Integration of Hydrogen and CO_2 Management within Refinery Planning

By

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ABSTRACT

The petroleum refining industry is considered to be one of the most important industries affecting daily life. However, this industry is facing many new and challenging situations, including such new trends as increased heavy crude markets, a shrinking market for fuel oils, clean-fuel legislation that encourages production of ultra low-sulfur (ULS) gasoline and diesel fuels, and strict green house gas (GHG) regulations to reduce CO_2 emissions into the atmosphere. Refineries thus face a serious need to increase the capacity of their conversion units, such as the hydrocracker and fluid catalytic cracking units (FCCs), and to increase their consumption of hydrogen to meet the new requirements. These increases should be planned with reference to allowable CO_2 emission limits. Refineries therefore need an appropriate tool for planning their operations and production.

This research focuses on refinery planning under hydrogen and carbon management considerations. A systematic method that uses mathematical programming techniques to integrate the management of hydrogen and CO_2 for refinery planning is proposed. Three different models for refinery planning, hydrogen management, and CO_2 management, are prepared and then properly integrated. Firstly, a Nonlinear Programming (NLP) model that provides a more accurate representation of the refinery processes and which is able to optimize the operating variables such as the Crude Distillation Unit (CDU) cut-point temperatures and the conversion of the FCC unit is developed. The model is able to evaluate properties of the final products to meet market specifications as well as required product demands, thereby achieving maximum refinery profit.

A systematic methodology for modeling the integration of hydrogen management and refinery planning was considered next. This resulted in a Mixed Integer Nonlinear Programming (MINLP) model that consists of two main building blocks: a set of nonlinear processing unit models and a hydrogen balance framework. The two blocks are integrated to produce a refinery-wide planning model with hydrogen management. The hydrogen alternatives considered in this research are hydrogen balancing, compressors, and purification processes. The model was illustrated on representative case studies and lead to an improvement in the hidden hydrogen unavailability that prevents refineries from achieving their maximum production and profit. It was found that an additional annual profit equivalent to $7 million could be achieved with a $13 million investment in a new purification unit.

The consideration of CO_2 management and the integration with refinery planning and the hydrogen network required the formulation of a CO_2 management model. This model focused on the refinery emission sources and the mitigation options. The refinery emissions sources are the fuel system, hydrogen plant, and FCC unit, and the mitigation options considered are load shifting, fuel switching, and capturing technology. The model performance was tested on different case studies with various reduction targets. The optimization results showed that CO_2 mitigation options worked successfully together to meet a given reduction target. The results show that load shifting can contribute up to a 3% reduction of CO_2 emissions, and fuel switching can provide up to 20% reduction. To achieve greater than 30% reductions, a refinery must employ capturing technology solutions. The proposed model provides an efficient tool for assisting production planning in refineries and at the same time determines the optimum hydrogen and CO_2 emissions strategies.

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I am thankful to my supervisors, Professor Ali Elkamel and Professor Peter Douglas, for their valuable comments, guidance, patience and encouragement throughout my study.

During my stay in Waterloo, I made so many good friends and new relations. Within the chemical engineering department, few colleagues in the Process System group were so influential and supported me academically and emotionally all the way to the end of my PhD program. Yousef Saif, Khalid Al-Qahtani and I used to discuss the best methodologies to achieve our final objectives on regular basis. We have a lot of unforgotten memories while attending classes, workshops and conferences. The three of us worked as a team and I hope that the bond between us will even get stronger by time.

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The greatest happiness of completing my thesis comes from my mother. My mother was always proud of my actions and now I made her even more proud. She took a lot of burden by agreeing on and approving my travel. My mother has a great vision and I believe her vision was inspired by my father. Her vision is to do our best to give back our motherland as we are taking from her since we were born. I hope that I will fulfill my parents’ vision in the near future.

To my mother
Nuwayer bint Mohammad

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NOMENCLATURE

Refinery Planning Model:

Indices:

i,j,m,b	Processing units
n,s	Streams
p	Properties
x	Operating Variables

Sets:

B	Final blending units (b), $B \in I$
E	Processing unit (e) received external raw material, $E \in I$
I	Processing units (i) in the refinery
J	Processing units (j) that can send products to unit (i) , $J \in I$
M	Processing unit (m) can received stream (s) from unit (i), $M \in I$
N	Streams (s) can sent from unit (i) to unit (j), $N \in S$
P	Properties (p) of stream (s)
PF	Properties (p) of feed to unit (i), $PF \in P$
S	Product streams (s) of unit (i)
X	Operating variables of unit (i)

Parameters

$a_{k,p}$	Coefficient for calculating the property (p) of stream (s)

ce_i	Cost of external material (raw material) to processing unit (*i*)
cx_i	Operating cost of processing unit i
sp_i	Selling price of final product from blending pool
TE_i^L	Lower bound of the end point (cut) temperature of stream (*s)* from *CDU* unit
TE_i^U	Upper bound of the end point (cut) temperature of stream (*s)* from *CDU* unit
UC_i	Maximum capacity of unit (*i*)

Variables

F_i	Volumetric flow rate of feed to unit (*i*), BPD
$FP_{i,p}$	Property (*p*) of feed to unit (*i*)
$PV_{i,s,p}$	Property (*p*) of stream (*s*) from unit (*i*)
$V_{i,s}$	Volumetric flow rate of stream (*s*) from unit (*i*), BPD
$VS_{i,s,m}$	Volumetric flow rate of stream (*s*) splited from product $V_{i,s}$ of unit (*i*) received by unit (*m*), BPD
$W_{i,s}$	Weight flow rate of stream (*s*) from unit (*i*), KLbPD
$wv_{s,p}$	Weight or volume fraction depending on the property (*p*) of stream (*s*)
$XU_{i,u}$	Operating variable *x* of unit *i*

Refinery Hydrogen Model:

Indices:

i	Sources
j	Sinks
k	Exist compressors
m	PSA units
n	New compressors
u	Processing units

Sets:

$Fuel$	Fuel System, $Fuel \in J$
I	Sources, $i \in I$
J	Sinks, $j \in J$
K	Exist compressors, $k \in K$
M	New purification units (PSA), $m \in M$
N	New compressors, $n \in N$
U	Processing units (hydrogen consumer), $u \in U$
$Iden\_u(U,U')$	Processing units U and U' are identical
$Iden\_n(N,N')$	New compressors N and N' are identical

Parameters

A	Binary parameter for flow existence (between ij, ik, iu, kj, ku, uj)
a, b	Capital cost function constants, for n, m

AF	Annual interest factor
$Cons_u$	Hydrogen consumption of processing unit (*u*)
FC_k^U	Maximum compressor flow rate, for *k*
LHV	Low heating value of fuel gas
OCE	Operating cost of electricity, compressors power ($/KWh)
OCF	Operating credit of fuel gas, gained by heating ($/MMBTU)
OCH	Operating cost of hydrogen production ($/MMSCF)
OD	Operating days per year
P	Pressure (psi), for *u, k, j, i*
$RCOV$	Recovery factor for PSA unit
UF, LF	Upper and lower bounds of flow rate
UP, LP	Upper and lower bounds of pressure difference
$UPwr$	Upper bound of compressor power
y_i	Purity of source (*i*) streams
y_{pr}	Purity of PSA (*m*) product streams

Variables

Cap	Capital cost of new compressors and PSA, for *n, m*
F	Flow rate (MMSCFD)
MU	Makeup streams

OC	Operating cost
PG	Purge streams
PI	Inlet pressure of new compressors and PSA, for *n, m*
PO	Outlet pressure of new compressors and PSA, for *n, m*
Pwr	Compressor power
R	Recycle streams
TAC	Total annual cost
y	Stream purity (hydrogen content %)

Binary Variables

X	Existence of new equipments (NC and PSA)
XF	Existence of flow rate streams

Refinery CO_2 Model:

Indices:

$fuel$	Refinery fuel
g	Mitigation alternative
i	Processing unit

Sets:

$FUEL$	Refinery fuels
G	Mitigation alternatives
I	Processing units

Parameters:

CFC	Carbon fraction in the coke burned
$Cost_{Capture}$	Cost of installing a capture process for each unit of flowrate
$Cost_{switch}$	Cost of switching furnace fuel for each unit of flowrate
EF_{fuel}	Emission factor of fuel
ERT	Emission reduction target level
$\varepsilon_{Capture}$	Efficiency of a given capture process
MVC	Molar volume conversion
MW_C	Molecular weight of carbon

MW_{CO_2}	Molecular weight of CO_2
RC	Rate of coke burn in units of mass per year
TE	Total CO_2 emission without any mitigation options
UCC_i	Upper limit on capturing cost of processing unit i
UCS_i	Upper limit on switching cost of processing unit i
UE_i	Upper limit on CO_2 emission from process i

Variables:

CAC_i	Capturing annualized cost on processing unit i
E_i	Overall emission flowrate of processing unit i
EP_i	Emission flowrate within process of processing unit i
F_i	Flowrate of feed stream to processing unit i
FC_i	Fuel consumption of unit i
HPR	Rate of hydrogen production in SCF/yr
RC	Rate of coke burn in units of mass per year
$SWAC_i$	Switching annualized cost (of fuel switching) on processing unit i

Binary Variables

$XC_{i,g}$	Selection of mitigation option g on processing unit i

ABBREVIATIONS

ATK	Aviation Turbine Kerosene
CDU	Crude Distillation Unit
CI	Cetane Index
CR	Catalytic Reformer
DHT	Diesel Hydrotreater
FCC	Fluid Catalytic Cracker
FLSH	Flash Point Temperature
FRZ	Freeze Point Temperature
GAMS	General Algebraic Modeling System
GOHT	Gas Oil Hydrotreater
GP	Gas Plant
HC	Hydrocracker
Kero	Kerosene
LP	Linear Programming
LSDSL	Low Sulfur Diesel
LSFO	Low Sulfur Fuel Oil
MINLP	Mixed Integer Non-Linear Programming
MEA	Mono Ethanol Amine

NHT	Naphtha Hydrotreater
NLP	Non-Linear Programming
OXG	Oxygenate weight %
PRG	Premium Gasoline
PSA	Pressure Swing Adsorption
RGG	Regular Gasoline
RHT	Residue Hydrotreater
RON	Research Octane Number
RVP	Reid Vapor Pressure
SUL	Sulfur weight %
ULS	Ultra Low-Sulfur
VISC	Viscosity @ 210°F

CHAPTER 1

INTRODUCTION

1.1 Motivation

The thrust of any modern oil refinery is to process crude oil into high value products at minimal cost and with minimal environmental burden. The refining industry remains a vital component of the national economy of many countries. It is forecasted that the world oil consumption will increase from 83.6 million barrels/day in 2005 to 113.0 million barrels/day in 2030 (EIA, 2006). Such expected increase in demand requires additional refining capacities, especially in developing countries. Refineries produce a wide range of petroleum products, including gasoline, diesel, heating oil, residual fuel, coke, lubricants, asphalt, and waxes, as well as non-hydrocarbon products such as sulfur and vanadium. The production of gasoline, which is one of the most important products, dominates the refinery production at over 46 percent, see Figure 1.1. Distillate and residual fuels comprise the next largest share, with about 35 percent of refinery production (Swaty, 2005; Radler, 2006).

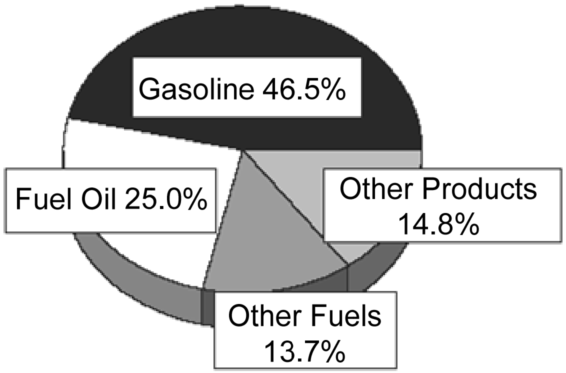

Figure 1.1. Refinery Production (Swaty, 2005)

The petroleum refining industry, as any other industry, aims to generate profit by converting crude oils into valuable products. However, a petroleum refinery is an extremely complex entity, which needs an accurate optimization of streams flow and process feed to achieve profitable operation. Currently, the optimization of refinery operations and production is mostly done through applying Linear Programming (LP) techniques that are based on yield victors (Uhlmann, 1988; Lee *et al*, 1996; Jia and Ierapetritou, 2003). This approach might give inaccurate results and lead to far from the optimal plans. Nevertheless, knowing that the oil refining industry is facing increasingly tight and stringent regulations with regards to products' specifications, such as the continuous reduction in the allowed sulfur content in fuel products, a rigorous model of refinery operations that can capture different refinery feed characteristics which mimics different refinery stages more accurately is necessary. Such model will be able to predict the effects of changing the conversion of a processing unit on the products quantity and properties, while LP models fail to do so. However, formulating and solving such rigorous models is considered one of the most difficult and challenging applications for the large-scale process industry, but the expected outcome outperforms these difficulties (Zhang and Zhu, 2000; Li, 2004). The main objective of this research is to develop a rigorous Nonlinear Programming (NLP) model (Chapter 3) for refinery planning problem and integrate the model with hydrogen and CO_2 management models.

In the last few years, several trends in the oil refinery industry have lead to an increased demand for hydrogen in refineries, resulting in dramatic changes in refinery processes. Figure 1.2 illustrates the current hydrogen situation in the petroleum refinery.

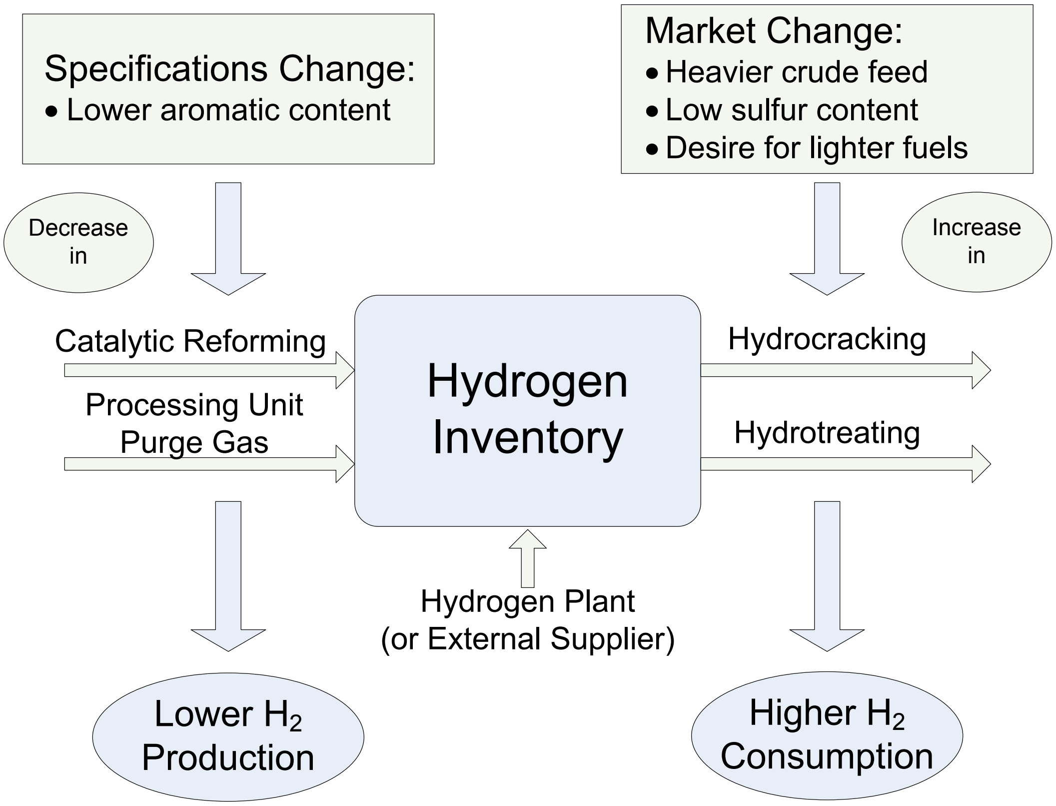

Figure 1.2. Overall Hydrogen Network in Petroleum Refinery

Hydrogen availability was not a major concern for most refineries, and hydrogen systems featured little or no integration. However, this situation is changed due to many new factors. First, stricter legislation on sulfur content in fuels increased the need for hydrotreating to produce Ultra Low Sulfur (ULS) fuel products. At the same time, regulations on gasoline aromatics composition are constraining the reformer operation which results in a decrease in hydrogen produced by this unit. Second, the shift towards processing heavier crude oils and the reduction in the demand for heavy fuel oil is forcing greater use of hydrocracking for upgrading. Increasing the throughput of a refinery also increases hydrogen requirements, causing the existing hydrogen production capacity to be a bottleneck. All these factors raise the need for integrating and optimizing the hydrogen refinery network to meet new market trends. This need was the motivation for integrating the hydrogen network within the refinery planning, which will be discussed in detail in Chapter 4.

