative or semicyclic	1.8 million b/d
Powerforming	Exxonmobil	Semiregenerative or cyclic	1.4 million b/d
Rheniforming	Chevron	Semiregenerative; low-pressure operation	1 million b/d
Ultraforming	Amoco	Semiregenerative or cyclic	0.5 million b/d
Zeoforming	SEC Zeosit	Semiregenerative; zeolite-based catalyst	Few small units

Since this project will focus on Kertih Refinery-1, KR1, which employed a semi regenerative unit so the functionality of the semi regenerative catalytic reforming unit must be fully understood. Reforming unit feedstock is usually prepared in an upstream naptha desulfurization unit which removes metals, nitrogen and sulfur components which could deactivate the reforming catalysts (Baird, 1983).

Typically, the operation of the unit is like this where the high pressure naptha feed is mixed with recycle hydrogen rich gas from the main compressor. The quantity of the recycle gas of 80 – 93% hydrogen purity depends again upon reactor design conditions. The mol ratio of hydrogen recycle to hydrocarbon feed may vary as low as 3/1 to as high as 12/1 (Baird, 1983).

Mixed feed is then partially preheated in exchange with hot reactor effluent, and possibly other heat exchange. Final feed preheat is provided by a fired heater, with heater outlet temperatures of 850 - 1050^{0}F. Then it charged to first reforming reactors containing palletized catalyst. The reactants typically undergo 60 – 120^{0}F decrease in temperature as they pass through the first reactor. This is due to the dehydrogenation of napthenes to form hydrogen and aromatic compounds. It is necessary to reheat the products prior to routing it to next reactor as it needs to reheat it to the desired temperature level. The second, third and fourth reactors all have upstream reheaters. The amount of reheat required is sequentially less due to changing character of the various reforming reactions (Baird, 1983).

Reactor pressure is a key design parameter which lower pressure will improved tolerance of coke on the catalyst so it permits higher reformate yields. Average reactor pressure may vary from 100psig to 500psig. Then, after exiting last reactor, effluent gases are cooled via heat exchange with feed and sometimes via reboil duty for the feed stripper and for product stabilizer which then fed to separator drum. Liquid from separator drum is charged to stabilizer where butane and lighter components are produced overhead to light ends recovery facilities where LPG which is the main concern in this project is produced. Stabilizer bottoms are cross exchanged with stabilizer feed and then are cooled and routed to storage. Where it is necessary to change the severity of operations to achieve a different reformate octane level, it can usually be accomplished by changing inlet temperatures to one or more of the four reactors (Baird, 1983).

Periodically, it is necessary to regenerate the reforming catalyst to remove carbon and to reactivate the metal sites in the catalyst. For semi-regenerative units this means the unit must periodically be shut down, purged with inert gas and then regenerated. This step requires the controlled burning, in situ of all carbon on the catalyst. Inert gas is typically circulated through the system, heated via fired fired furnace to the level necessary to support combustion. Air is then slowly and continuously introduced into the circulating gas. After the completion of carbon burning, the metal on catalyst is redistributed and rejuvenated by the circulation of air in inert gas for a period of time at proper temperature levels. Finally, chlorides are introduced into the system to replace those stripped from the catalyst by water vapor during previous operations and regeneration procedures. It will reactivate the catalyst to original activity levels (Baird, 1983).

Six months is a typical cycle length for a semi regenerative unit. The time required for regeneration is 3 to 6 days and depends primarily upon the amount of carbon to be burned off the catalyst (Baird, 1983).

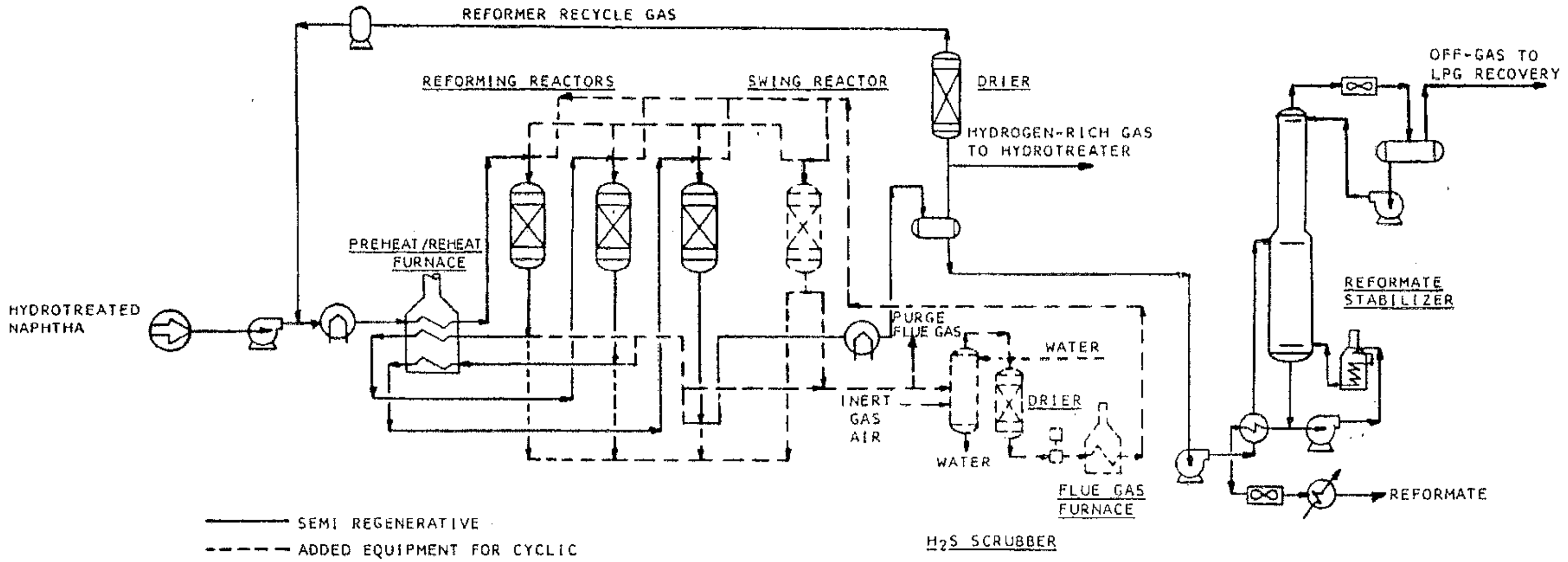

Figure 3: Semi-regenerative catalytic reforming processes (Baird, 1983)

There are several process variables that will determine the optimum production of reformate and LPG. (PPTSBa)

1. Reactor Temperature (PPTSBa)

   The temperature at which reactor catalyst beds are held is the major control parameter used to meet the product quality requirements. Platforming Catalyst is capable of operation over wide temperature range with little adverse affect on the product yield & catalyst stability. However, above 560°C may cause thermal reactions which will decrease reformate & hydrogen yield and increase the rate of coke laydown. Reactor temperature can be defined in two fashions, such as:

   a. Weighted Average Inlet Temperature (WAIT).
   b. Weighted Average Bed Temperature (WABT).

   WAIT = Weight Fraction of Catalyst in bed * Reactor inlet temperature.
   WABT = Weight Fraction of Catalyst in bed * Avg of reactor bed inlet & outlet temperature.

   As the reactor temperature is increased, the product octane increases and the product yield decreases. Thus, the reactor temperature should only be set to give the desired octane and no higher.

2. Space Velocity (PPTSBa)

   Space velocity is a measurement of Naptha which is processed over a given amount of catalyst over a set length of time. When the hourly volume charge rate of naptha and the volume of catalyst are used, the term is called liquid hourly space velocity (LHSV). When the hourly weight charge rate of naphtha and the weight of catalyst are used, the term is Weight Hourly Space Velocity (WHSV).

LHSV, hr^{-1} is commonly used since most refiners define their charge rate on volume basis and hourly rates give conveniently sized numbers.

Space velocity has a major effect on product quality (octane number). The higher the space velocity (lower residence time), the lower the product quality or the less the amount of reaction allowed at a fixed WAIT which is lower the product research octane number (RON). Increasing reactor temperatures will offset the effect but again limited to certain extent due to thermal reactions. At very low space velocities, thermal reactions can occur to a sufficient degree to decrease reformate yields. At very low LHSV, thermal reactions can occur & decrease reformates & hydrogen yields.

It should become a regular practice always to lower reactor inlet temperatures before lowering charge rate and not the reverse or severe hydrocracking may occur which would result in rapid hydrogen consumption and catalyst coking.

When increasing charge rate and temperatures, the charge rate should always be raised first. It is not desirable to operate at charge rate less than half of the design charge rate or at a rate which would give a minimum liquid hourly space velocity less than $0.75hr^{-1}$. Also before increasing the charge, the recycle gas flow must be checked so that a suitable H_2/HC ratio will exist after the increase.