Recently, the production of greenhouse gases (GHG) and CO_2 emissions are getting great attention in many international arenas and the petroleum refining industry is no exception. The Kyoto Protocol on GHG, which mandates more stringent emissions measures, left many countries facing a challenging situation. The new CO_2 legislation forces many industries to review their operations and processes to cope with the new limitation. Petroleum refineries started to consider the CO_2 impacts of their operations, and to adopt a CO_2 management strategy across their various processes (IEA, 2007). The integration of a CO_2 strategy model within the integrated refinery model (hydrogen network and refinery planning) will be discussed in Chapter 5 of this thesis.

1.2 Research Objectives

The overall objective of this research is to determine the best strategy for a refinery to meet a given hydrogen requirements and CO_2 emissions limitation while maintaining or increasing desired production level with minimal overall cost. The problem will be formulated as a Mixed Integer Nonlinear Programming (MINLP) model. This goal can be achieved successfully through the accomplishment of:

Refinery processes planning: the objective here is to formulate a mathematical model that aims to maximize the profit of selling final products with meeting properties specifications and market demands. This is because the production activities area represents the most important area in the refinery, and these activities profitability depends on operating the refinery processes with optimal conditions. Therefore, an accurate planning model is necessary for refineries to meet this objective. Rigorous units' models will be used, rather than the traditional used linear models, to achieve the accuracy needed to represent the refinery processes. With this in mind, a NLP refinery processes planning model that integrates the processing units' models with the blending correlations, to form a complete refinery planning tool is formulated and implemented in General Algebraic Modeling System (GAMS).

Refinery hydrogen management: the objective here is to offer a mathematical model that is able to attain the refinery planning objective at the same time and meet the hydrogen requirements with least cost. The new environmental regulations, as mentioned earlier, are driving this part of the research. A deeper study of hydrogen within refinery will change the whole picture from dealing with hydrogen as a utility to be an asset. The overall hydrogen network will be investigated in terms of sources, sinks, and recovery methods. Three potential hydrogen management options are considered, for this research, namely; balancing, purification process, and compressor. The balancing is achieved by changing the processing units load to maintain the hydrogen balance. The purification process option allows installing new processes to increase the high purity hydrogen streams in the refinery hydrogen network. The compressor option allows installing new compressors to raise high purity streams' pressure to the required pressure by the refinery hydrogen network. To achieve this objective, a MINLP hydrogen management model is formulated and integrated within the refinery planning model.

Refinery CO_2 management: the objective here is to formulate a mathematical model that is able to find the best CO_2 management strategies for the refinery while achieving the refinery profit and appropriate hydrogen management. As in the previous discussion, the cost of carbon emissions is a new additional variable to be considered when establishing the optimum operation in a petroleum refinery. The refinery CO_2 emissions mitigation options considered in this research are load balancing, fuel switching, and capture processes. Balancing or load shifting considers the adjustment of production throughput across the refinery units to reduce CO_2 emissions. In fuel switching, emissions are reduced by selecting to switch from one type of fuel to another (essentially switching from fuel oil to natural gas). Capture technology, considers the installation of capture processes to reach high levels of CO_2 reduction. To achieve this objective, an integrated MINLP model that integrates the planning model, the hydrogen model, and CO_2 considerations is formulated.

1.3 Research Contributions

The major contributions of this research can be summarized as follows:

- The optimization program is written in a general style that will allow it to be transferable to other industries with many applications.
- The refinery processing unit rigorous models can be used to predict the product yield and properties for different feedstocks charged to the processing units.
- The NLP refinery production planning model not only optimizes the production flow rate for final and/or intermediate products, but also optimizes the properties of each stream in the refinery.
- The MINLP hydrogen management model can select the best hydrogen strategies for a refinery. In addition, it can be easily integrated with different industries other than the refining industry.
- The MINLP CO_2 management model can select the best CO_2 mitigation strategies for the refinery. This model can be applied on other industries such as the power generation industry.
- The integrated plant-wide planning model that simultaneously take into account the refinery processing unit production, the hydrogen management strategies, and the CO_2 management strategies.
- The optimization programs can be used as tools for evaluating various strategies that might be suggested by the petroleum refinery and petrochemical industry.

1.4 Organization of the thesis

The organization of this thesis is as follows:

Chapter 1: *INTRODUCTION*

This chapter addresses the latest issues in petroleum refining industry, and provides the motivation for this research. Also, it states the research objectives, contributions, and organization of the thesis.

Chapter 2: *BACKGROUND AND LITERATURE REVIEW*

This chapter provides a background about the petroleum refining industry and describes the major processing units in the refinery. In addition, it gives an overview of refinery hydrogen network and CO_2 emissions. It also presents a review of many previous studies related to the thesis topics (i.e. refinery planning, hydrogen management, and CO_2 management).

Chapter 3: *MATHEMATICAL MODEL FOR REFINERY PLANNING*

This chapter presents the rigorous models for each processing unit within a refinery and different correlations for blending products' properties. The general mathematical refinery planning model is developed through simultaneously connecting the processing units models with the blending properties correlations. The model is tested through different case studies.

Chapter 4: *INTEGRATION OF HYDROGEN MANAGEMENT WITHIN REFINERY PLANNING*

This chapter discusses the proposed general plant-wide planning model for the hydrogen management. Initially, it develops the superstructure representation, which illustrates alternative options of hydrogen management strategies. The hydrogen network elements models are provided; the sources, sinks, processing units, compressors, and purification processes. The resulted MINLP hydrogen management model will be connected to the NLP planning model to form the refinery-wide planning model. The model performance is tested through different case studies.

Chapter 5: *INTEGRATION OF HYDROGEN AND CO_2 MANAGEMENT WITHIN REFINERY PLANNING*

This chapter presents the MINLP CO_2 management model through developing the superstructure representation that illustrates alternative CO_2 emissions sources and mitigation options. The CO_2 emissions sources considered are fuel, hydrogen plant, and FCC regenerator. The CO_2 mitigation options are balancing, fuel switching and capturing processes. The mathematical plant-wide refinery planning model is developed through simultaneously connecting the NLP planning model, the MINLP hydrogen management model, and the MINLP CO_2 management model. The model is tested on different case studies.

Chapter 6: *CONCLUSIONS AND RECOMMENDATIONS*

This chapter gives the conclusions gained from this research and suggests recommendations for future work.

CHAPTER 2

BACKGROUND AND LITERATURE REVIEW

2.1 Introduction

Petroleum refineries extract and upgrade the valuable components of crude oil to produce a variety of marketable petroleum products that are vital to everyday life. Figure 2.1 shows the overall refinery flow diagram. In the next decade, the total worldwide demand for crude oil is expected to be increased by 15 million barrels per day more than the current consumption. Much of the growth in oil consumption is projected for the emerging Asian nations, where strong economic growth results in a robust increase in oil demand. Emerging Asia, including China and India, accounts for 45 percent of the total world increase in oil use over the forecast period (IEO, 2006).

Examples of valuable refinery products are gasoline, jet fuel and diesel. The petroleum refining industry employs a wide variety of processes. It begins with the distillation, or fractionation, of crude oils into separate hydrocarbon groups. The resultant products are directly related to the characteristics of the crude processed. Most distillation products are further converted into more usable products by changing the size and structure of the hydrocarbon molecules through cracking, reforming, and other conversion processes. These converted products are then subjected to various treatment and separation processes such as hydrotreating and sweetening to remove undesirable constituents and improve product quality.

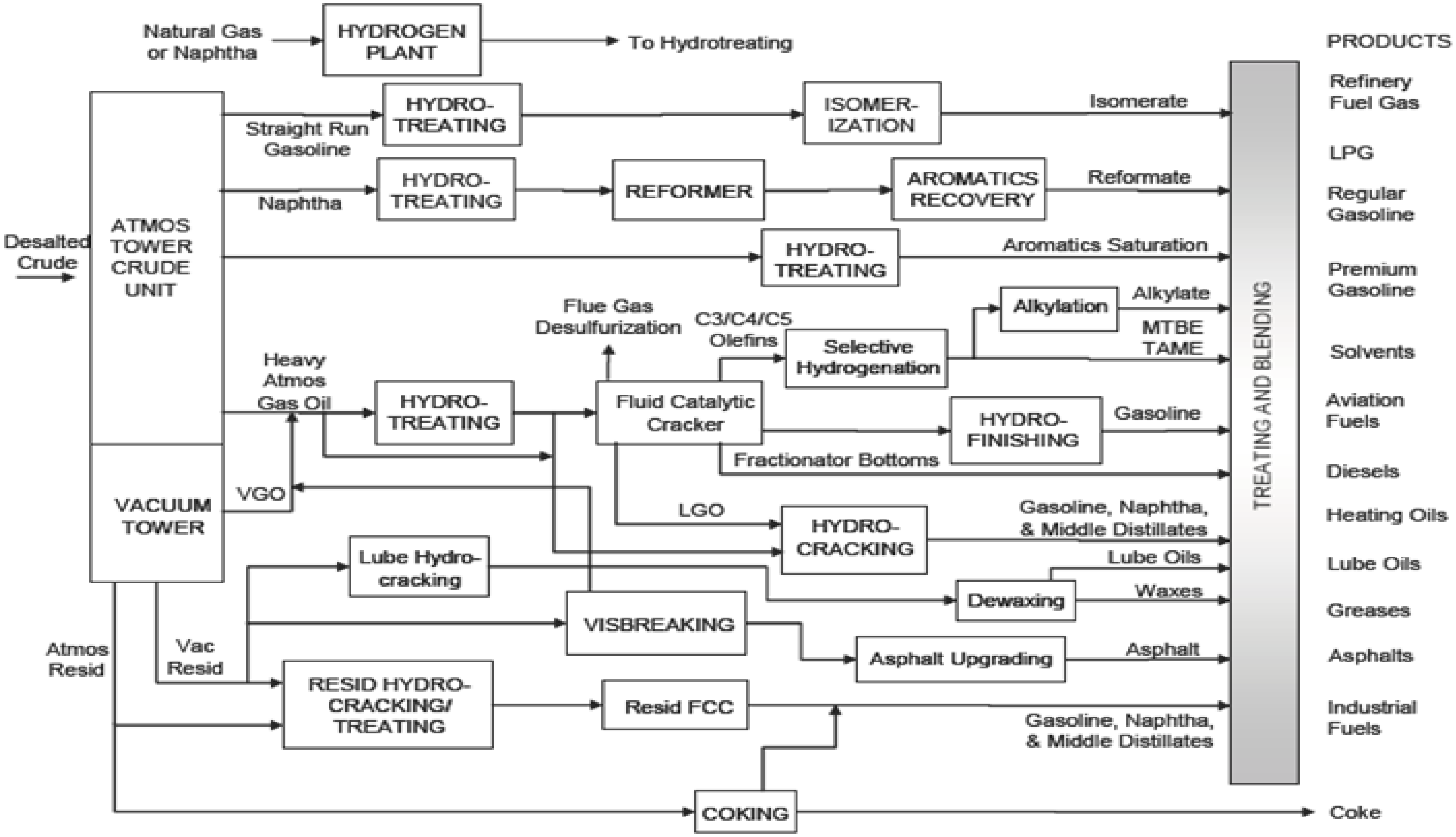

Figure 2.1. Typical Petroleum Refinery Flow Diagram (ODE 2007)

The objective of this chapter is to give a background on the petroleum refinery processing and the latest concerns (hydrogen and CO_2) in refining industry.

The remainder of this chapter is organized as follows. In the following section, a description for the main processing units included in this research will be provided. Then, an overview of hydrogen problem in refinery will be explained, in section 3. In section 4, an illustration of the refinery CO2 problem will be presented. This chapter ends with literature review.

2.2 Overview of Refinery Processes

Crude oil is a mixture of hundreds of hydrocarbon compounds ranging in size from the smallest, methane, to the large compounds containing 100 or more carbon atoms. Crudes are characterized based on a number of qualities, including sulfur content, density, and distillation fraction (Jones, 1995; Gary, 2001). Crude oil density is measured using a specific gravity scale developed by the American Petroleum Institute (API). Lighter crude oils (high API) have a greater value than heavier oils (lower API). Over the past two decades, the average API gravity of crude oil inputs has decreased from 32.5 to 30.2 degrees (Henderson et. al., 2005).

Refinery configurations are different from one refinery to another, which depends on the type of crude oil processed, the processing units operated (complexity), and the desired product slate. Complex refineries have a variety of processing and treatment options, which can change in response to the availability of certain types of crude oil (Jones, 1995; Gary, 2001).

Refinery operations essentially fall into four categories (Gary, 2001; OSHA, 2007):
1) Fractionation involve in separating crude oil, in atmospheric and vacuum distillation, into different hydrocarbon groups, or fractions.
2) Conversion processes:

A. Cracking (thermal and catalytic) involve in breaking large and heavy hydrocarbon molecules into smaller ones. Cracking can be achieved either through the application of heat (delayed coking) or by catalysts (FCC).

B. Rearrangement involve in restructuring the molecule and producing a new molecule with different characteristics, but the same number of carbon atoms (catalytic reforming and isomerisation).

C. Combination involve in linking molecules together to form a larger molecule (alkylation and polymerization).

3) Treating processes involve in preparing streams for additional processing, and in removing impurities (hydrotreating).

4) Blending is used get the final product, and it considers as the last phase of the refining process.

Different processes from each category are selected to be included in this research. In the next section, each category and the selected processes will be explained in more details.

2.2.1 Distillation (Fractionation)

Crude distillation unit (CDU) is the first major processing unit in refinery. The basic function of the CDU is to separate the crude oil into fractions appropriate for further processing. According to the boiling points, ranging from 90^{o}F to over 800^{o}F, crude oil is separated into many fractions. As the boiling points of different hydrocarbons are reached, the vapors condense and are collected in streams. Lighter fractions are collected through atmospheric distillation; heavier fractions are collected in a vacuum tower at lower pressure due to their high boiling points (Maples, 1993; Gary, 2001).

Desalted crude oil is separate into specific hydrocarbon groups with similar boiling points at the atmospheric distillation column. Boiling ranges of fractions produced in atmospheric distillation go up to about 700^{o}F. In this process, the crude is preheated with hot products, and finally it is heated to about 700^{o}F in a tubular furnace, see Figure 2.2. Many different configurations can be used for the furnace, but most use hot furnace flue gases to preheat pipes (Watkins, 1979; Maples, 1993; Jones. 1995; Gary, 2001).

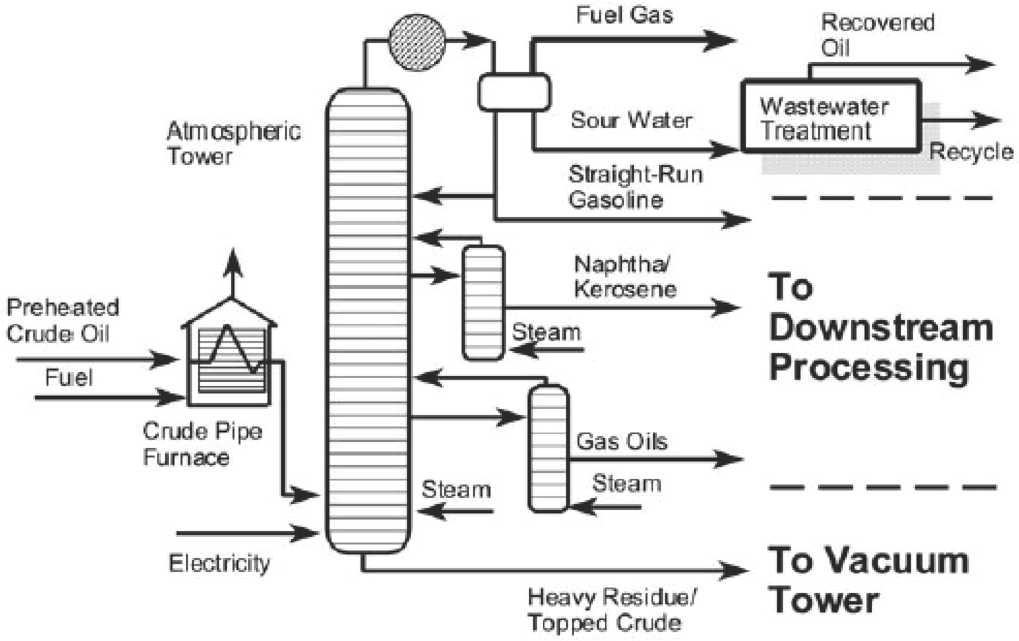

Figure 2.2. Crude Oil Atmospheric Distillation Unit Flow Diagram (ODE 2007)

Atmospheric distillation products are often referred to as straight-run products. The major products of CDU are gasoline, naphtha, kerosene, gas oils, and heavy crude residue. The straight-run liquids are further processed to make final products or blended with products from downstream processes. Atmospheric columns also produce a light non-condensable fuel gas composed mostly of methane and ethane that is often referred to as refinery gas.

Further heating of the atmospheric residue, grater then 750^{o}F, might decompose the fractions in the residue. Also, excessive heat can lead to the formation of coke deposits, which must be removed. Vacuum distillation is effectively able to lower the boiling points of the fractions and permit separation at lower temperatures. Vacuum distillation column products are vacuum gas oil, and heavy bottom residue. The vacuum gas oil can be used as feed to the catalytic cracker downstream. Vacuum bottoms can be used as fuel, or can be further processed in coking units where they can be converted to gasoline components, petroleum coke, and refinery gases (Watkins, 1979; Maples, 1993; Jones. 1995; Gary, 2001).

2.2.2 Fluidized Catalytic Cracking (FCC)

Fluidized catalytic cracking (FCC) is the most widely-used catalytic cracking process, and many refiners consider FCC the primary conversion process, see Figure 2.3. FCC has been the workhorse of the petroleum refinery. It consists of a reactor/regenerator section and a fractionation section. Heavy gas oil flows from the atmospheric column, and vacuum distillation unit to the FCC preheat furnace to the reactor riser, where it is contacted with the catalyst returning from the regenerator. The resulting oil-catalyst fluid mixture flows up the riser, in which the majority of the cracking reactions occur, and into the reactor vessel. Catalyst fines are separated from the hydrocarbon product through the use of cyclones within the reactor vessel. The product stream from the reactor flows to the fractionation section, from which three product streams leave. These are namely, gasoline, light catalytic gas oil (LCGO) and heavy catalytic gas oil (HCGO). On the other hand, FCC is the major source of the olefin feed to the alkylation's process (Sadeghbeigi, 1995; Wilson, 1997; Gary, 2001; Meyers 2004).

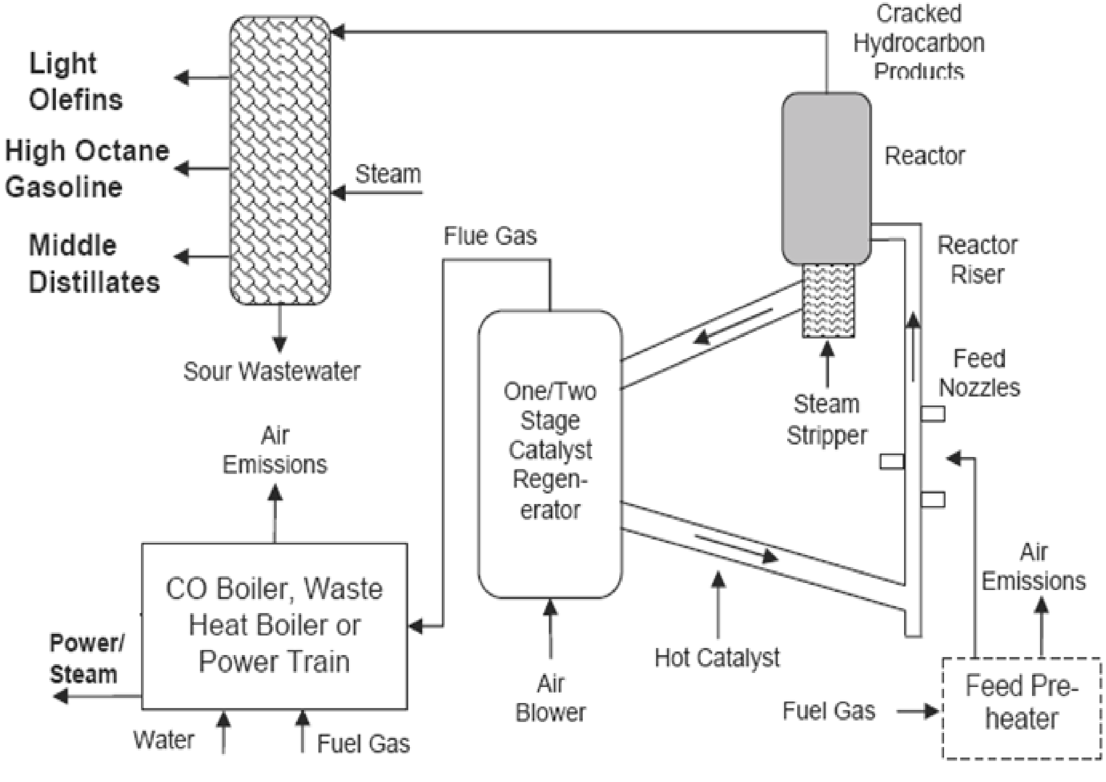

Figure 2.3. Fluid Catalytic Cracking Unit Flow Diagram (ODE 2007)

2.2.3 Hydrocracking Process (HC)

The aim of hydrocracking is the transformation of the heavy fractions of crude oil into light fractions. The use of this process is determined by the high quality of some of the products obtained, such as the jet fuel, see Figure 2.4. Hydrocracking is the appropriate process for all feedstocks that are difficult to process by either catalytic cracking or reforming. The process employs high pressure, high temperature, a catalyst, and hydrogen. Therefore, the hydrocracking process is more expensive than catalytic cracking process. Hydrocracking process heavy aromatic feedstock is converted into lighter products under a wide range of high pressures (1000-3000 psi) and high temperatures (750°-1500° F), and existence of hydrogen. Hydrogen has another important role in the hydrocracking process, which is reducing tar formation and preventing buildup of coke on the catalyst. Hydrogenation also serves to convert sulfur compounds and nitrogen compounds present in the feedstock to hydrogen sulfide and ammonia (Maples, 1993; Elkamel et. al., 1999; Gary, 2001; Raseev, 2003; Meyers 2004).

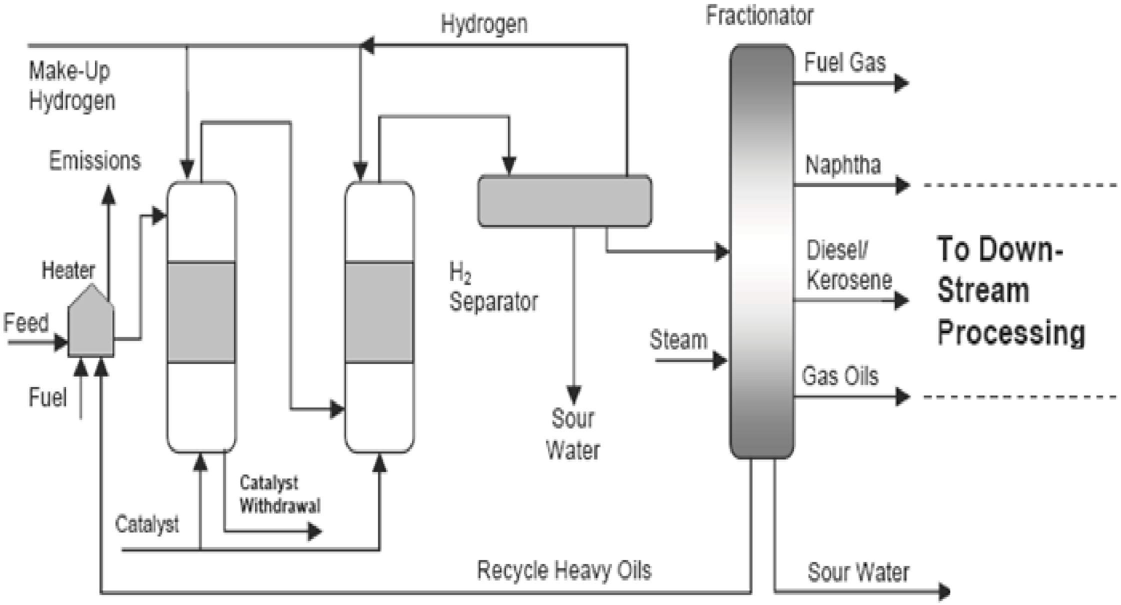

Figure 2.4. Hydrocracker Unit Flow Diagram (ODE 2007)

2.2.4 Catalytic Reforming (CR)

Catalytic reforming is employed to increase the octane rating of naphtha and heavy, straight-run gasoline produced by atmospheric crude oil distillation, see Figure 2.5. In addition to reformate, the process produces significant yields of aromatic hydrocarbons, used as petrochemical feedstocks, and hydrogen gas, used in many other refinery processes. Catalytic reforming process restructures hydrocarbon molecules to the desired molecular configuration or structure without altering the number of carbon atoms in the molecule. There are four major reactions take place in during reforming, namely; dehydrogenation of napthenes to form aromatic compounds, isomerization of paraffins and naphthenes, dehydrocyclization of paraffins to aromatic compounds, and hydrocracking (Little, 1985; Antos, 1995; Gary, 2001; Meyers 2004).

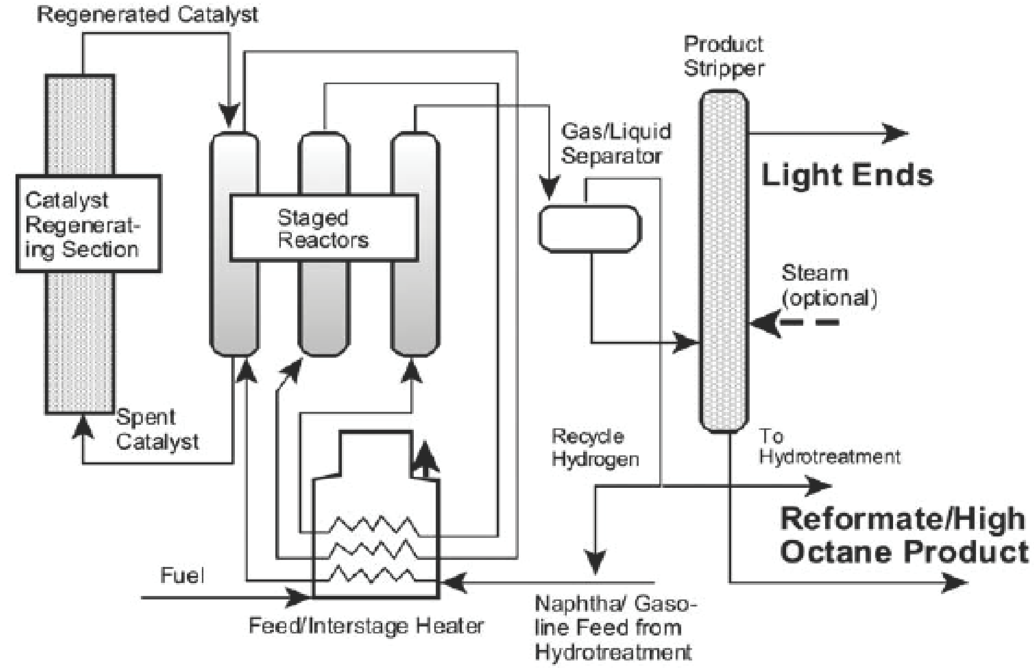

Figure 2.5. Catalytic Reforming Unit Flow Diagram (ODE 2007)

2.2.5 Hydrotreating Processes (Treatment)

Hydrotreating processes are used to remove impurities such as sulfur, nitrogen, oxygen, and metals from petroleum fractions, see Figure 2.6. Usually hydrotreating units are placed ahead of processing units using catalyst, so that the catalyst is not contaminated by untreated feedstock, such as FCC, HC, and CR. The use of hydrotreating process is improving economics of conversion processes by lowering sulfur content. The main hydrotreating process variables affecting the treatment process are the reaction temperature, hydrogen partial pressure, and space velocity. Hydrogen is added to the feed to improve product yields and quality in conversion units. The amount of hydrogen required by the hydrotreating unit to reach the desired objective must be considered in early stage. It would be necessary to have a hydrogen balance for the refinery to know how much hydrogen maybe available for the addition. It might be end with a need for extra source of hydrogen, and this raise the need of appropriate hydrogen management (Maples, 1993; Gary, 2001; Meyers 2004).