3. Reactor Pressure (PPTSBa)

Because of its inherent effect on reaction rates, hydrogen partial pressure is the basic variable but for ease of use, the total reactor pressure can be used and the hydrogen purity is not needed.

Reactor pressure is most accurately defined as the average catalyst pressure. Since 50% of the catalyst is usually in the last reactor, a close approximation is the last reactor inlet pressure. Separator pressure as an operating parameter is of limited value since the pressure drop from unit to unit can be considerably different and even within the same unit it may vary.

The reactor pressure effects the reformate yields, reactor temperature requirement, and catalyst stability (cycle length). Reactor pressure has no theoretical limitations although practical design limitations have an effect.

Decreasing the reactor pressure will increase the hydrogen and reformate yield, decrease the temperature requirement to make the product quality (research octane number) and shorten the catalyst cycle (increase catalyst coking rate).

4. Hydrogen/Hydrocarbon Ratio (PPTSBa)

The ratio is defined as the moles of recycle hydrogen per mole of naptha charge to the unit. The recycle hydrogen is giving the sweeping effect of the reaction product on the catalyst and it is necessary to reduce the catalyst coking rate.

An increase in H_2/HC ratio will move the reaction products through the reactor at a faster rate and supply a greater heat sink for the endothermic heat of reaction. The end result of this is decreased catalyst coking rate. The effect of H_2/HC ratio on the catalyst coking rate is more in the last reactor and has less effect on the first reactor as most of the net hydrogen is produced in the first reactor.

2.2 LIQUEFIED PETROLEUM GAS

LPG and its uses:

Liquefied petroleum gas is a mixture of hydrocarbon gases used as a fuel in heating appliances and vehicles, and increasingly replacing chlorofluorocarbons as an aerosol propellant and a refrigerant to reduce damage to the ozone layer.

Varieties of LPG bought and sold include mixes that are primarily propane, mixes that are primarily butane, and the more common, mixes including propane (60%) and butane (40%). Propylene and butylenes are usually also present in small concentration.

At normal temperatures and pressures, LPG will evaporate. Because of this, LPG is supplied in pressurized steel bottles. In order to allow for thermal expansion of the contained liquid, these bottles are not filled completely; typically, they are filled to between 80% and 85% of their capacity.

LPG can be use as an alternative fuel for spark ignition engines. More recently, it has also been used in diesel engines. Its advantage is that it is non-toxic, non-corrosive and free of tetra-ethyl lead or any additives and has a high octane rating (108 RON). It burns more cleanly than petrol or diesel and is especially free of the particulates from the latter.

In highly purified form, various blends of the LPG constituent's propane and iso-butane are used to make hydrocarbon refrigerants. Hydrocarbons are more energy efficient, run at the same or lower pressure and are generally cheaper than refrigerant-134a. However, a major concern relating to the use of LPG hydrocarbons is that the refrigerant-143a does not present a significant flammability hazard. The flammability of LPG hydrocarbons restricts their use to specially designed systems where the risk of ignition is mitigated especially considering leaks and accidents.

2.3 CATALYTIC REFORMING CORRELATIONS

The catalytic reforming correlation has been developed to estimate product yields and reformate properties for reforming full boiling range (175/375^{0}F) napthas. The base yields represent a modern catalytic reformer employing platinum rhenium catalyst and operating at a pressure of 200psig and a weight hourly space velocity (WHSV) of 2.0. The most important factors governing the yield pattern are (Baird, 1983):

1. The feedstock quality as represented by the N2A content
2. The operating severity as measured by the clear research octane number of the C_5+ reformates

Adjustment factors have been developed for different operating pressures, but it has been assumed that within normal operating conditions space velocity has little effect on the yields and product properties. In other words, temperature and space velocity are interrelated in such a way it makes little difference in the yield structure whether the reformate octane level is achieved through higher temperatures or lower space velocities. It's valid for RON range from 75-102. (Baird, 1983)

Catalytic reformer correlation (Baird, 1983):

1. Base reformate yield at 200psig, volume percentage.

$$REFBASE = (0.404258 - 4.21563(N2A) - 2.10686(N2A)(N2A) + 5.418305(RON) + 5.72875(N2A)(RON) - 5.491635(RON)(RON))/(0.001 - 0.04374(N2A) - 0.016164(N2A)(N2A) + 0.064142(RON) + 0.047072(RON)(N2A) - 0.055155(RON)(RON))$$

Pressure corrected reformate yield, volume percentage.

$$
\begin{aligned}
REFORMATE \\
&= (REFBASE) \\
&+ \big(2.0 \\
&- 0.01(P)\big)\big(\exp\big(1.4245 - 13.225(N2A) \\
&+ 12.0(N2A)(RON)\big)\big)
\end{aligned}
$$

2. Base propane yield at 200psig, volume percentage.

$$
\begin{aligned}
C3BASE \\
&= (-1.494159 - 0.859401(N2A) + 4.072991(N2A)(N2A) \\
&+ 4.378753(RON) - 7.824259(N2A)(RON) \\
&+ 1.861973(RON)(RON))/(0.0001 - 1.220596(N2A) \\
&- 0.042877(N2A)(N2A) + 1.470481(RON) \\
&+ 1.049342(RON)(N2A) - 1.226394(RON)(RON))
\end{aligned}
$$

Pressure corrected propane yield, volume percentage.

$$PROPANE = C3BASE + (P - 200.0)(0.0126(SGF) + 0.00159(C3BASE))$$

3. Base isobutene yield, volume percentage.

$$
\begin{aligned}
IC4BASE \\
&= (0.914553 - 0.551547(N2A) - 1.980982(N2A)(N2A) \\
&- 1.802567(RON) + 4.027941(N2A)(RON) \\
&- 0.151577(RON)(RON))/(0.01 + 1.893071(N2A) \\
&+ 0.355879(N2A)(N2A) - 0.779086(RON) \\
&- 1.819559(RON)(N2A) + 0.689810(RON)(RON))
\end{aligned}
$$

Pressure corrected isobutene yield, volume percentage.

$$ISOBUTANE = IC4BASE + (P - 200.0)(0.00447 + 0.00163(IC4BASE))$$

4. Base normal butane yield, volume percentage.

$$\begin{aligned} NC4BASE & \\ &= (-0.703152 - 0.119072(N2A) + 2.920369(N2A)(N2A) \\ &+ 2.911147(RON) - 6.678879(N2A)(RON) \\ &+ 1.404543(RON)(RON))/(1.0 - 1.207616(N2A) \\ &- 0.437298(N2A)(N2A) - 0.460191(RON) \\ &+ 1.339366(RON)(N2A) - 0.352645(RON)(RON)) \end{aligned}$$

Pressure corrected normal butane yield, volume percentage.

$$N - BUTANE = NC4BASE + (P - 200.0)(0.00647 + 0.00153(NC4BASE))$$

CHAPTER III
METHODOLOGY

An important part in the final year project of modeling the catalytic reforming unit in Petronas Penapisan Terengganu Sdn Bhd is familiarization of the unit itself in term of its operation and process flow in the plant. It will help to know on how the naptha are reacted to produce high octane number in reformate production and also butane and propane production that contributes to LPG product.

From the HPI Consultant catalytic reforming correlation, the equation acts as a model to obtain the yield of reformate propane and butane. The equation has variable that can accept different ranges of input as to know the trend of yield of LPG and reformate to pressure, naptha quality to yield and effect of research octane number requirement also to the yield. Moreover, the tradeoff between both yields can be seen clearly and this can be manipulated to achieve the best production.

Meanwhile, several tags point is identified by referring to the P&ID. Then, the actual data from the plant is gathered. The required tags point data is PONA composition for inlet of catalytic reformer unit, octane number of reformate produce, temperature and pressure of the unit, specific gravity of feed and flow readings at selected tagging point. These data are the input for the correlation.

As the actual data have known, there is a different of between the actual and correlation results for the production of LPG and reformate in the unit. The analysis is required to make the correlation can be used to model the catalytic reformer unit at PPTSB. From the diverted model, the prediction of LPG and reformate in PPTSB can be done earlier. It is advantageous so that it will help notify the personnel if there is a short of production and any problem that may occur.

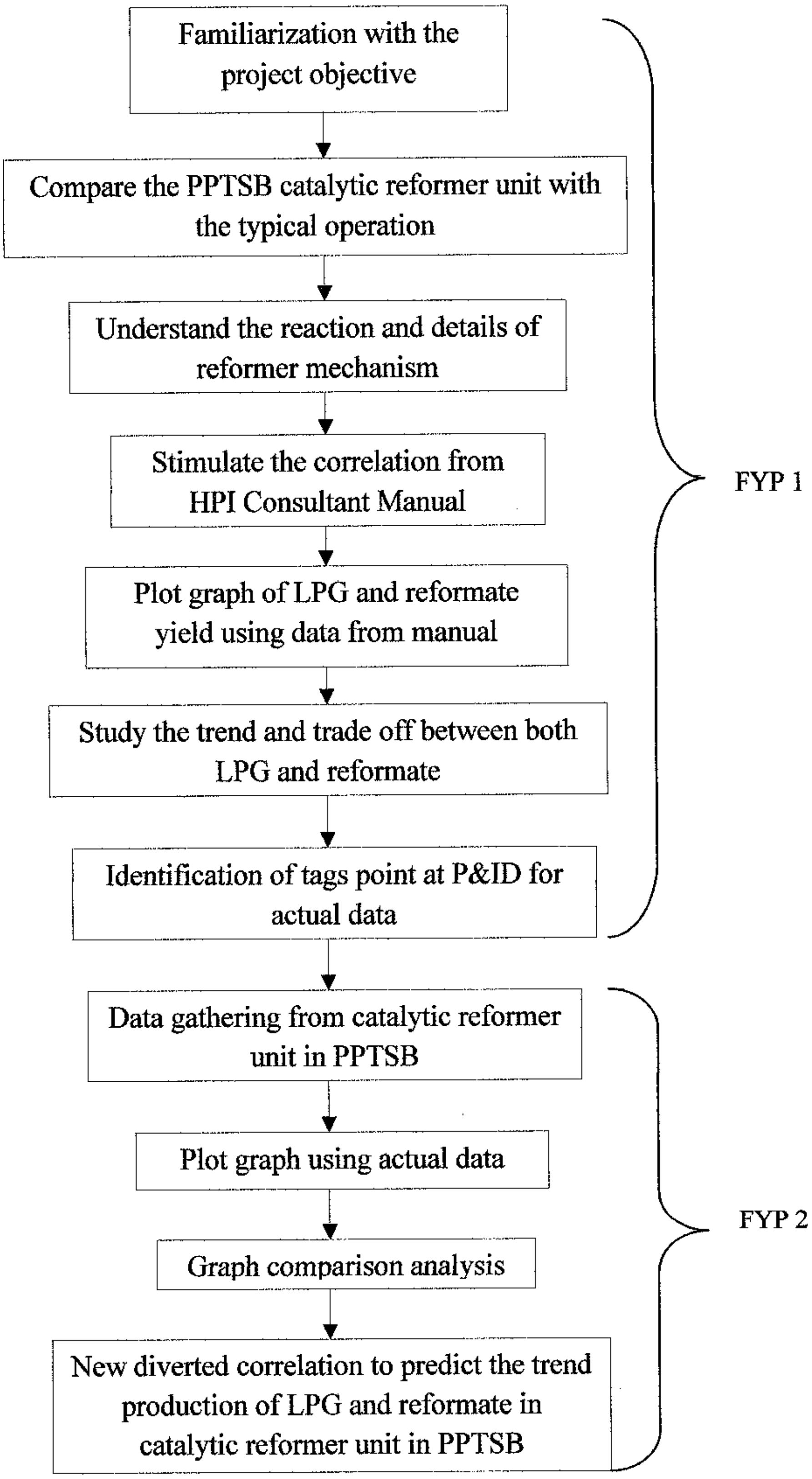

Figure 4: Methodology of final year project

CHAPTER IV

RESULTS AND DISCUSSION

4.1 PRODUCTION TREND

In the step of familiarization with the process and operating principles of catalytic reformer unit, the trend of yield of LPG and reformate to pressure, naphtha feed quality and RON requirements must known. From that, the trend from the graph can be evaluated. The value of input in the correlation is given by HPI Consultant Manual are as follows:

Example (Baird, 1983):
Operating pressure = 250psig
Yields:

Table 4: Yields of Products from Catalytic Reforming Unit

Products	SCF/Bbl	Volume Percent	Specific Gravity	Weight Percent
Hydrogen	766	-	-	1.61
Methane		4.03	0.3000	1.67
Ethane		6.30	0.3564	3.10
Propane		7.99	0.5077	5.60
Isobutane		3.60	0.5631	2.80
Normal Butane		5.39	0.5844	4.35
C_5+ Reformate		79.37	0.7379	80.87
Total		**106.68**		**100.00**

Feedstock and reformate properties (Baird, 1983):

Table 5: Feedstock and Reformate Properties

Property	Feedstock	Reformate
Specific Gravity ($60^0F/60^0F$)	0.7242	0.7379
RON (Clear)	-	96.0
Paraffins, LV PCT.	50.0	-
Napthenes, LV PCT.	40.0	-
Aromatics, LV PCT.	5.0	-

The trends of production are as follows:

1. Yield of Reformate and LPG as function of reformer pressure.

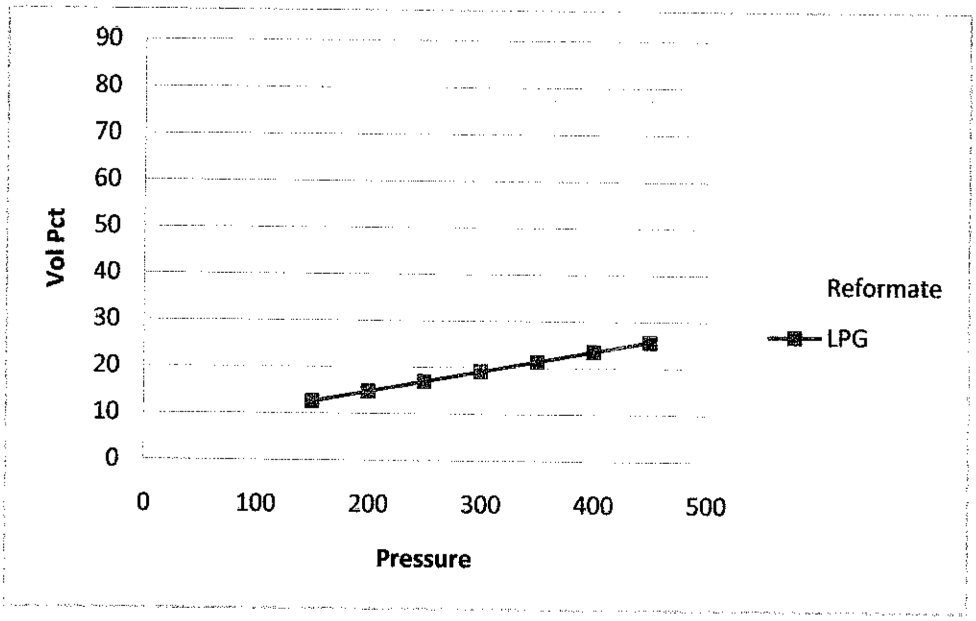

Figure 5: Graph of Yield of Reformate and LPG versus Pressure

Constant:

Specific gravity, RON, N2A (naptha quality)

Variables:

Pressure, Yield of reformate and LPG

As pressure increases, the production yield of LPG also increase while the productions yield of reformate decreases. This is the trade off that the unit offers when operating at higher pressure. One constraint or drawback that may occurs is that the catalyst used may coked and results in less yield of both products. As operating pressure is increases, the unit is working in higher severity of the operating system.

2. Yield of LPG as function of research octane number.

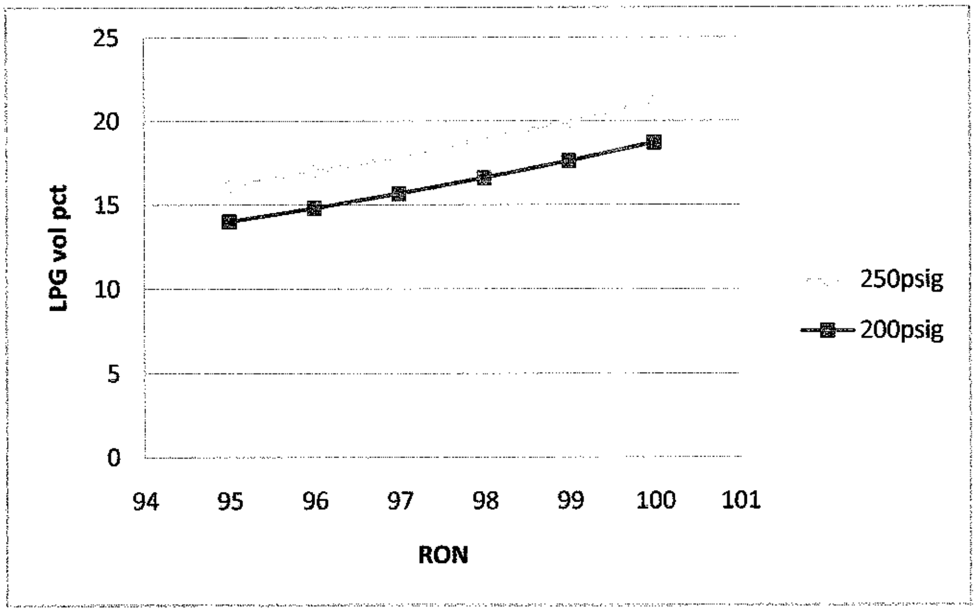

Figure 6: Graph of Yield of LPG versus RON

Constant:

N2A (naptha quality), specific gravity

Variables:

Pressure, RON, Yield of LPG

For both operating pressure, as the research octane number requirements is increased, the yield of LPG in the catalytic reforming unit also increases. Higher RON requirement means that the unit must work in higher severity of operating systems. Meanwhile, an increase in operating pressure will tend to increase the yield of LPG. Higher operating pressure also means that the catalytic reforming unit is working in higher severity of the process.