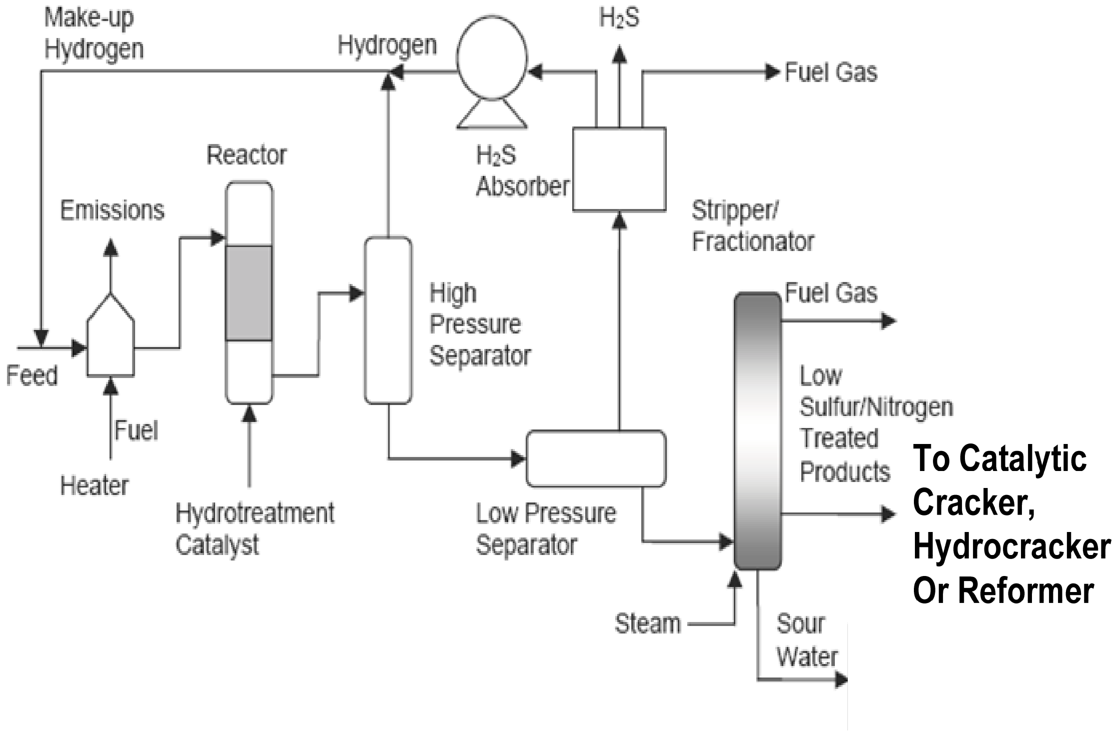

Figure 2.6. Catalytic Hydrotreating Unit Flow Diagram (ODE 2007)

2.3 Overview of Refinery Hydrogen Management

Refineries are being forced to increase their use of conversion units because the increased market for heavy crude oils requires the use of such units for hydrocracking, which is required to upgrade the heavy crude to more valuable products. In addition, the hydrotreating processes used by refineries must be more effective due to the promulgation of increasingly stringent air emissions regulations that require reductions in the amount of sulfur in fuel products, such as ultra low-sulfur (ULS) gasoline and diesel fuel. Among all the processes in a refinery, hydrocrackers and hydrotreaters consume the most hydrogen. At the same time that oil refineries are being required to use increasingly large quantities of hydrogen, stricter environmental regulations on the product specifications of low-aromatic gasoline have resulted in decreased hydrogen production by catalytic reformers, which are major sources of hydrogen for the refining industry, thereby lowering the overall availability of hydrogen in the refinery. As a result, it has been necessary for the petroleum refining industry to seek innovative approaches for dealing with the hydrogen balance issue. Also, the assistance of many technical consultants has been sought to develop strategies for increasing the availability of hydrogen or reducing its consumption (Ratan and Vales 2002, Hofer *et al.* 2004, Davis and Patel 2004, Girardin *et al.* 2006).

Therefore, in oil refineries, hydrogen management is vitally important in meeting production requirements while simultaneously complying with environmental regulations. The hydrogen network in the refinery consists of three elements: hydrogen sources, mainly the hydrogen plant and catalytic reformers; hydrogen sinks, e.g., hydrotreating and hydrocracking processes; and hydrogen recovery methods or purification units. The interactions between these three elements define the performance of the hydrogen network in the refinery. Once the hydrogen network is defined in a refinery, an effective and optimized hydrogen management plan for the overall refinery should be established. A general overview on the hydrogen network elements are presented in detail from an integrated perspective.

2.3.1 Hydrogen sources

While the primary sources of hydrogen in the refinery are hydrogen plants and catalytic reformers, the off gases from hydroprocessing units can be a secondary source if the hydrogen in these off gases can be recovered for use rather than sending it to the fuel system of the refinery. Many recent studies have addressed approaches for using the refinery fuel gas as a source of hydrogen (Oh *et al.* 2002, Grover and Zanno 2007).

2.3.1.1 Catalytic reformer

Hydrogen yields are primarily a function of the properties of the feed naphtha, severity, catalyst and operating pressure. A number of methods are available to increase the hydrogen production of the catalytic reformer. Also, hydrogen yields can be improved by changing the naphtha feed, by decreasing pressure, or by replacing the catalyst charge with one that can provide a higher hydrogen yield. In general, the design of the catalytic reformer unit is determined by overall refinery economics, the gasoline pool, rather than the need for hydrogen (Wier *et al.* 1998, Beshears 2000).

2.3.1.2 Hydrogen plant

Hydrogen plants produce hydrogen primarily with steam reforming and water gas shift reaction, see Figure 2.7. The steam-to-carbon ratio is a critical operating variable that affects conversion and coking. A number of approaches exist to revamp hydrogen plants to achieve higher capacities, and increases of up to 25% are common (Fleshman 2001, Kruse *et al.* 2002).

2.3.2 Hydrogen Sinks

Hydrotreaters and hydrocrackers are the major consumers of hydrogen in refinery, where hydrogen used in a series of reactions that convert organic sulfur compounds and nitrogen compounds to hydrogen sulfide and ammonia. Hydrocracking reactions convert heavier oils to diesel fuel and naphtha. All of these reactions increase the products’ value and contribute to the refinery’s gross margin (Pacheco and Dassori 2002, Turner and Reisdorf 2004).

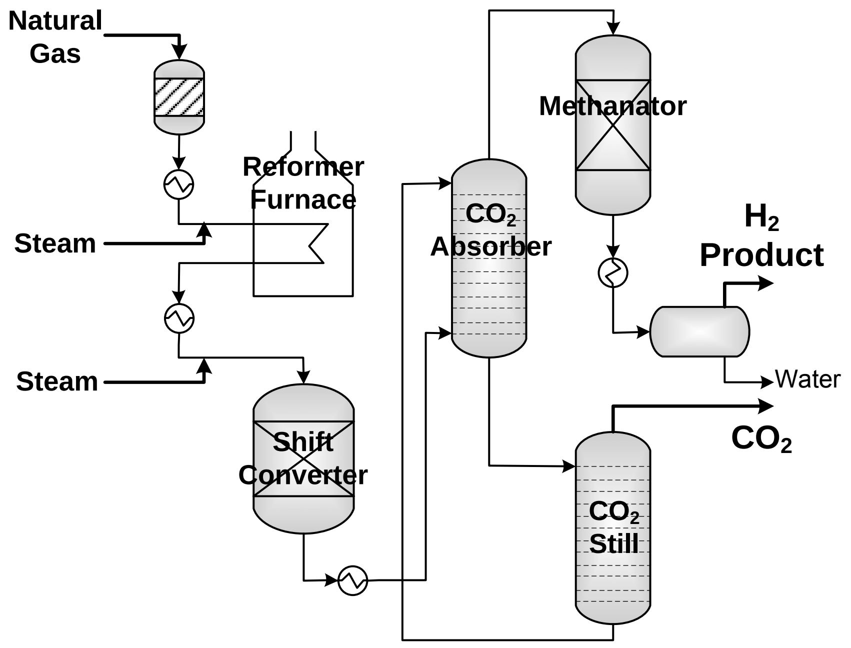

Figure 2.7. Steam-Methane Reforming Hydrogen Unit Flow Diagram

The partial pressure of hydrogen drives these reactions and suppresses unwanted coke formation. A minimum partial pressure, usually determined by measuring purity of reactor inlet stream or recycle gas purity, is required to operate with a reasonable catalyst life and reactor temperature. Makeup stream purity is often confused with the partial pressure of hydrogen. For a given set of operating conditions, the partial pressure of hydrogen is determined by the combination of makeup stream purity and purge flow. It is possible to adjust the partial pressure without modifying makeup stream purity. Conversely, it is possible to utilize a different makeup stream, with a different purity, and maintain the same partial pressure of hydrogen.

To maximize the profitability of these units, one must have a good understanding of process characteristics and refinery economics. Detailed process models that reflect the performance of the units as a function of the partial pressure of hydrogen are required.

2.3.3 Hydrogen Recovery

Many refinery streams that contain hydrogen, such as hydrotreater off gases or excess hydrogen streams are sent to fuel gas or hydrogen plant feed. The recover of the hydrogen in these streams in particular is powerfully beneficial for the refinery, because the cost of hydrogen recovery can be as low as 50% of the cost of producing hydrogen. Generally, the economic feasibility of recovering hydrogen from various streams in the refinery will be the determining factor.

2.3.3.1 Purification technology

The stream purity of the hydrogen available to consumer units can have a significant effect on the design and operation of the consuming units, which are generally hydro-processing units. The three main hydrogen purification technologies used in refineries are pressure-swing adsorption (PSA), selective permeation using polymer membranes, and cryogenic separation. Each of these processes is based on a different separation principle, and, consequently, the process characteristics differ significantly (Whysall and Picioccio 1999, Peramanu *et al.*1999). Selecting the appropriate technology for hydrogen purification depends on economics and on other project considerations, such as process flexibility, reliability, and ease of future expansion.

PSA units for hydrogen purification are based on the ability of adsorbents to adsorb more impurities at high gas-phase partial pressures than at low partial pressures. This process has been in commercial operation since 1966 for various refinery and petrochemical applications worldwide, see Figure 2.8. Impurities are adsorbed in an adsorber at high partial pressure and then desorbed at low partial pressure. The partial pressures of impurities are lowered by varying the adsorber pressure from the feed pressure to the tail-gas pressure and by using a high-purity purge gas. High-purity hydrogen is recovered at high pressure, multiple absorbers are used to provide constant product and tail-gas flows. Commercial units normally use between four and twelve absorbers (Malek *et al.* 1998, Picioccio and Reyes 2000, Sircar and Golden 2000). Table 2.1 summarizes the performance criteria and operational requirements for the PSA technology.

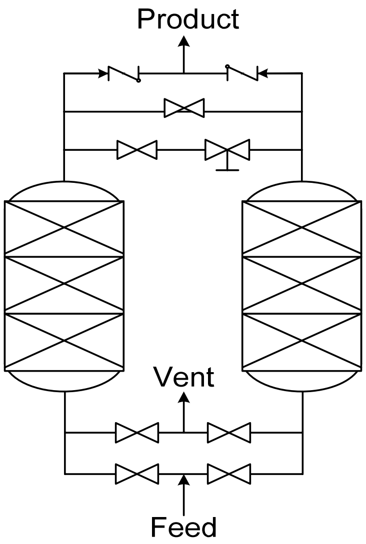

Figure 2.8. PSA Unit Flow Diagram (Ruthven 1994)

Table 2.1. Process and Operational Considerations for PSA Process

Process Factors		**Operational Factors**	
Minimum feed H_2,%	50	Feed pretreatment	No
Feed pressure, psig	150-1,000	Flexibility	Very high
H_2 purity, %	99,9+	Reliability	High
H_2 recovery, %	Up to 90	By-product recovery	No
CO + CO_2 removal	Yes	Ease of expansion	Average
H_2 product pressure	Approximately feed		

2.3.3.2 Compressors

The pressure of recovered hydrogen streams must be equal to or higher than the sink pressure in order to maintain the specified pressure within the hydrogen sink. This means that low-pressure source streams, which are to be sent to a sink with higher pressure, must be compressed to the required sink pressure. The pressure drop associated with the hydrogen recovery methods must be considered when determining the pressure of the recovered hydrogen. In the case of a PSA unit, the pressure drop is relatively low (i.e., approximately 10 psig).

2.4 Overview of Refinery CO_2 Management

CO_2 emissions in refineries are dominated by the emissions resulting from burning of fuel in fired heaters and in utility boilers. In general, the refinery CO_2 emissions can be modeled through the main three sources of emissions, namely; fuel for process heating, hydrogen production, and coke burning from the FCC regenerator. Therefore, a general overview of the refinery emission sources and the available CO_2 emission mitigation option is illustrated in this section.

2.4.1 Fuel System Emissions

Most of the refineries worldwide consider the fuel system as the largest contributor to the refinery emissions. The nature of the refinery fuel-derived emission will therefore depend on the type of units found and their capacity. Many international agencies carried out emissions test on different fuels to assign an emission factor for each fuel. The fuel emission factor used in this research is the one developed by the United States Environmental Protection Agency (Ritter et al., 2005).

Table 2.2 demonstrates the amount of CO_2 emitted per unit energy (MBTU) for different fuels. The CO_2 emissions will be calculated via multiplying each fuel quantity consumed by processing unit with its relative emission factor. Thus, the emission of CO_2 from a fuel obviously depends on its carbon content.

Table 2.2. Fuel Emission Factor (Ritter et al., 2005)

Fuel	Emission Factor (EF) Ton CO_2/MBTU
Fuel Oil	0.0811
Crude Oil	0.0741
Diesel	0.0731
Jet Fuel	0.0721
Gasoline Oil	0.0711
Natural Gas	0.0531

2.4.2 Hydrogen Plant Emissions

The pressures on hydrogen availability and consumption are well known and understood, as discussed in the previous section. As the specifications for modern, low-sulfur transportation fuels, require many refineries to produce hydrogen on-site. Although, most refiners were able to avoid this via better hydrogen management, it is expected that there will a dramatic increase in the need for hydrogen and hence further installed hydrogen generation capacity.

Hydrogen management effectively tracks hydrogen within the fuel system and recovers large amount of hydrogen to use it in the refinery as a process stream. However, from a CO_2 emissions standpoint, it is wanted to enrich fuel streams with hydrogen to reduce fuel emissions. Thus, the refinery hydrogen management is raising a conflict on fuel emissions (Ratan and Uffelen, 2008).

In some refineries, it is been found that hydrogen recovery from fuel gas to avoid hydrogen production via hydrogen plant is beneficial from a CO_2 production standpoint. This can be clarified through comparing the CO_2 emissions on an energy equivalent basis. Burning 1 MW of natural gas will release 198 kg/hr of CO_2, while burning 1 MW of hydrogen will emit 0 kg/hr. However, if this hydrogen came from a hydrogen plant, then it would have emitted 286 kg/hr of CO_2 in producing it (Clarke, 2001).

Hydrogen production is often a large source of CO_2 emissions on a refinery and this makes the hydrogen-production plant a prime target for carbon sequestration, which will be discussed in more detailed. This is significant, as the emissions from a hydrogen plant can therefore be lowered via CO_2 capture from the process, which is considerably easier and cheaper than recovery from flue gas.

2.4.3 FCC Unit Emissions

The catalytic cracking unit is one of largest non-fuel-derived source of CO_2 within the refinery. The catalytic cracker rejects a quantity of carbon in the form of coke, as CO_2 is emitted from the regenerator as the coke is burnt off the catalyst. Usually, the FCC regenerator is responsible for 15-20% of the refinery CO_2 emissions (Mertens et al., 2006).

In addition, revamping FCC units to take heavier feedstocks, thereby allowing a portion of atmospheric residue in the feed, and deep catalytic cracking (DCC) for maximum light olefins production is another emerging trend. All these options are increasing CO_2 emission from the unit.

Accordingly, FCC must be viewed as a CO_2 emitter and to reduce the emissions step must be taken through process changes, namely; coke (concarbon) management, capacity management, and alternative processes (Mertens et al., 2006; Stockle et al., 2008).

Coke management involves in minimizing coke yield while maintaining the product slate. Capacity management can take two forms: 1) reduce unit capacity, which will reduce emissions from the refinery, 2) separate out feedstocks into high coke and low coke yields, and running the unit in blocked operation mode. Hydrocracking processes are the alternative processes to catalytic cracking processes. A hydrocracking process has lower emissions than a catalytic cracking process. However, it is important to remember the required amount of hydrogen for hydrocracking process, and the resulted CO_2 produced.

The emission reduction effectiveness is varying from one option to another. Concarbon management has the potential to lower refinery emissions by up to 6%, capacity management by up to 20%, and alternative processing by up to 25%. The results show the sort of decisions the refiner might have to take in the future in order to lower CO_2 emissions (Moore, 2005). On the other hand, for effective (high) emissions reduction, capturing process can be the solution, although this solution shifts the economics to some extent. However, it should be kept in mind that this could obviously capture most of the emitted CO_2.

2.4.4 Capturing Processes

The idea of separating CO_2 from flue gas streams started in the 1970s, not with concern about the greenhouse effect, but as a potentially economic source of CO_2, mainly for enhanced oil recovery (EOR) operations. The capture processes of CO_2 emission are technologies that remove carbon dioxide from flue gases. Usually through contact with some chemical solvent, most commercially available processes are amine-based. Figure 2.9 illustrates wide ranges of technologies currently exist for separation and capture of CO_2 from gas streams (Rao and Rubin, 2002).

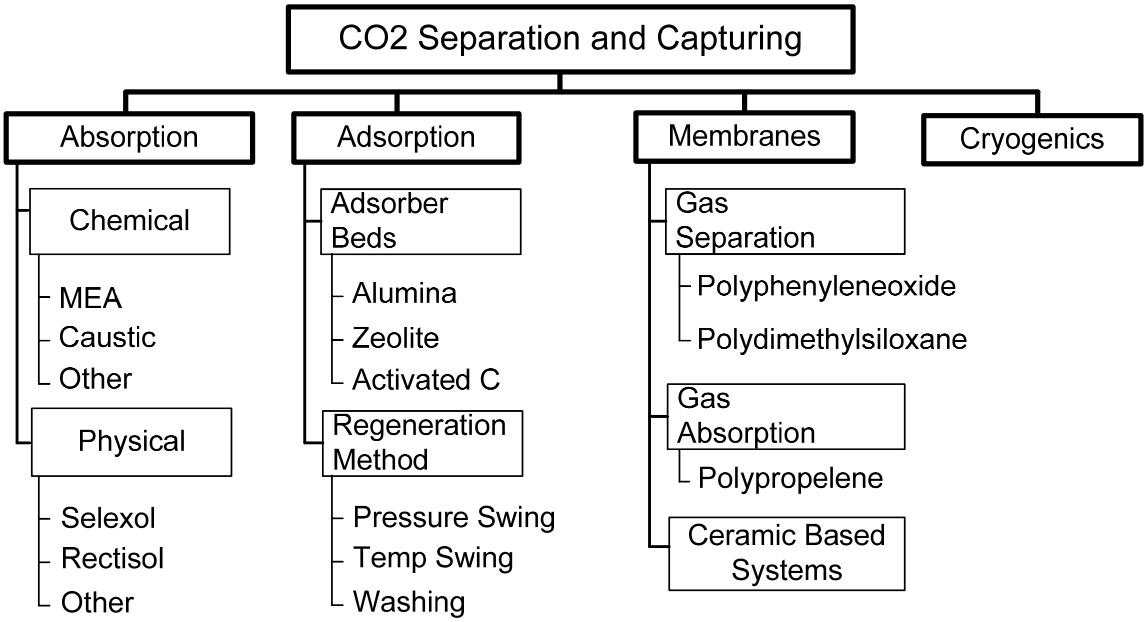

Figure 2.9. Technology Option for CO2 Separation and Capturing (Rao and Rubin, 2002)

Most of the commercial capturing plants capture CO_2 with processes based on chemical absorption using a monoethanolamine (MEA) - based solvent. MEA is an organic chemical belonging to the family of compounds known as amines. It was developed over 60 years ago as a general, nonselective solvent to remove acidic gas impurities from natural gas streams. The process was then adapted to treat flue gas streams for CO_2 capture (Romeo *et al.*, 2008). MAE processes typically involve some form of contacting vessel where the flue gas is contacted with the solvent, and a solvent regenerator, usually thermal in nature. A continuous scrubbing system is used to separate CO_2 from the flue gas stream. As demonstrated in Figure 2.10, the system consists of two main elements: an absorber where CO_2 is removed and a regenerator, where CO_2 is released and the original solvent is recovered.

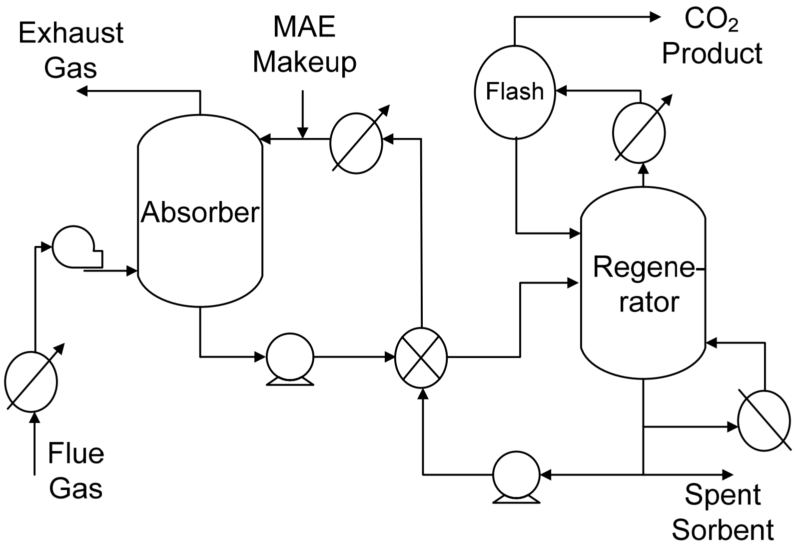

Figure 2.10. Flowsheet of MAE Process (Romeo et al., 2008)

One of the disadvantages of the capturing processes in a refinery is that they work best on large single emissions. For example, capturing process works very well in power industrial sectors. In refinery, process-drive emissions are considered as a large-scale emission source, for example hydrogen plant. Capturing technology can reduce the emissions by 70-90%, although there is an issue with utility use, based on the process efficiency (Creek, 2004).

2.5 Literature Review

This section will cover the previous studies done on the three subjects under study in this research.

2.5.1 Refinery Planning Problem

Production planning is the discipline related to allocation of production capacity and production time (with less emphasis on the latter); raw materials, intermediate products, and final products inventories; as well as labor and energy resources. Its primary objective is to determine a feasible operating plan consisting of production goals that optimizes a suitable economic criterion, typically of maximizing total profit (or equivalently, of minimizing total costs). This plan is over a specific extended period of time into the future, typically in the order of a few months to a few years, given marketing forecasts for prices, market demands for products, and considerations of equipment availability and inventories (Birewar and Grossmann, 1995). In essence, its fundamental function is to develop a good set of operating goals for the future period. In the present settings of the oil and gas or hydrocarbon industry, planning requirements have become increasingly difficult and demanding arising from the need to produce more varied, higher-quality products while simultaneously meeting increasingly tighter environmental legislations and policies as reported by Fisher and Zellhart (Bodington, 1995).

As was mentioned in the previous section, oil refinery is one of the most complex chemical industries involving different processes with various possible connections. The aim in refinery operation is to generate as much profit as possible by converting crude oils into valuable products. Mathematical programming or optimization has become indispensable tools to realize this goal. Linear programming (LP) is the most widely used technique in refinery operation optimization, which is called planning and scheduling in industry. The goal in planning is to determine high-level decisions such as production levels and product inventories for given marketing demands.

Linear programming is an approach to the solution of a particular class of optimization problems. It is concerned with finding values for a set of variables which maximize or minimize a linear objective function of the variables, subject to a set of linear inequality constraints. Linear programming was first proposed by Dantzig in 1947 (Edgar, 2001) to refer to the optimization problems in which both the objective function and the constraints are linear. LP problems exhibit the special characteristic that the optimal solution of the problem must lay on some constraints or at the intersection of several constraints.

Despite the many contributions that have been reported on planning models, very few can be found that specifically address the petroleum refining industry. Symonds (1956) developed an LP model for solving a simplified gasoline refining and blending problem. The advantage of LP is its quick convergence and ease of implementation. Allen (1971) presented in his paper an LP model for a simple refinery that consists mainly of three units; distillation, cracking and blending.

One of the first contributions to consider nonlinearity in production planning is that of Moro et al. (1998). The main objective of their study was to develop a nonlinear planning model for refinery production. The model is able to represent a general refinery topology and a real world application is developed for the planning of diesel production in the refineries. The model is solved and the results are compared to the actual data where no computer algorithm is being used. Pinto and Moro (2000) developed also a nonlinear planning model for refinery production. The described model represents a general petroleum refinery and its framework allows for the implementation of nonlinear process models as well as blending relations. This model assumes the existence of several processing units, producing a variety of intermediate streams, with different properties, that can be blended to constitute the desired kinds of products. However, the model was based on two assumptions; (1) the nonlinearity represent the deviation from the linear yield vector; and (2) that many of the refinery processes are linear. These two assumptions affect the overall predictability of the model.

Pinto et al. (2000) discussed planning and scheduling application for oil refinery operations. They presented a nonlinear planning model in the first part similar to the one developed earlier by Moro et al. (1998). In the second part, they addressed scheduling problems in oil refineries that are formulated as mixed integer optimization models and rely on both continuous and discrete time representations. The paper considered the development and solution of optimization models for short term scheduling of a set of operations including products received from processing units, storage and inventory management in intermediate tanks, blending in order to attend oil specifications and demands, and transport sequencing in oil pipelines. Important real-world examples on refinery production and distribution are reported. The diesel distribution problem at one refinery in Brazil and the production problems related to fuel oil, asphalt and LPG were considered.

Zhang and Zhu (2000) showed in their paper a novel decomposition strategy to tackle large scale overall refinery optimization problems. The approach is derived from an analysis of the mathematical structure of a general overall plant model. This understanding forms the basis for decomposing the model into two levels. These levels are a site level (master model) and a process model (submodels). The master model determines common issues among the processes. Then, submodels optimize individual processes. The results from these submodels are fed back to the master model for further optimization. Zhang et al. (2001) studied a simultaneous optimization strategy for overall integration in refinery planning. They presented a method for overall refinery optimization through integration of the hydrogen network and the utility system with the material processing system. To make the problem of overall optimization solvable, the current practice adopts a decomposition approach, in which material processing is optimized first using linear programming (LP) techniques to maximize the overall profit. Then, supporting systems, including the hydrogen network and the utility system, are optimized to reduce operating costs for the fixed process conditions determined from the LP optimization.

Recently, Li et al. (2005) conducted a study on integrating crude distillation, FCC and product blending modules into refinery planning models. They presented a refinery planning model utilizing simplified empirical nonlinear process models with considerations for crude characteristics, products yields and qualities. Neiro and pinto (2005) studied multi-period optimization for production planning of petroleum refineries. The given model is based on a nonlinear programming formulation that was developed to plan production over a single period of time. Uncertainties related to petroleum and product prices as well as demand is then included as a set of discrete probabilities.

From the previous discussion, the need is clear to have an efficient refinery planning model with more accurate outcome for the petroleum refinery decision maker. The model should be capable to deal with different types of crudes without major changes in the model. Also, the model should represent refinery operation planning in order to optimize the operating variable in individual processing units. The most important operating variable will be the CDU cut points which will affect the products flow rates and properties for all the streams in the refinery as well as the conversion in the other processing units. The model should also meet market demand with quality constraints for each final blended product. Nonlinear rigorous unit models will be used rather than the linear models which are based on yield vectors. A general model will embed the different rigorous refinery process models and the blending model. Products properties as well as market demand will be taken into account.

2.5.2 Optimization of Refinery Hydrogen Problem

In the refinery business, hydrogen is viewed as a utility that must be available to operate, much like other utilities such as electricity and water. However, in this research, the development and implementation of a good overall management policy for the hydrogen needed and available in the refinery will allow the handling of hydrogen as an asset for the refinery. Most of the publications about refinery hydrogen have been focused on individual hydrogen production and/or consuming units rather on the overall hydrogen system in the refinery.

A lot of work has been performed in the past in the area of hydrogen purification systems. There are many methods of purification systems in oil refineries, such as pressure-swing adsorption (PSA), membrane separation, cryogenic separation, and liquid absorption. For example, Whysall and Picioccio (1999) explained the commonly used purification methods in a refinery and presented criteria for selection and revamping of each of them, and Peramanu *et al.* (1999) determined the options that were economically and technically suitable for pressure-swing adsorption, membranes, and countercurrent gas-liquid contacting.

All this research is important, and it has improved the refinery hydrogen system by modifying individual refinery processes and units. However, the whole refinery hydrogen system should be integrated in order to achieve more improvements. The first study of the refinery hydrogen system was done by Towler *et al.* (1996). Towler analyzed the hydrogen network from an economic point of view, and he compared the cost of recovering hydrogen and the value added by hydrogen in refinery processes. The pinch technique was applied, and the driving force to recover hydrogen was economics. However, the physical constraints that manipulate the network were not taken into account. The study nevertheless gave a great indication for researchers to consider the whole network of the refinery hydrogen system.

Alves and Towler (2002) gave an excellent analysis of the hydrogen distribution system in a refinery. Alves identified the sources and sinks of hydrogen and proposed a systematic method for setting the target for the minimum supply of fresh hydrogen to a hydrogen distribution system that was independent of the design of the distribution system. Unfortunately, Alves' study did not take into account the pressure constraint, which is a significant concern in the refinery hydrogen network.

Hallale and Liu (2001) introduced an efficient mathematical method for refineries to optimize a refinery hydrogen network to maximize the amount of hydrogen recovered throughout the refinery. It is proposed here to improve upon the Hallale model to take care of these considerations. In addition, the hydrogen management model will be integrated within the refinery-planning model of the previous work.