3. Yield of reformate as a function of research octane number.

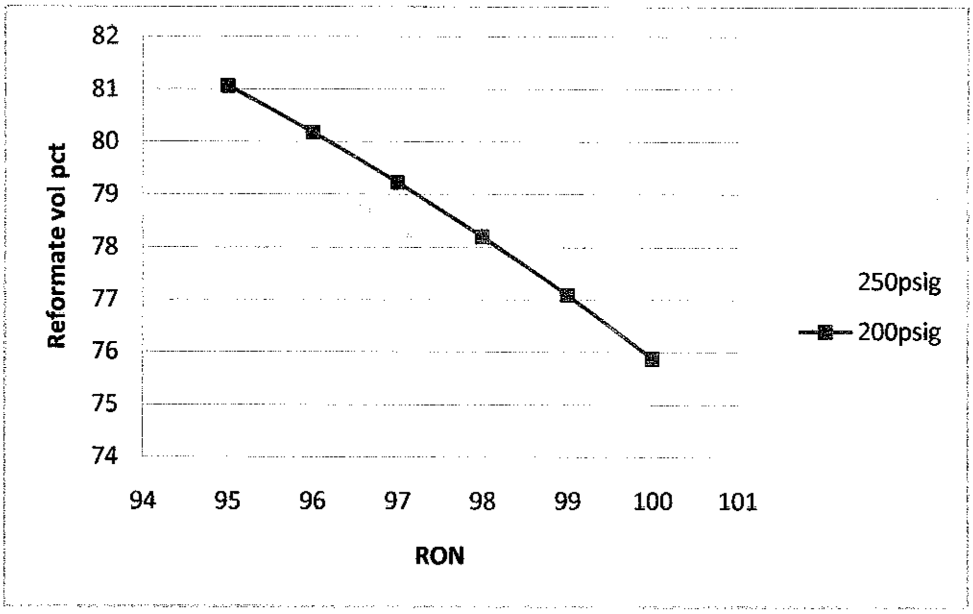

Figure 7: Graph of Yield of Reformate versus RON

Constant:

N2A (naptha quality), specific gravity

Variables:

Pressure, RON, Yield of reformate

For both operating pressure, as the research octane number requirements is increased, the yield of reformate in the catalytic reforming unit decreases. Higher RON requirement means that the unit must work in higher severity of operating systems. Meanwhile, an increase in operating pressure will tend to decrease the yield of reformate. Higher operating pressure also means that the catalytic reforming unit is working in higher severity of the process.

4. Yield of LPG as a function of naphtha feed quality at constant research octane number.

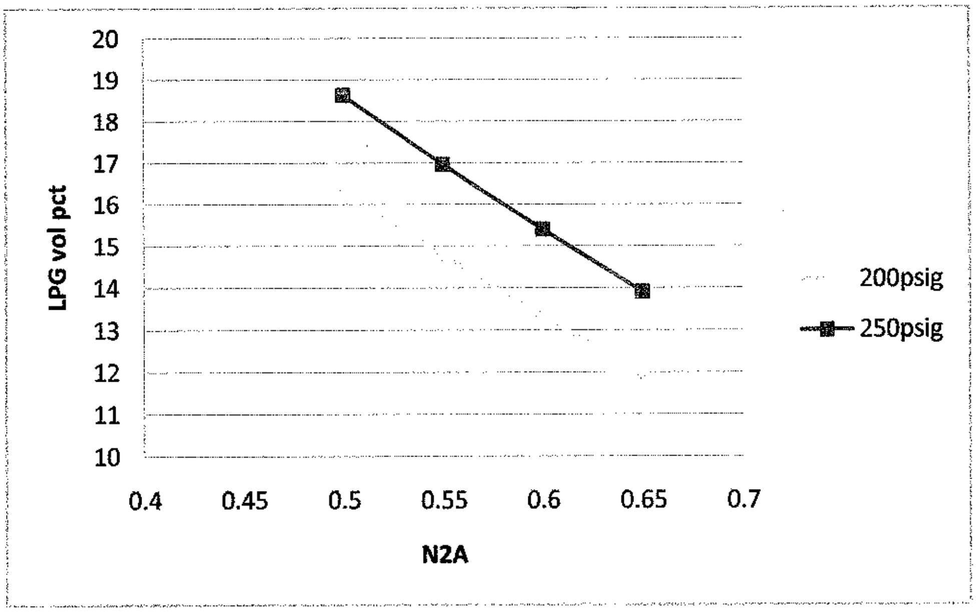

Figure 8: Graph of Yield of LPG versus N2A

Constant:
RON, specific gravity

Variables:
Pressure, N2A (naphtha feed quality), Yield of LPG

For both operating pressure, as the N2A quality (naphtha feed quality) increased, the yield of LPG in catalytic reforming unit is decreases. Naphtha feed quality means that the naphtha has high percentage of naphthenes and aromatics that can be easily converted into products in the catalytic reforming unit. Meanwhile, as pressure increases, higher yield of LPG tends to occur. Higher operating pressure also means that the catalytic reforming unit is working in higher severity of the process.

5. Yield of reformate as function of naphtha feed quality at constant research octane number.

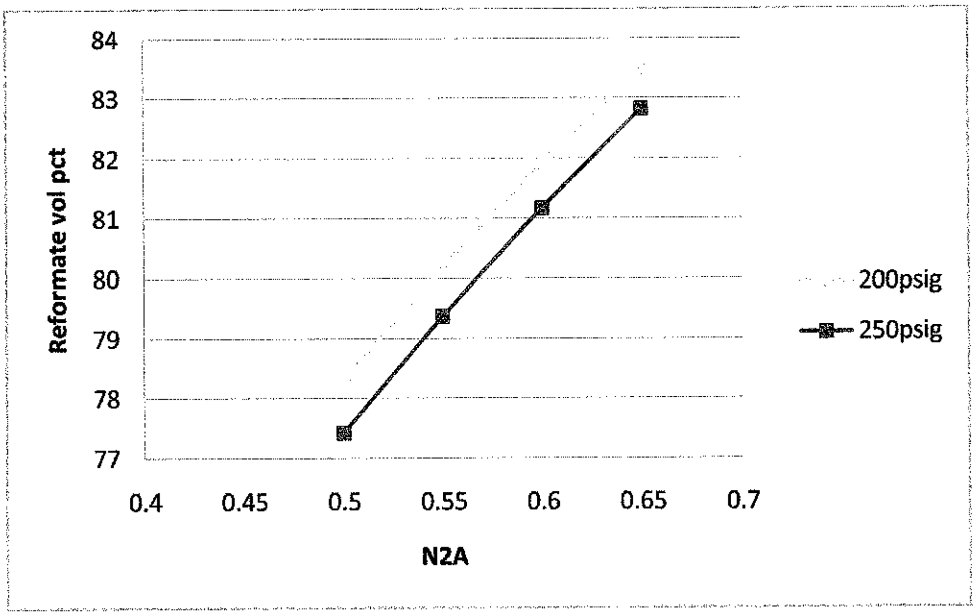

Figure 9: Graph of Yield of Reformate versus N2A

Constant:

RON, specific gravity

Variables:

Pressure, N2A (naphtha feed quality), Yield of reformate

For both operating pressure, as the N2A quality (naphtha feed quality) increased, the yield of reformate in catalytic reforming unit is also increases. Naphtha feed quality means that the naphtha has high percentage of naphthenes and aromatics that can be easily converted into products in the catalytic reforming unit. Meanwhile, as pressure increases, less yield of reformate tends to occur. Higher operating pressure also means that the catalytic reforming unit is working in higher severity of the process.