Zagoria *et al.* (1999) discussed the hydrogen network and the possibility of dealing with sink streams purity as an optimization variable rather than fixing it to a specific value. They proposed that increasing the partial pressure of hydrogen in consuming processes has great impact on profitability due to the associated effect on throughput, product quality, and catalyst life. Zhang *et al.* (2001) studied a simultaneous optimization for overall integration of the hydrogen network, the utility system, and the material processing system in a refinery. Zhang and his colleagues used a linear programming (LP) model to represent the network, which prevented them from exploring the discrete components of the hydrogen network.

Hallale *et al.* (2002) treated hydrogen as an asset rather than a liability and used pinch technology and mathematical programming to account for the physical constraints in the network. Liu and Zhang (2004) proposed a systematic methodology for selecting appropriate purifier technology for the hydrogen network in the refinery and considered operating and capital costs in order to evaluate economic trade-offs.

From the previous discussion, it is apparent that there is a need for an efficient, integrated, refinery-planning model for products and the hydrogen network. It is imperative that the model provides for meeting production objectives and incorporates a proper hydrogen management strategy. The model must represent refinery operation planning in such a way as to optimize the operating variables in individual processing units as well as to optimize hydrogen requirements. The model should also account for the installation of new equipment, such as purification units or compressors. The hydrogen network model must include models of the purification unit, compressor, hydrogen requirements of the processing units, and the economic aspects of each process component. Therefore, it is a main aim of this research to propose a general model that embeds the different rigorous nonlinear refinery process models and the hydrogen model, allowing product quality and market demand to be taken into account.

2.5.3 Optimization of Refinery CO_2 Problem

Several researches have been developed in GHG emissions reduction and CO_2 emissions in particular. Most of these researches are in the power generation industries followed by transportation sector and fuel consumption. In the last five years, the petroleum refining industry has a considerable attention, although it is not a major contributor in the global CO_2 emissions.

There are a few academic researches done on the CO_2 emissions problem in petroleum refinery. Therefore, the literature review will be divided into two parts, academic and industrial.

In academic research, many researchers studied the allocation of the refinery CO_2 emissions (Babusiaux, 2003; Babusiaux and Pierru, 2007; Tehrani, 2007a; Tehrani, 2007b), were they investigate the CO_2 emissions related to the oil refinery inputs and outputs. However, they did not study the amount produced by the refinery processing units. The first work done on the CO_2 reduction in petroleum refinery was by Bashammakh (2007). In their work, they studied the refinery strategies to meet certain CO_2 reduction target, and the associated actions and cost with each strategy selected. However, they only considered the fuel firing emissions and did not include the process-derived emissions, which may not adequately reflect the full picture of CO_2 emissions in refinery.

In the industrial side, the major oil consulting companies are deriving the CO_2 reduction research in the petroleum refining industry. Greek (2004) emphasized the importance of the pre-combustion and gasification solutions to reduce refinery CO_2 emissions and claimed that capturing processes will be an expensive option for the refiner to choose. Moore (2005) explained the possible areas of CO_2 reduction in refinery, namely; fuel switching, utility systems and hydrogen plant. Moore suggested an approach to refinery CO_2 reduction including utilities management, fuel gas optimization, energy integration, and hydrogen management. Ritter et al. (2005) proposed a systematic methodology for estimating CO_2 emissions in oil-and-gas industry. Stockle et al. (2008) clarified the best way for optimizing refinery CO_2 emissions. Stockle highlighted three main emission sources, namely; fuel, hydrogen production, and FCC coke. Ratan and Uffelen (2008) studied the hydrogen plant process and find out that with appropriate improvements the refinery CO_2 emissions can be reduced by 45%. Nevertheless, the industrial research gives a great idea about the CO2 emission in petroleum refinery, but lack to give a mathematical model that represents the CO2 management in refinery.

All these research are assuring that the refining industry is facing new challenges, and the cost of carbon emissions should be considered when establishing the optimum operation for a refinery. However, the integration of CO_2 management problem within refinery planning and hydrogen management was not properly addressed. This research is aiming to propose a mathematical model to solve the CO_2 emission problem in refinery. The model will include refinery hydrogen management and all other CO_2 emission sources. The strategy is to build an MINLP model that incorporates the mitigation alternatives efficiency and cost. The integrated model can have different objective functions according to refiner needs, such as economic, operation, and production objectives.

CHAPTER 3

MATHEMATICAL MODEL FOR REFINERY PLANNING

3.1 Introduction

This chapter focuses on the development of models for the refinery processing units under study. These models are then integrated with blending correlations in order to provide a complete refinery planning tool.

The objective of the planning model is to maximize the profit from selling the final products with specific properties constraints.

This chapter is organized as follows. In the next section, problem statement of the petroleum refinery planning problem is presented, and provides the equivalent mathematical formulation that will allow solving the planning problem in this study. In section 3.3, an NLP planning model is presented through embedding the different rigorous refinery process models and the blending correlations. In section 3.4, different case studies will be provided to illustrate the petroleum refinery planning model. This chapter ends with concluding remarks.

The refinery processing units' models and the blending correlations are explained in more details in appendix A and B, respectively.

3.2 Problem Statement

A Petroleum refinery is an extremely complex entity. The profitable operation of a refinery, therefore, requires the optimization of different intermediate and final products in addition to process feeds. Several trends in the oil refinery industry are also leading to a tight production of deferent products with the new more stringent specifications. A rigorous model of refinery operations which can capture the different refinery feed characteristics and which mimics the different refinery stages more accurately is attempted in this chapter.

We consider an oil refinery that consists of several processing units, splitters, and mixers. The final refinery products $V_{i,s}$, i={refinery processing units} and s={streams}, have to meet market demand and specification. The processing units have operating variables $XU_{i,x}$, x ={operating variables} that affect the products flow rates and properties. Splitters and mixers connect the different processing units. The overall objective is to maximize the refinery profit by adjusting the flow rates of different streams, intermediates or final products, as well as the operating variables for the processing units.

The refinery planning problem to be addressed in this chapter can be stated as follows, "*what is the best operating condition, production capacity, and blending strategy for a refinery to follow, in order to meet a given product demand and specifications ?*"

The mathematical statement of the problem statement above consists of maximizing an objective function while observing equality and inequality constraints. The problem is modeled mathematically and can be written as the following NLP (Non-Linear Programming):

$$\max_{x} f(x) \qquad \text{(Objective function)}$$

such that,

$$h(x) = 0 \qquad \text{(Equality constraints)}$$

$$g(x) \leq 0 \qquad \text{(Inequality constraints)}$$

$$x \in X \leq R^{n} \qquad (x \text{ is a vector of continuous variables})$$

Variables

Continuous variables, x, are real numbers that may represent streams flow rate from processing units, streams properties, and operating conditions.

Objective Function

In this chapter, the objective is to maximize the overall refinery profit. $f(x)$ is an objective function which represents the profit including revenues from selling the final products subtracted from it the operating cost of each unit and the raw material cost.

Constraints

- $h(x) = 0$, are the equality constraints which correspond to balance equations.
  a) Mass balance constraints: the material balance over a processing unit and at the blending area.
  b) Streams properties constraints: the properties of the blended streams as intermediate for further processing or as final products.
- $g(x) \leq 0$ are the inequality constraints which correspond to design specifications, restrictions, feasibility constraints.
  a) Market demand constraints: the minimum quantity required by market for different final products.
  b) Products specifications constraints: the upper and lower product properties specifications.
  c) Processing unit constraints: the properties of the feed, operating variables, and the capacity of the processing unit.

3.3 Model Formulation

In this section, the mathematical models were developed to represent the refinery processing units operation. The model consists of an objective function and a system of equalities and inequalities describing the performance of each processing unit.

An individual nonlinear mathematical model is developed for each unit in the refinery prior to the development of a planning model, the connections between the streams, and the blending pool, see Figure 3.1. The processing units in this study are modeled using nonlinear regression correlations. The correlations are developed for: crude distillation unit (CDU), naphtha hydrotreaters (NHT), diesel hydrotreaters (DHT), gasoil hydrotreaters (GOHT), residue hydrotreaters (RHT), naphtha reformer (CR), fluid catalytic cracking (FCC), and hydrocracker (HC). Our final aim is to provide methods of determining optimal operational plans for a petroleum refinery including the fractions cut points of the CDU and the severity or conversion of the processing units. The most important variables in operational planning models are the processing units operating variables, feed flow rates, feed properties, products flow rates, and products properties.

Objective Function

The mathematical formulation and representation in this study is written in a general way, so it can compile with any defined objective, and new/modified constraints. The objective function for this section will be the maximization of the total profit of the refinery, i.e.

$$\text{Maximize} \qquad \sum_{i \in B} sp_i \; F_i \; - \sum_{i \in E} ce_i \; F_i \; - \; \sum_{i \in I} cx_i \; F_i \tag{3.1}$$

Equation (3.1) expresses the overall refinery profit as revenues from selling all products, subtracting costs of purchasing feedstock and costs of operating process units in the refinery. B represents the set of blending units for the final products and their sales price (sp_i). The cost (ce_i) of the feedstock purchased from external sources defined under the set (E) for all the units that receive such material from outside. Finally, there is an operating cost (cx_i) for each processing unit (i) in the refinery where it is usually expressed as a function of the quantity fed to the unit.

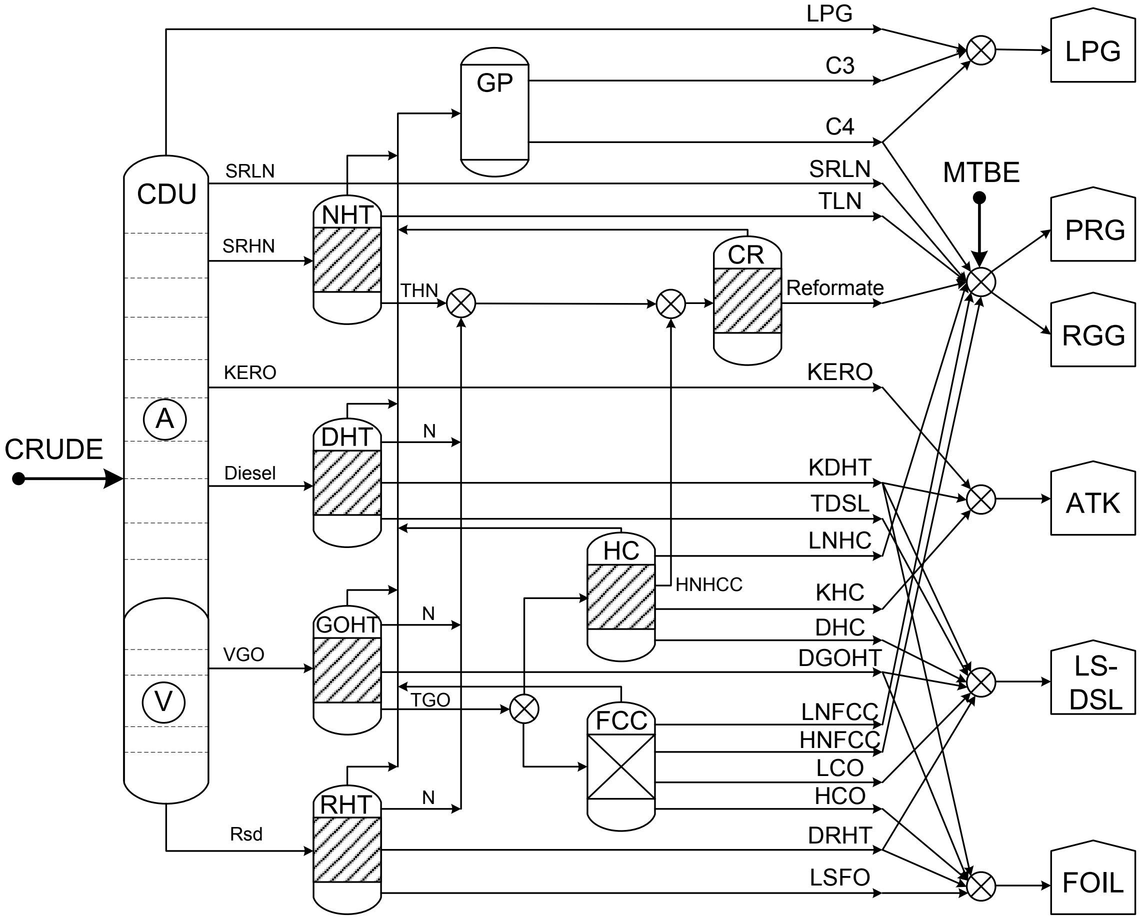

Figure 3.1. Refinery Flowchart

3.3.1 General Model

A generic processing unit drawing is shown in Figure 3.2 to illustrate the mathematical representation. The general mathematical model consists of the following sets of constraints:

Feed flow rate of processing units:

$$F_i = \sum_{j \in J} \sum_{s \in N} VS_{j,s,i} \qquad \forall i \in I \qquad (3.2)$$

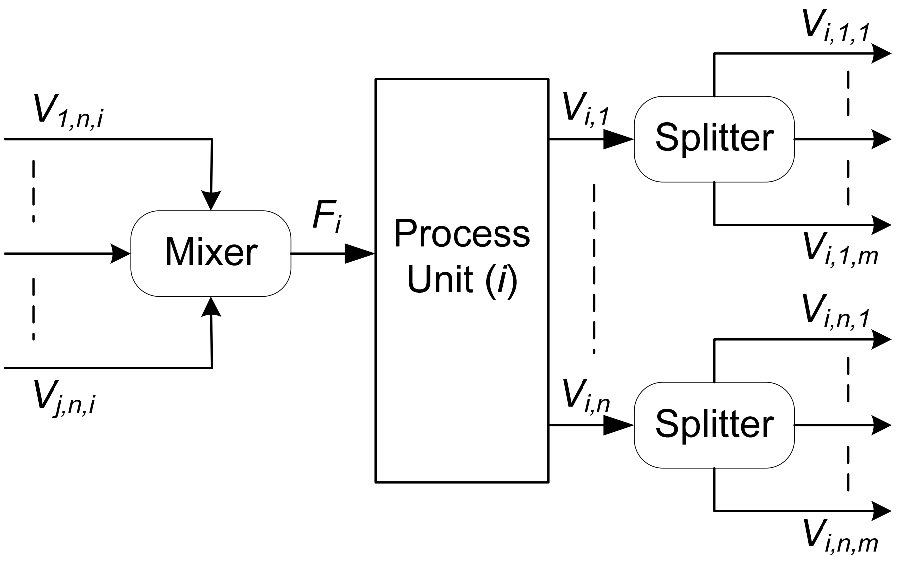

Figure 3.2. General Processing Unit Model

The feed F_i for any processing unit ($i \in I$, I is the defined set of all the units in the refinery) is the summation of all flow rates $VS_{j,s,i}$ of the possible streams (*s*) that can be received by unit (*i*) from units ($j \in J$), where J is defined as the set of all units that can send streams (*s*) to unit (*i*) and N is defined as the set of all streams (*s*) that can be sent from unit (*j*) to unit (*i*).

Feed properties of processing units:

$$FP_{i,p} = f\left(VS_{j,s,i}\,,\,PV_{j,s,p}\right) \qquad \forall i \in I,\ p \in PF_i \tag{3.3}$$

Properties (*p*) of the feed to unit (*i*) are represented by $FP_{i,p}$ and PF_i is the set of all feed properties to unit (*i*). The properties are functions of the quantities and properties of all streams (*s*) from unit (*j*), $VS_{j,s,i}$, and $PV_{j,s,p}$ respectively. For example, the sulfur weight percent on the catalytic reformer unit feed is written as:

$$FP_{CR,SUL} = \left(\sum_j VS_{j,Naph,CR} * PV_{j,Naph,SUL}\right) \Big/ \ \left(F_{CR} * FP_{CR,SG}\right)$$

Product flow rates of processing units are given as:

$$V_{i,s} = f\left(F_i , FP_{i,p} , XU_{i,x}\right) \qquad \forall\, i \in I , s \in S_i , x \in X \qquad (3.4)$$

The product flow rate from unit (i) for stream (s) is represented by $V_{i,s}$ ($s \in S_i$; S_i is the defined set of all the streams produced from unit i) are functions of the unit (i) feed quantity F_i and property $FP_{i,p}$ as well as the operating variables $XU_{i,x}$ ($x \in X$; X is the defined set of all the operating variables). For example, the light naphtha produced from the fluid catalytic cracking unit is written as:

$$V_{FCC,LN} = F_{FCC} * FP_{FCC,SG} * \left[\sum_{h=0}^{4} (a_h + b_h * FP_{FCC,K}) * XU_{FCC,CONV\,\%} \right]$$

where a_h and b_h are constants.

Products properties of processing units:

$$PV_{i,s,p} = f\left(FP_{i,p} , XU_{i,x}\right) \qquad \forall\, i \in I , s \in S_i , p \in P_i \qquad (3.5)$$

$PV_{i,s,p}$ is the product property (p) for product stream (s) from unit (i) which is a function of unit (i) feed properties $FP_{i,p}$ and the operating variables $XU_{i,x}$. For example, the flash point temperature of the kerosene produced by the hydrocracker unit is written as:

$$PV_{HC,Kero,FLSH} = 120 - 4 * \left[\left((FP_{HC,VABP} + 460)\text{^}0.333\right) / FP_{HC,SG} \right] - \left[0.05 * XU_{HC,CONV\,\%} \right]$$

Product splitting:

$$V_{i,s} = \sum_{m \in M} VS_{i,s,m} \qquad \forall\, i \in I , s \in S_i \qquad (3.6)$$

The above equation represents the possibility for each product from unit (i) to be split into many streams either as final product or feed to other processing units. Product stream

(s) from unit (i) is represented by $V_{i,s}$ can be sent to different destinations (m) define by streams $VS_{i,s,m}$ ($m \in$ M; M is defined as the set of all the possible units or final products pool blending that can receive the splitted streams).

Processing unit capacity:

$$F_i \le UC_i \qquad \forall i \in I \tag{3.7}$$

The feed of processing unit (i) cannot exceed its maximum capacity, which is represented by UC_i.

Final products market demand:

$$F_i \ge D_i \qquad \forall i \in B \tag{3.8}$$

The final products flow rate of the blending units must be equal or greater than the market demand D_i.

Equations (3.2) and (3.3) represent the feed quantities and properties of the processing unit models, which play an important role in the products flow rates and properties, as defined by equation (3.4) and (3.5), respectively. Clearly, equations (3.2), (3.6), (3.7) and (3.8) are linear whereas equations (3.3), (3.4) and (3.5) are nonlinear due to mixing.

3.3.2 Processing units Models

The processing units have different operating variables. The aim of the refinery processing unit models is to predict and evaluate feedstocks and operating conditions to plan the refining operations. In this study, simplified nonlinear process correlations are used to predict product yields and properties for every processing unit. Table 3.1 lists the processing units feed and products as well their properties. The operating variables for the different processing units are listed in Table 3.2.

Table 3.1. Processing Units Feed and Product Streams and Properties

Unit	Feed Streams	Feed Properties[1]	Products Streams	Products Properties[1]
CDU	Crude oil	TBP	SRLN	RON, RVP
			SRHN	ARO%,NAPH%, N%
			KERO	FLSH, FRZ
			Diesel	CI, FLSH, N%
			VGO	N%, Metal
			Residue	N%, Metal
CR	Naphtha HT's HNHC	ARO% NAPH%	Reformate	RON RVP
FCC	TGO	VABP K_f	LNFCC	RON, RVP
			HNFCC	RON, RVP
			LCOFCC	CI, FLSH
			HCOFCC	VISCO
HC	TGO	K_f	LNHC	RON, RVP
			HNHC	RON, RVP
			KHC	FLSH, FRZ
			DHC	CI, FLSH
NHT	SRHN	N%	TLN	ARO%, NAPH%
			THN	ARO%, NAPH%
DHT	Diesel	N%	NDHT	ARO%, NAPH%
			KDHT	FLSH, FRZ
			TDiesel	CI, FLSH
GOHT	VGO	N%, Metal	NGOHT	ARO%, NAPH%
			DGOHT	CI, FLSH
			TGO	VABP, AP
RHT	RSD	N%, Metal	NRHT	ARO%, NAPH%
			DRHT	CI, FLSH, VISCO
			LSFO	VISCO

[1] API and S% are required in all streams.

Table 3.2. Operating Variables Used for Predicting Product Yields and Properties

Processing unit	Operating Variable
Crude Distillation (CDU)	Cut-point Temperature
Catalytic Reforming (CR)	Reformate Octane Number
Fluid Catalytic Cracking (FCC)	Conversion
Hydrocracking (HC)	Conversion
Hydrotreating (HT)	Conversion

The detailed mathematical model of all refinery processing units is presented in Appendix A.

3.3.3 Blending Correlations

Refinery products are typically the result of blending several components or streams. The purpose of the blending process is to obtain petroleum products from refined components that meet certain quality specifications. Increased operating flexibility and profits result when refinery operations produce basic intermediate streams that can be blended to produce a variety of on-specification finished products. In this study, several blending properties are included in the general model. Blending indices for each property are used throughout the paper. The method of finding any blending property is via finding the blending indices (*BI*) for each stream by a property equation for a given property (*p*) to be blended and averaged the blending index (*BI*) can be expressed by the following general equation:

$$BI_p = \sum_s PI_{s,p} * wv_{s,p} \qquad \forall p \in P \qquad (3.9)$$

Where BI_p represents the blending index for a property p. PI_s is the property index for the property p of a stream s and $wv_{s,p}$ is either weight or volume fraction depending on the property. The properties covered in this study are given in Appendix B.

3.4 Results and Discussions

In order to illustrate the model of the previous section, different case studies are considered. Figure 3.1 shows a simplified flow diagram for the oil refinery under consideration. First unit is the distillation column unit (CDU), which consists of an atmospheric and vacuum distillation tower. Also, the refinery includes four hydrotreating units; naphtha hydrotreater (NHT), diesel hydrotreater (DHT), gas oil hydrotreater (GOHT), and residue hydrotreater (RHT). Beside the catalytic reforming unit (CR), there are two conversion units; Fluidized Catalytic Cracking (FCC) unit and the hydrocracker (HC) unit. Table 3.3 shows the maximum capacity of processing units.

Table 3.3. Processing Unit Capacity

Processing Unit	Maximum Capacity BBL/D
CDU	100,000
CR	14,000
HC	25,000
FCC	25,000

A single or mixture of crude oils can be charged to the CDU unit. Different fractions are then withdrawn from the unit including straight run light naphtha (SRLN), straight run heavy naphtha (SRHN), kerosene (Kero), diesel, vacuum gas oil (VGO) and residue. The overhead gases are sent directly to a liquefied petroleum gas (LPG) pool.

The hydrotreating is utilized to remove the sulfur from the intermediate streams. The SRLN stream from the top of the distillation column is sent to a gasoline pool for blending. The SRHN stream from the crude distillation unit after being hydrotreated in

NHT unit is fed to a CR. The CR process reforms the molecular structure of the heavy naphtha to increase the percentage of high-octane (for gasoline blending).

The diesel stream from the distillation column, after being hydrotreated in DHT unit, is sent to a low-sulfur diesel (LSDSL) pool. The residue from the bottom of the distillation column is hydrotreated in RHT unit and then directed to fuel oil pool. The VGO stream, after being hydrotreated in GOHT unit, is fed to the FCC unit and the HC unit.

The FCC process converts heavy gas oils into lighter products which are then used as blendstocks for gasoline and diesel fuels. The HC unit is similar to the FCC unit to the extent that this process catalytically cracks the heavy molecules that comprise gas oils by splitting them into smaller molecules which boil in the gasoline, kerosene, and diesel fuel boiling ranges.

The model was implemented in the General Algebraic Modeling System (GAMS) Brooke et al. (1998) and solved with the CONOPT solver (Drud, 1994). Different initial starting points were used and the best solution was retained. The model optimizes all intermediate and final products streams across the oil refinery subject to connectivity, capacity, demand, and quality constraints. These constraints can be easily modified to either include new data or guide the model to acceptable solutions.

3.4.1 Base Case Study

The refinery for this base case study imports crude oil and MTBE to produce five final products. The crude oil feed to the refinery is assumed to be constant with a 100,000 BBL/D Alaska crude oil. The MTBE used for improving the octane number of the gasoline pool (Energy Information Administration, 2006). The refinery has to meet the market demand for different products as well as the product specifications. Table 3.4 and Table 3.5, show the products demand and specifications, respectively. The objective is to maximize the overall refinery revenue while meeting both market demand (in terms of both quantity and quality).

Table 3.4. Products Demand

Final Product	Demand BBL/D
PRG	15,000
RGG	15,000
ATK (Jet Fuel)	15,000
LSDSL	15,000
FOIL	15,000

Table 3.5. Products Specifications

Final Product	Property	Specification requirement
PRG	API	≥ 45.0
	SUL %	≤ 0.05
	RON	≥ 92.0
	RVP, psi	≤ 8.8
	OXG %	≤ 2.2
RGG	API	≥ 45.0
	SUL %	≤ 0.05
	RON	≥ 89.0
	RVP, psi	≤ 8.8
	OXG %	≤ 2.2
ATK	API	≤ 37.0
	SUL %	≤ 0.30
	FLSH, °F	≥ 130
	FRZ, °F	≤ -40
LSDSL	API	≥ 35.0
	SUL %	≤ 0.05
	CI	≥ 45
	FLSH, °F	≥ 100
FOIL	API	≥ 10
	SUL %	≤ 1.0
	VISC, cSt	≤ 350

A summary of each blending pool final product stream flow rates and properties is given in Table 3.6. The table shows the solution of the base case study. The optimization procedure leads to the production of profitable products and to meeting all product demands and quality restrictions. The intermediate products were blended first in order to meet the model constraints and to maximize the overall refinery profit. For example, the intermediate streams are sent to a less profitable blending pool rather than profitable ones. Also, the distillate produced by the diesel hydrotreater (KDHT) is chosen to be blended with the fuel oil pool rather than kerosene or diesel, the reason for this is the property specification limitation on the fuel oil viscosity. On the other hand, when the quality constraints are met, the model opts to send the streams to the profitable pool. For example, in the case of DGOHT and DRHT (5100 and 1320 BBL/D respectively), the model recommends sending these streams to the LSDSL pool instead of the fuel oil pool.

3.4.2 Maximum products Case Study

In this case, we consider the maximization of production in anticipation of increased market demand. The quality specification constraints are still enforced. Two different cases are presented each dealing with the maximization of a specific product (gasoline and ATK). Table 3.7 – 3.8 show the final products flow rates and the quality specifications for each product in each case.

3.4.2.1 Maximum Gasoline

In the gasoline case (Table 3.7), the objective was to maximize both PRG and RGG with a minimum of 5,000 BBL/D each. The optimization results show an increase in the RGG rather than the PRG due to the lower RON value of the RGG and because maximizing the profit is not any more the objective. Moreover, from this case, we can see the importance of the nonlinear model in meeting the properties specifications as depicted by the operating variables in the different refinery processes. For example, when maximizing gasoline, the expected result was to run the FCC with full throughput rather than running the HC. However, the bottleneck was the ATK freezing point, which forced the model to select to run HC rather than a production rate of 5,990 BBL/D.

Table 3.6. Final Products Flow Rate and Properties

Blending Pool	Product Stream	Flow Rate BBL/D	Final Product BBL/D	Product Property	Property value
PRG	SRLN	5,570	**20,350**		
	TLN	0		API	45.0
	REFORMATE	10,730		SUL %	0.003
	LNHC	650		RON	92.8
	LNFCC	0		RVP	8.8
	HNFCC	560		OXG %	2.0
	C_4	580			
	MTBE	2,260			
RGG	SRLN	0	**16,650**		
	TLN	1,260		API	56.9
	REFORMATE	1,260		SUL %	0.002
	LNHC	540		RON	90.2
	LNFCC	6,770		RVP	8.8
	HNFCC	4,570		OXG %	2.0
	C_4	400			
	MTBE	1,850			
ATK	Kero (CDU)	8,540	**17,510**	API	40.4
	KHC	7,870		SUL %	0.145
	KDHT	1,100		FLSH	166.9
				FRZ	-42.7
LSDSL	TDSL	12,170	**29,610**		
	DHC	8,210		API	35.0
	LCO	2,810		SUL %	0.034
	KDHT	0		CI	57.4
	DGOHT	5,100		FLSH	217.5
	DRHT	1,320			
FOIL	LSFO	15560	**18,430**		
	LCO	0		API	10.1
	HCO	995		SUL %	0.198
	KDHT	1,875		VISC	350.0
	DGHOT	0			
	DRHT	0			

Table 3.7. Maximum Gasoline Results

Final Product	Flow Rate BBL/D	Product Property	Property Value
PRG	**23,125**	API	47.4
		SUL %	0.05
		RON	92.8
		RVP	8.8
		OXG %	2.0
RGG	**17,290**	API	55.2
		SUL %	0.007
		RON	92.0
		RVP	8.8
		OXG %	2.0
ATK	**8,390**	API	41.5
		SUL %	0.107
		FLSH	167.2
		FRZ	-40.0
LSDSL	**29,580**	API	35.6
		SUL %	0.032
		CN	56.1
		FLSH	222.8
FOIL	**22,180**	API	11.0
		SUL %	0.18
		VISC	49.9

3.4.2.2 Maximum ATK

For the ATK case, the refinery maximum ATK production achieved was 28,610 BBL/D, see Table 3.8. This cap of production was due to the properties constraints of the other products. The refinery has to produce an 8,225 BBL/D of PRG due to the gasoline property constraints (API, SUL, and RON). Although MTBE was added to improve the gasoline RON, OXG limit was reached (2.0%). In addition, the viscosity of the FOIL forced the refinery to produce 19,000 BBL/D of FOIL.