6. Yield of LPG as a function of naphtha feed quality at constant pressure.

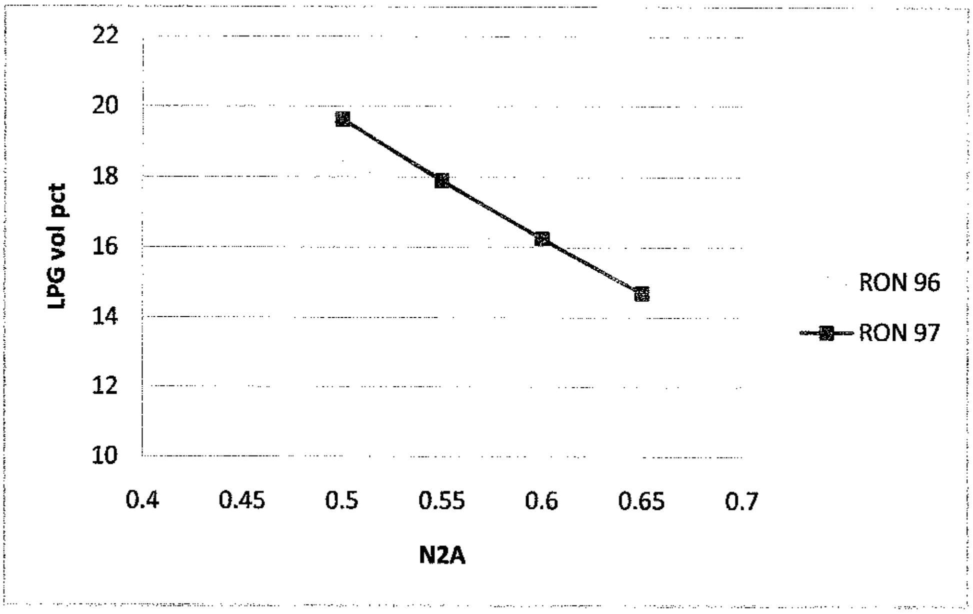

Figure 10: Graph of Yield of LPG versus N2A

Constant:

Pressure, specific gravity

Variables:

RON, N2A (naphtha feed quality), Yield of LPG

For both research octane numbers, as the N2A quality (naphtha feed quality) increased, the yield of LPG in catalytic reforming unit is decreases. Naphtha feed quality means that the naphtha has high percentage of naphthenes and aromatics that can be easily converted into products in the catalytic reforming unit. Meanwhile, as RON requirement increases, higher yield of LPG tends to occur. Higher RON requirement also means that the catalytic reforming unit is working in higher severity of the process.

7. Yield of reformate as a function of naphtha feed quality at constant pressure.

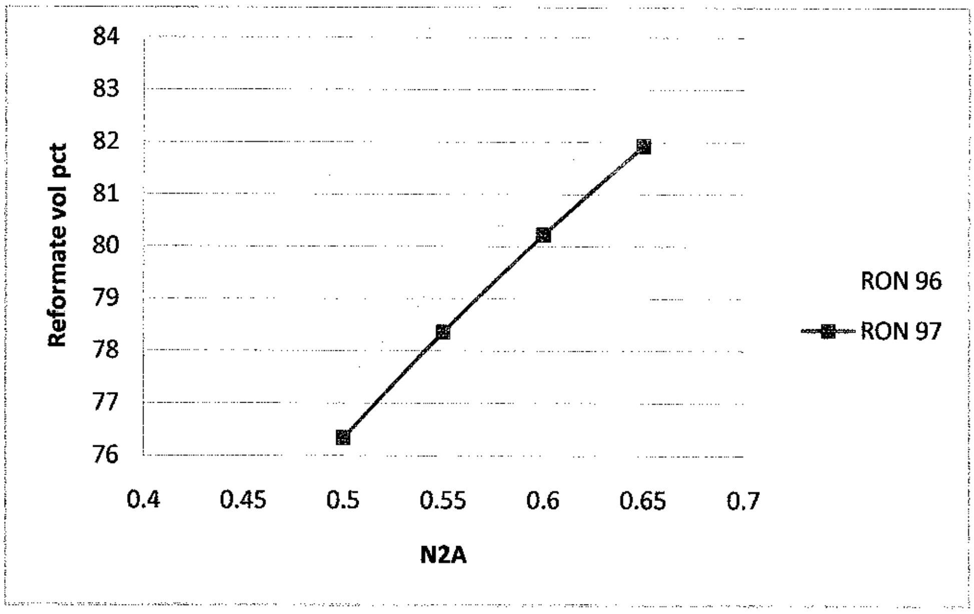

Figure 11: Graph of Yield of Reformate versus N2A

Constant:

Pressure, specific gravity

Variables:

RON, N2A (naphtha feed quality), Yield of reformate

For both research octane number, as the N2A quality (naphtha feed quality) increased, the yield of reformate in catalytic reforming unit is also increases. Naphtha feed quality means that the naphtha has high percentage of naphthenes and aromatics that can be easily converted into products in the catalytic reforming unit. Meanwhile, as RON requirement increases, less yield of reformate tends to occur. Higher RON requirement also means that the catalytic reforming unit is working in higher severity of the process.

4.2 REFINERY DATA

The trend of production of both products of LPG and reformate has been seen clearly in the previous pages. The actual data from Petronas Penapisan Terengganu Sdn Bhd (PPTSB) which employed semi regenerative catalytic reformer unit at Kerteh Refinery 1 are as follows:

1. PONA composition for inlet catalytic reformer unit.

Table 6: Effect of case on Specific Gravity and PNA by volume

Case	Specific gravity	PNA by volume
Naphthenic	0.755	54.7/29.3/16.0
Paraffinic	0.749	64.7/20.3/15.0

For this project, only naphthenic case is considered. Moreover, the naphthenic feed is most likely to occur in Petronas Penapisan Terengganu Sdn Bhd.

2. Octane number of reformate produce.

Research octane number = RON 99

3. Process temperature of reformer unit.

The process temperature reading is taken at tag point TICA 1103.

Table 7: Value of process temperature

Process temperature (TICA 1103)	Value (^{0}C)
Minimum	503.77
Average	**504.49**
Maximum	505.15

The input for catalytic reformer correlation is only dealing with the average process temperature given.

4. Inlet pressure for reformer.

Average pressure $= 14$ barg ≈ 203.0528 psig

The input for catalytic reformer correlation is only dealing with the average inlet reformer pressure given.

5. Flow indicator

Inlet of stabilizer (C-1113) flowrate

Table 8: Value of inlet of stabilizer flowrate

Inlet stabilizer (FI 1135)	Value (m^3/hr)
Minimum	38.75
Average	**40.25**
Maximum	41.71

LPG production flowrate

Table 9: Value of LPG production flowrate

LPG flowrate (FI 1125)	Value (m^3/hr)
Minimum	0.5
Average	**0.9**
Maximum	1.2

Reformate production flowrate

Table 10: Value of reformate production flowrate

Reformate flowrate (FI 1126)	Value (m^3/hr)
Minimum	38.1
Average	**39.6**
Maximum	40.8

The input for catalytic reformer correlation is only dealing with the average flowrate given.

4.3 ACTUAL PRODUCTION TREND

From the above actual data from refinery plant, the value is input to the catalytic reformer correlation which produces the following yield of products:

Reformate = 79.439 vol%
LPG = 15.627 vol%

Meanwhile, an actual production of LPG and reformate from Petronas Penapisan Terengganu Sdn Bhd can be calculated as follows:

Reformate:

$$= \frac{(Average\ reformate\ flowrate\ FI1126)}{(Average\ inlet\ stabilizer\ flowrate\ FI1135)} \times 100\%$$

$$= \frac{(39.6)}{(40.25)} \times 100\%$$

$$= 98.385\ vol\%$$

LPG:

$$= \frac{(Average\ LPG\ flowrate\ FI1125)}{(Average\ inlet\ stabilizer\ flowrate\ FI1135)} \times 100\%$$

$$= \frac{(0.9)}{(40.25)} \times 100\%$$

$$= 2.236\ vol\%$$

A comparison between actual production yield and theoretical production yield using the catalytic reformer correlation is represented in the graph in next page:

1. Yield of LPG and reformate as function of pressure.

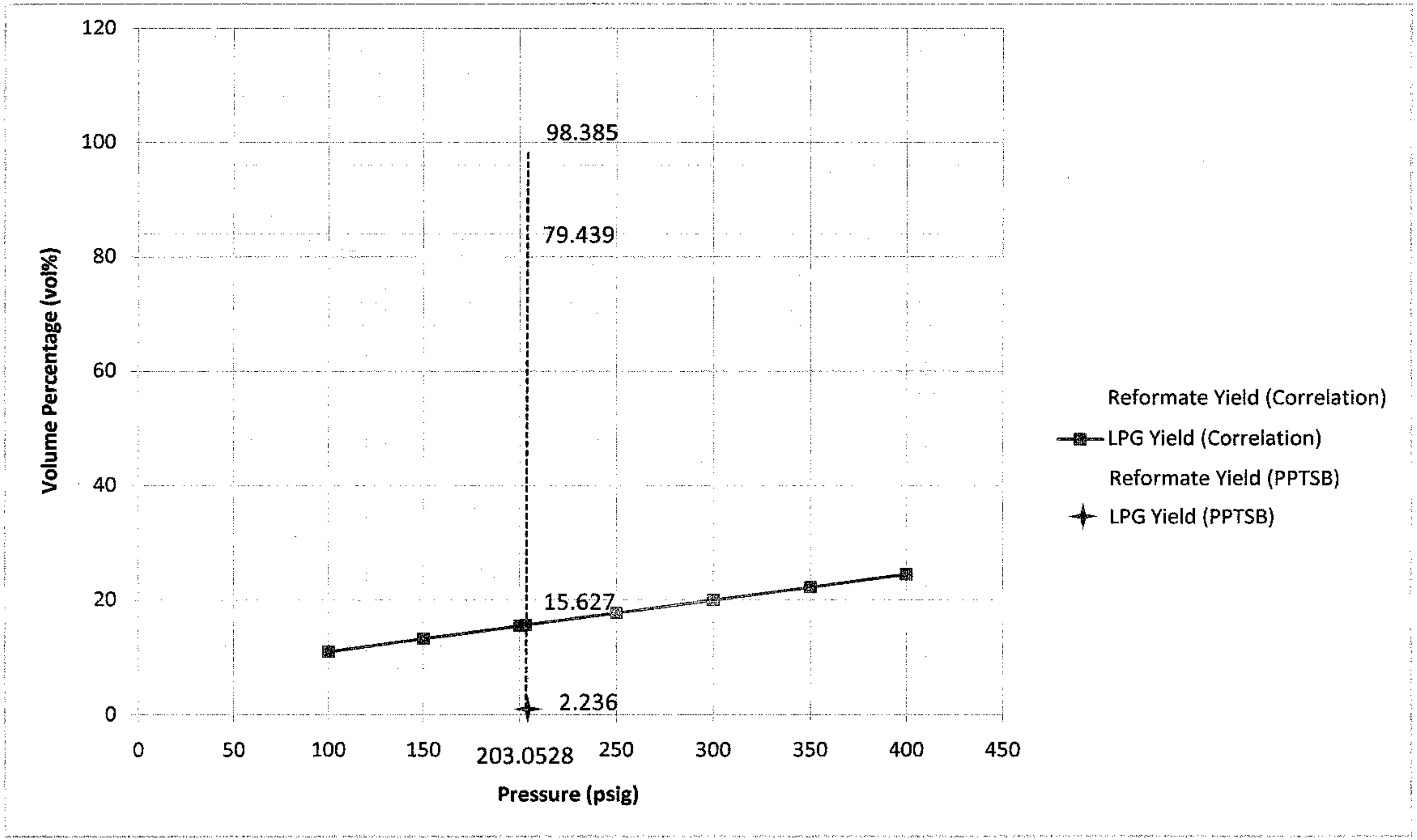

Figure 12: Graph of Yield of Reformate and LPG versus Pressure

2. Yield of LPG as a function of research octane number at pressure 203.0528psig.

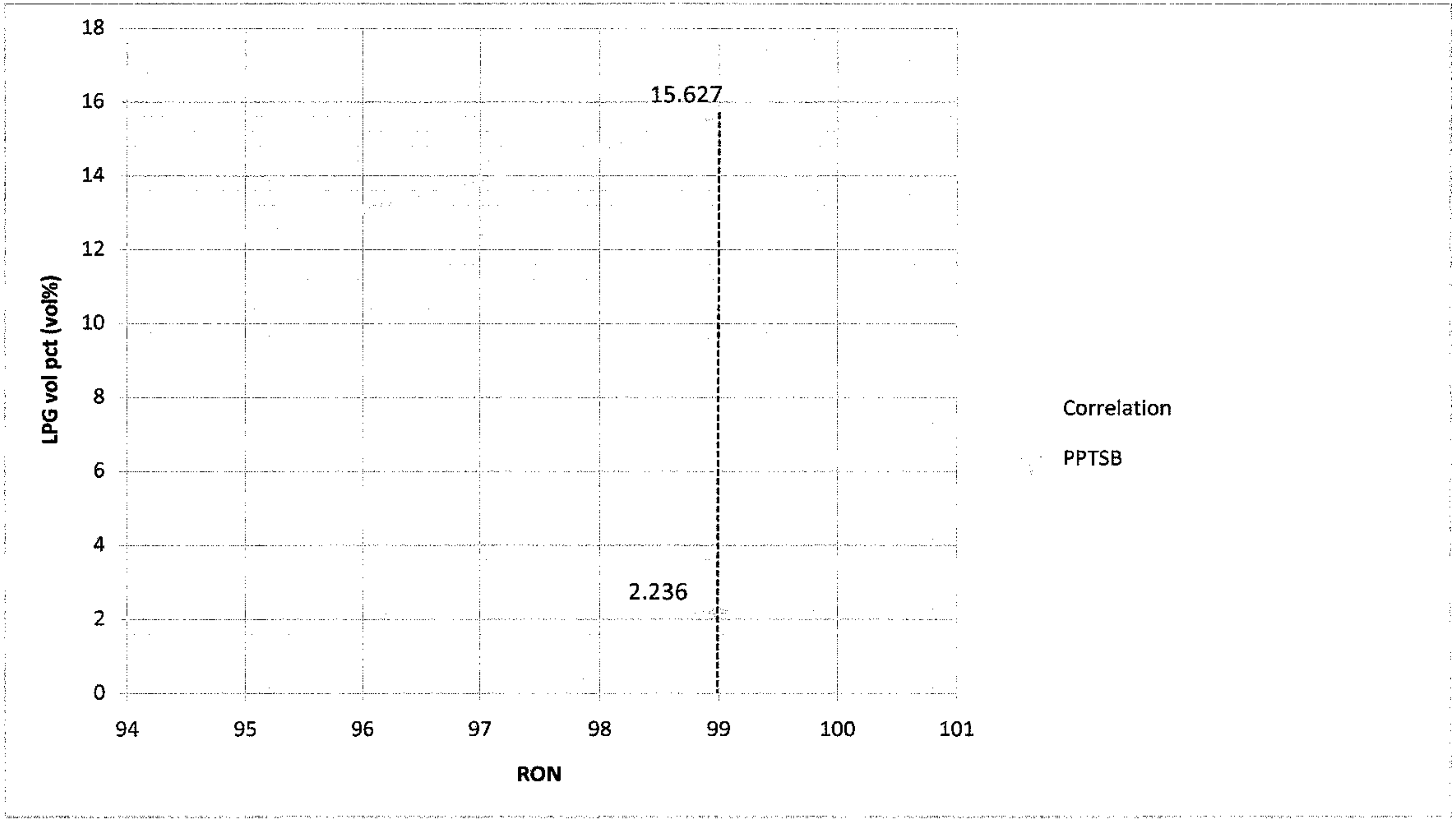

Figure 13: Graph of Yield of LPG versus RON

3. Yield of LPG as a function of N2A (naphtha feed quality) at pressure 203.0528psig and RON 99.

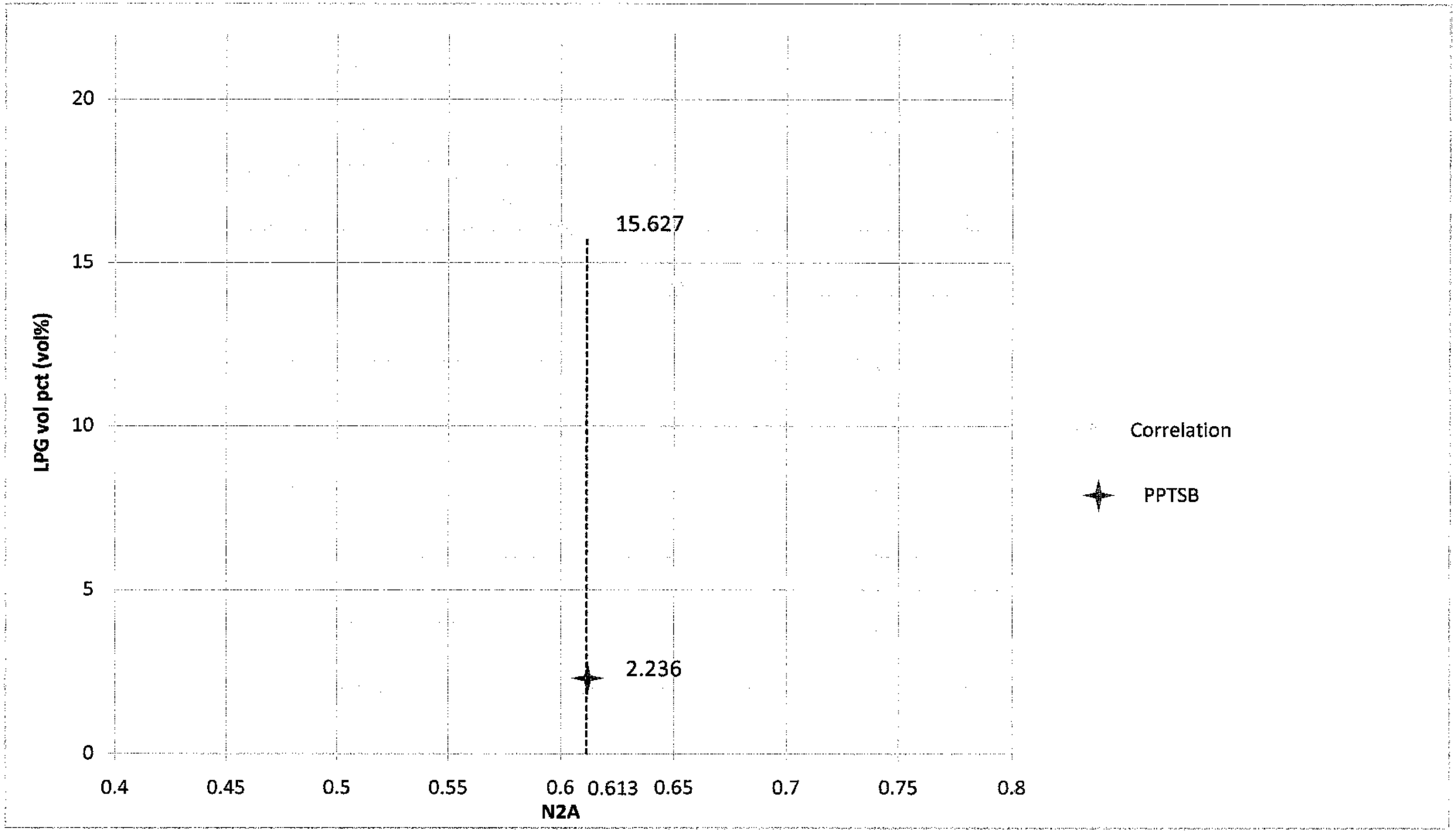

Figure 14: Graph of Yield of LPG versus N2A

4. Yield of reformate as function of research octane number at pressure 203.0528psig.

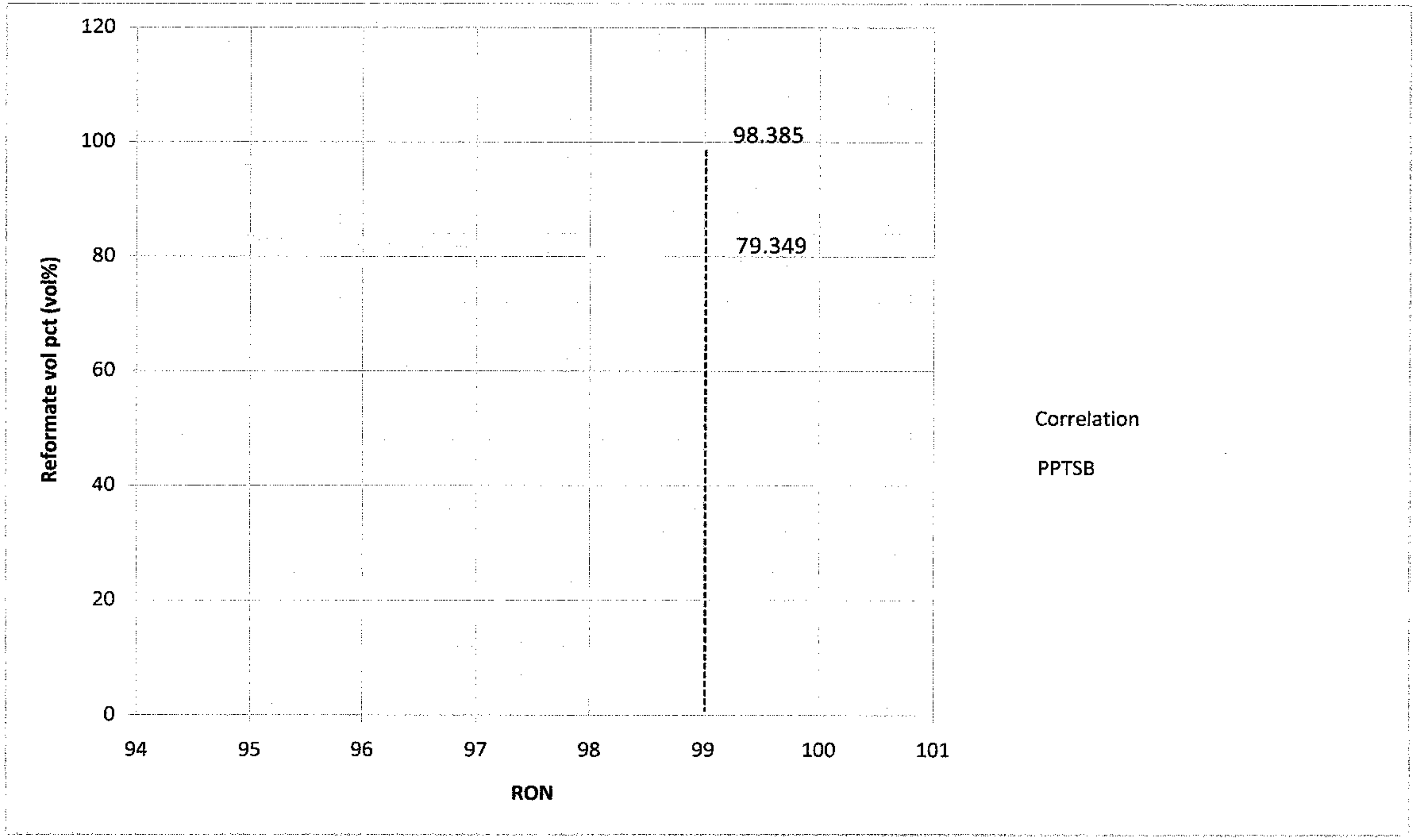

Figure 15: Graph of Yield of Reformate versus RON

5. Yield of reformate as a function of N2A (naphtha feed quality) at pressure 203.0528psig and RON 99.

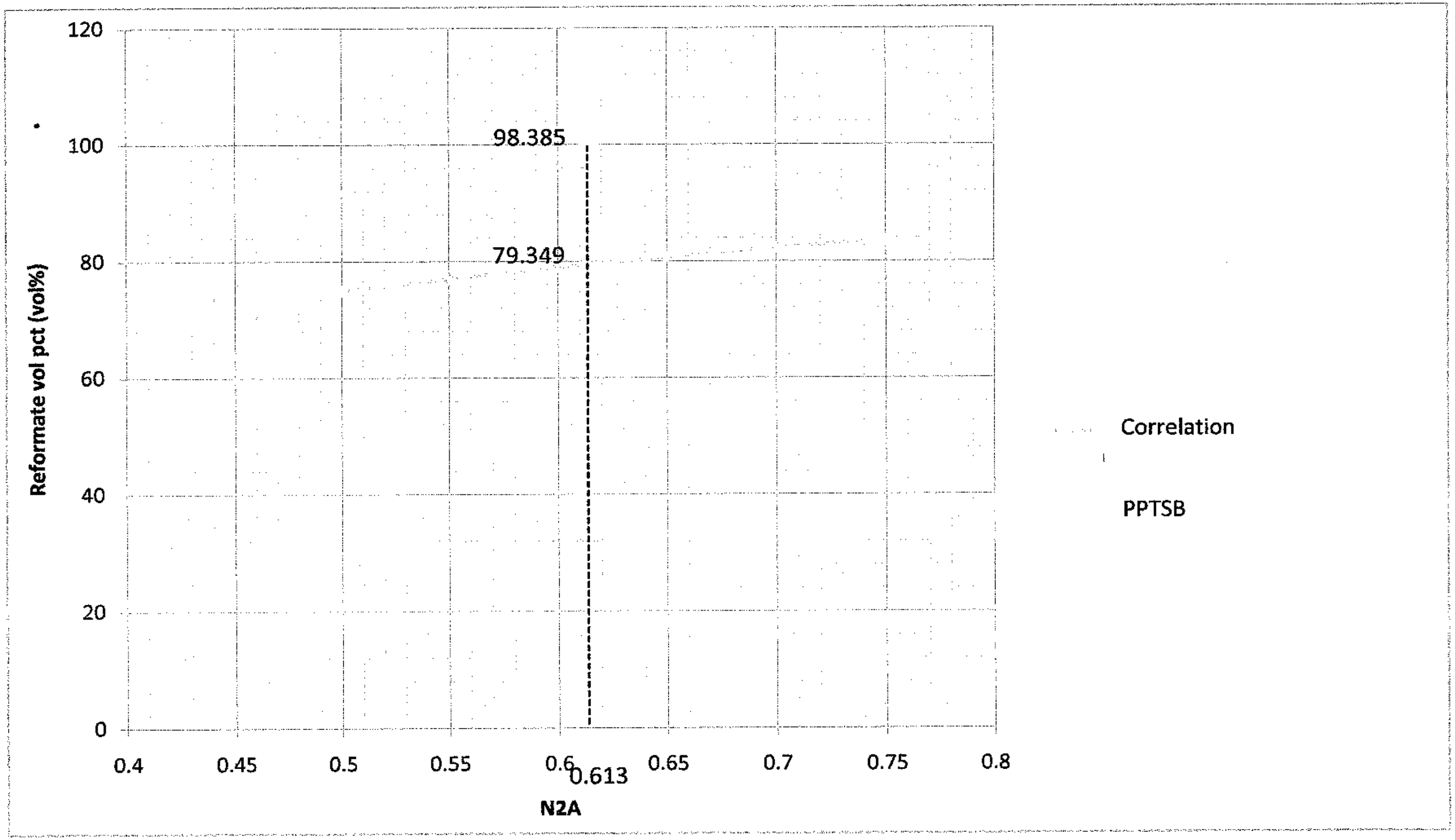

Figure 16: Graph of Yield of Reformate versus N2A

4.4 ANALYSIS

4.4.1 Correction Factor

From the graph, a value of a correction factor need to be finding as to model the catalytic reformer unit using the correlation provided. Different correction factor is applied differently on LPG and reformate correlation. By that, an analysis is done and the correction factors calculated are as follows:

Reformate

Table 11: Volume percentage of yield of reformate

Volume percentage %	**Correlation**	**PPTSB**
	79.439	98.385

$$\alpha = \frac{98.385}{79.439} = \mathbf{1.238}$$

An α value of 1.238 will be multiply to pressure corrected reformate correlation so that it fit the yield of reformate in PPTSB.

Reformate yield at PPTSB:

Pressure corrected reformate yield = (Base reformate yield at 200psig) × **1.238**

$$\begin{aligned} REFORMATE = {} & [(REFBASE) \\ & + \big(2.0 \\ & - 0.01(P)\big)\big(\exp\big(1.4245 - 13.225(N2A) + 12.0(N2A)(RON)\big)\big)] \\ & \times \mathbf{1.238} \end{aligned}$$

LPG

Table 12: Volume percentage of yield of LPG

Volume percentage %	Correlation	PPTSB
	15.627	2.236

$$\beta = \frac{2.236}{15.627} = \mathbf{0.143}$$

A β value of 0.143 will be multiply to pressure corrected propane, iso-butane and butane correlation respectively so that it fit the total yield of LPG in PPTSB.

Propane yield at PPTSB:

Pressure corrected propane yield = (Base propane yield at 200psig) × **0.143**

$$PROPANE = [C3BASE + (P - 200.0)(0.0126(SGF) + 0.00159(C3BASE))] \times \mathbf{0.143}$$

Isobutene yield at PPTSB:

Pressure corrected isobutene yield = (Base isobutene yield at 200psig) × **0.143**

$$ISOBUTANE = [IC4BASE + (P - 200.0)(0.00447 + 0.00163(IC4BASE))] \times \mathbf{0.143}$$

Butane yield at PPTSB:

Pressure corrected butane yield = (Base butane yield at 200psig) × **0.143**

$$N - BUTANE = [NC4BASE + (P - 200.0)(0.00647 + 0.00153(NC4BASE))] \times \mathbf{0.143}$$

The amount or yield produces by correlation of propane, isobutene and butane is sum up to give the total amount of yield of LPG.

4.4.2 Standard Deviation

It is important to calculate the value of standard deviation between the yield values of LPG and reformate using the correlation that has applied the correction factor and actual yield of LPG and reformate in PPTSB. The equation used is:

$$\varepsilon = \left|\frac{Yield\ using\ correlation\ with\ correction\ factor - Actual\ yield\ in\ PPTSB}{Actual\ yield\ in\ PPTSB}\right| \times 100\%$$

Reformate

Table 13: Volume percentage of yield of reformate

Volume percentage %	**Correlation with correction factor**	**PPTSB**
	98.3454	98.385

$$\varepsilon = \left| \frac{98.3454 - 98.385}{98.385} \right| \times 100\% = \mathbf{0.04\%}$$

LPG

Table 14: Volume percentage of yield of LPG

Volume percentage %	**Correlation with correction factor**	**PPTSB**
	2.2346	2.236

$$\varepsilon = \left| \frac{2.2346 - 2.236}{2.236} \right| \times 100\% = \mathbf{0.06\%}$$

For the correction factor to be acceptable or used as an addition to the correlation to model the catalytic reformer unit at PPTSB, the value must has to be less than 5%. For both reformate and LPG, the standard deviation value gives the value of 0.04% and 0.06% respectively, so the correction factor of 1.238 for reformate correlation and 0.143 for each component of LPG is accepted and can be applied in the correlation.

4.5 SUMMARY

As a summary, the models of catalytic reformer unit employed at Petronas Penapisan Terengganu Sdn Bhd are as follows:

Reformate yield at PPTSB:

$$\begin{aligned}\boldsymbol{REFORMATE}\\ &= [(\boldsymbol{REFBASE})\\ &+ (\mathbf{2.0}\\ &- \mathbf{0.01}(\boldsymbol{P}))(\mathbf{exp}(\mathbf{1.4245} - \mathbf{13.225}(\boldsymbol{N2A}) + \mathbf{12.0}(\boldsymbol{N2A})(\boldsymbol{RON})))]\\ &\times \mathbf{1.238}\end{aligned}$$

Propane yield at PPTSB:

$$\begin{aligned}\boldsymbol{PROPANE} &= [\boldsymbol{C3BASE} + (\boldsymbol{P} - \mathbf{200.0})(\mathbf{0.0126}(\boldsymbol{SGF}) + \mathbf{0.00159}(\boldsymbol{C3BASE}))]\\ &\times \mathbf{0.143}\end{aligned}$$

Isobutene yield at PPTSB:

$$\begin{aligned}\boldsymbol{ISOBUTANE} &= [\boldsymbol{IC4BASE} + (\boldsymbol{P} - \mathbf{200.0})(\mathbf{0.00447} + \mathbf{0.00163}(\boldsymbol{IC4BASE}))]\\ &\times \mathbf{0.143}\end{aligned}$$

Butane yield at PPTSB:

$$\begin{aligned}\boldsymbol{N - BUTANE}\\ &= [\boldsymbol{NC4BASE} + (\boldsymbol{P} - \mathbf{200.0})(\mathbf{0.00647} + \mathbf{0.00153}(\boldsymbol{NC4BASE}))]\\ &\times \mathbf{0.143}\end{aligned}$$

The amount or yield produces by correlation of propane, isobutene and butane is sum up to give the total amount of yield of LPG.

The significance of modeling the unit is that the personnel in PPTSB can predict the amount of LPG and reformate that will produced by the unit. If at a time when there is a shortage of production yield, it will give them an earlier indication that the unit or the process flow of the unit may have a problem and prompt for their actions.

CHAPTER V
CONCLUSION AND RECOMMENDATION

5.1 CONCLUSION

Catalytic reformer unit at Petronas Penapisan Terengganu Sdn Bhd has been modeled accordingly by comparison of actual production trend with the production trend produced by the catalytic reformer correlation. By analysis study, a correction factor is applied to the catalytic reformer correlation so that it fit in the model to produce the same amount or yield of LPG and reformate at PPTSB. Moreover, the correction factor applied is acceptable in a manner that its standard deviation is lower than 5%.

The advantages of modeling the catalytic reformer unit at the refinery is when there is such a shortage in production yield of products as compared to predicted amount of products calculated by the model, the personnel in the refinery can acts promptly to fix the unit or the process flows of the unit. This shortage of production yield may have effect in income of the refinery and most likely the management of the refinery won't want it to happen.

In conclusion, the objective of the final year project of modeling the catalytic reformer unit at Petronas Penapisan Terengganu Sdn Bhd has been accomplished. The trend of production and trade off between LPG and reformate, also with the actual data taken from the refinery has led to the understanding of the process flow of the catalytic reformer unit and development of its model.

5.2 RECOMMENDATION

For the success and maintaining the objectives of final year project, there must be collaboration between the university and industry especially between Universiti Teknologi Petronas and Petronas Penapisan Terengganu Sdn Bhd itself. The industry must have realized that all the data taken from them are just for educational purposes and not more than that. The sharing of information between both parties can be beneficial to both in term of operation of the plant and also to the capabilities of the university.

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APPENDIX: GANTT CHART

NO	**DETAIL/WEEK (JULY 2008)**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Selection of project topic	▨	▨												
2	Preliminary research work		▨	▨	▨										
3	Submission preliminary report				▨										
4	Project work					▨	▨	▨							
5	Submission progress report								▨						
6	Seminar									▨					
7	Project work								▨	▨	▨	▨	▨		
8	Submission of interim report													▨	
9	Oral presentation														▨
NO	**DETAIL/WEEK (JANUARY 2009)**	**1**	**2**	**3**	**4**	**5**	**6**	**7**	**8**	**9**	**10**	**11**	**12**	**13**	**14**
1	Project work	▨	▨	▨											
2	Submission progress report 1				▨										
3	Project work				▨	▨	▨	▨							
4	Submission progress report 2								▨						
5	Project work								▨	▨	▨	▨			
6	Poster exhibition										▨				
7	Submission of dissertation (softbound)												▨		
8	Oral presentation													▨	
9	Submission of dissertation (hardbound)														▨