Table 3.8. Maximum ATK Results

Product	Flow Rate BBL/D	Product Property	Property Value
PRG	**8,225**	API	47.4
		SUL %	0.05
		RON	92.0
		RVP	6.88
		OXG %	2.0
RGG	**16,915**	API	61.8
		SUL %	0.0005
		RON	89.0
		RVP	8.24
		OXG %	2.0
ATK	**28,610**	API	40.6
		SUL %	0.131
		FLSH	167.6
		FRZ	-40.0
LSDSL	**31,075**	API	35.2
		SUL %	0.035
		CN	59.0
		FLSH	211.0
FOIL	**18,935**	API	12.4
		SUL %	0.183
		VISC	150.0

3.4.3 Maximum Profit Case Study

This case study was undertaken in order to determine the production plan of the refinery in terms of intermediate and final products to achieve the maximum possible profit for the refinery without paying attention to market demand. It is implicitly assumed here that the refinery is able to sell all what it can produce. A minimum production rate of 5,000 BBL/D was imposed on every product. The results, as illustrated in Table 3.9, show clearly a focus on production of LSDSL and ATK rather than gasoline. Again, the viscosity restriction on FOIL forced the model to produce a large quantity of FOIL. The profit is improved in this case by a margin of 2.3% compared to the base case.

Table 3.9. Maximum Profit Results

Product	Flow Rate (BBL/D)	Product Property	Property Value
PRG	**5,000**	API	48.1
		SUL %	0.001
		RON	92
		RVP	8.8
		OXG %	2.0
RGG	**22,145**	API	54.2
		SUL %	0
		RON	89.6
		RVP	8.8
		OXG %	2.0
ATK	**28,225**	API	42.3
		SUL %	0.077
		FLSH	166.6
		FRZ	-40.0
LSDSL	**30,480**	API	35.2
		SUL %	0.034
		CN	57.9
		FLSH	217.7
FOIL	**17,890**	API	10.0
		SUL %	0.197
		VISC	150.0

Table 3.10 provides a comparative summary of the different case studies considered. The optimal temperature cut for the CDU fractions and the optimal FCC conversion are different for the different case studies. It is important to note that the model was able in each case to provide the best operational capacity of the refinery processing units. The optimization chose to reduce capacity and conversion of the FCC unit in the maximization case studies of ATK and free market demand.

Table 3.10. Comparison between selected variables for different case studies

	Base Case	**Max Gasoline**	**Max ATK**	**Max Profit**
CDU Cut Point (°F)				
SRLN	220.0	220.0	194.1	220.0
SRHN	380.0	380.0	330.0	330.0
KERO	465.8	420.0	520.0	490.4
Diesel	610.0	610.0	610.0	610.0
VGO	1050.0	1050.0	1050.0	1050.0
FCC Conversion (%)	78.0	78.0	72.0	72.0
Final Products (BBL/D)				
PRG	20350	23125	8225	5000
RGG	16650	18290	16915	22145
ATK	17510	8390	28610	28225
LSDSL	29610	29580	31075	30480
FOIL	18430	22180	18935	17890
Refinery Profit (10^6x$/D)	2.0191	1.8652	1.9871	2.0788

3.5 Summary

In this chapter, an efficient nonlinear refinery-planning model has been presented. The model integrates the processing unit models with the blending correlations, and optimizes the operating variables of each individual unit. The CDU fractions cut-point temperature and the operating variables show the greatest effect on the final products flow rates and quality. The results from the case studies show how the model can be utilized to minimize quality give-away.

The optimization results show that refinery profit can reach up to $758.8\text{x}10^6$\$/yr by changing the CDU cut point temperature and other operating variables in the processing units. also, the model was able to cooperate with different objective function, such as maximizing production of certain product rather than the refinery profit. In ATK case, the FCC unit was chosen to work with the minimum capacity and to run the HC unit with its full maximum capacity.

One of the main advantages of the nonlinear planning model, which can be inferred from the previous discussion and results, is that it can provide an optimal operating strategy for the refinery while at the same time meet products properties and production rates. Quality give-away is also minimized hence resulting in large savings for the petroleum refinery. This of course is in addition to the more accurate representation of the refinery units. The model proved to be computationally tractable and is able to integrate new processing units or replace the existing units with new ones without major modifications. Finally, the model will be the base to formulate and solve other problems in refinery: hydrogen and CO_2 management strategies.

CHAPTER 4

INTEGRATION OF HYDROGEN MANAGEMENT WITHIN REFINERY PLANNING

4.1 Introduction

Refineries are being forced to increase their use of conversion units due to the increased market for heavy crude oils. In addition, the hydrotreating processes used by refineries must be more effective due to the promulgation of increasingly stringent air emissions regulations that require reductions in the amount of sulfur in fuel products. At the same time, stricter environmental regulations on the product specifications of low-aromatic gasoline have resulted in decreased hydrogen production by catalytic reformers, thereby lowering the overall availability of hydrogen in the refinery. As a result, it has been necessary for the petroleum refining industry to seek innovative approaches for dealing with the hydrogen balance issue (Ratan and Vales 2002, Hofer *et al.* 2004, Davis and Patel 2004, Girardin *et al.* 2006).

Therefore, hydrogen management is vitally important in meeting production requirements while simultaneously complying with environmental regulations. The goal of this chapter is to develop an integrated model of process operations and the hydrogen network in refineries that will allow assessment and maximization of overall profits.

This chapter is organized as follows. In next section, the refinery hydrogen problem statement will be presented. In section 4.3, a MINLP hydrogen management model will be proposed. Then, different case studies will be provided to illustrate the model performance, in section 4.4. This chapter ends with a concluding remark.

4.2 Problem Statement

Hydrogen plays an important role in the treating and upgrading processes. Recently, refineries have to operate under huge pressure and tight margins due to the environmental regulations that requires reduction the sulfur content allowed in fuels and due to the trend toward a heavier crude oil market in which more hydrogen is required for cracking.

The hydrogen network in a refinery consists of Sources i = {Suppliers} and Sinks j = {Consumers}. Between these two, there is a set of equipment that improves the exchange between the suppliers and the consumers, i.e., recovery units, k, n = {compressors} and m = {purification units}. The gas stream (F) fed to the processing units, u = {work as both source and sink}, as well as the purity (y) of this stream are optimization variables.

The processing units are the link between the planning model and the hydrogen management model. The overall objective is to maximize the refinery profit function, which includes the hydrogen alternatives operating and capital cost.

The refinery hydrogen problem to be addressed in this chapter can be stated as follows, "*what is the best hydrogen strategies a refiner can select in order to meet a given product demand and specifications and satisfy the hydrogen requirements quantity and purity?*"

The mathematical equivalent of the problem statement above consists of maximizing an objective function while observing equality and inequality constraints. The problem is modelled mathematically and can be written as the following Mixed Integer Non-Linear Programming (MINLP):

$$\max_{x,y} f(x,y) \qquad \text{(objective function)}$$

such that,

$$h(x,y) = 0 \qquad \text{(equality constraints)}$$

$$g(x,y) \leq 0 \qquad \text{(inequality constraints)}$$

$$x \in X \leq R^n \qquad (x \text{ is a vector of continuous variables})$$

$$y \in Y = \{0,1\} \qquad (y \text{ is a vector of binary variables})$$

Variables

- Continuous variables, x, are real numbers that may represent streams (hydrogen) flow rate, streams purity, and inlet and outlet pressure.
- Binary variables, y, are assigned (0-1) to represent the potential of existence or nonexistence of units such as new compressors, and PSA processes.

Objective Function

The objective is to maximize the overall refinery profit. In this chapter, $f(x,y)$ is the same objective function in Chapter 3, adding on it the retrofitting cost associated with hydrogen network, and capital and operating costs of the new pieces of equipment installed.

Constraints

- $h(x,y) = 0$
  - a) Hydrogen balance constraints: the hydrogen balance over a processing unit, compressors, and PSA units.
  - b) Hydrogen purity constraints: the hydrogen purity of the streams fed to a sink or leaving a source unit.
- $g(x,y) \leq 0$
  - a) Capacity constraints: the capacity of compressors and PSA units.
  - b) Assignment constraints: the upper and lower constraints to assign value to a variable, such as hydrogen flow rate or pressure.

4.3 Model Formulation

The refinery hydrogen management model can be formulated once the hydrogen network sources and sinks within the crude oil refinery are identified. Constraints can be added to the model to ensure that hydrogen sink requirements are achieved, including, but not limited to, total hydrogen flow and hydrogen partial pressure. Additionally, connectivity constraints, such as hydrogen availability in source streams, pressure compatibility between source streams, recovery methods, and hydrogen sinks, are also be included in the model. The final model will incorporate sub-models for processing units, compressors, purification (PSA) units. The hydrogen network elements' models are explained in more details in Appendix C.

Hydrogen network is assumed to have three different types of unit operations. Compressors are necessary to raise the pressure of different streams. PSA units separate single feeds with low hydrogen purity to product, with high purity, and tail streams. Processing units can exchange their purge streams with each other, or they can be sent to compressors or PSA units. With the view of a superstructure, one should allow all possible connections between the inlet hydrogen streams supply the network the unit operations, and the unit-operations exit streams. Figure 4.1 depicts the proposed superstructure for hydrogen network.

The superstructure is split into three parts, inlet hydrogen streams, different unit operations, and outlet streams. The set of inlet streams represents different hydrogen streams that provide the network with its requirements of hydrogen. Every inlet stream is distributed over all the unit-operations, the set of final streams. The set of unit operations (processing units in refinery, compressors and PSA units), can have similar units and they operate under different conditions. The units operations can exchange streams between each other's or sent it to the outlet streams set. The abovementioned representation of hydrogen superstructure gives all the possible alternatives for a potential hydrogen network.

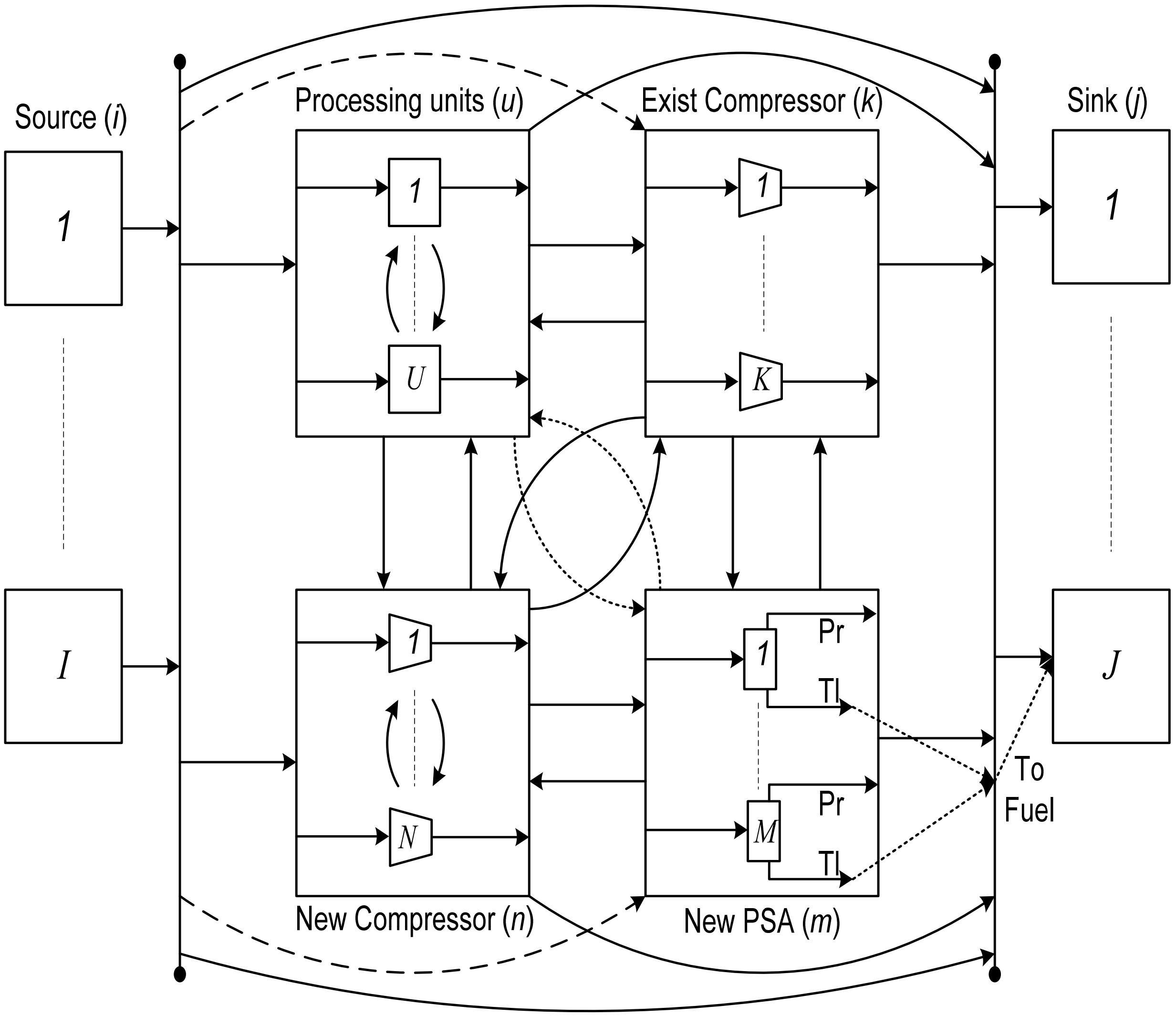

Figure 4.1. Hydrogen Management Super Structure

- Flow Assignment

The flow rate stream between any two destinations is defined by a binary variable ($XF_{q,w}$) that allows the flow if the upstream pressure is equal to or higher than the downstream pressure. For the existing units (sources, processing units, existing compressors, and sinks), the pressure is known as a fixed parameter. Therefore, the flow rate binary variable is defined by a binary parameter ($a_{q,w}$) to reduce the number of variables in the network.

$$XF_{q,w}\ ,\ a_{q,w} = \begin{cases} 1 & P_q - P_w \geq 0 \\ 0 & Otherwise \end{cases}$$

This can be mathematically reformulated as follows:

$$UP(XF_{qw} - 1) \leq \left(P_q - P_w\right) \leq XF_{qw}UP - \varepsilon \qquad \forall\, \boldsymbol{q, w}\, ;\ \begin{matrix} \boldsymbol{q \in i, u, k, n, m} \\ \boldsymbol{w \in u, k, n, m, j} \end{matrix} \tag{4.1}$$

$$F_{q,w} \leq XF_{q,w}UF \qquad \forall\, q, w;\ \begin{matrix} \boldsymbol{q \in i, u, k, n, m} \\ \boldsymbol{w \in u, k, n, m, j} \end{matrix} \tag{4.2}$$

where *UP*, *UF*, ε represent the upper pressure difference bound, the upper flow rate bound and a small value number, respectively.

- New Equipments

The selection of any new equipment is represented by a binary variable (*X*). For new compressor (*n*), the compressor exists if there is a minimum pressure difference (*LPNC*) between the suction (*PI*) and discharge (*PO*) pressures.

$$UP(X_n - 1) + LPNC \leq (PO_n - PI_n) \leq X_n\, UP + LPNC - \varepsilon \quad \forall\, \boldsymbol{n = 1, 2, ..., N} \tag{4.3}$$

The new compressors and PSA units exists if there is a minimum design flow rate (*LF*).

$$X_w\, LF \leq F_{in,w} \leq X_w\, UF \qquad \forall\, \boldsymbol{w};\ \ \boldsymbol{w \in n, m} \tag{4.4}$$

- Purification Unit (PSA)

The objective of the PSA unit is to supply the hydrogen network with high-purity product. The product stream can be exchanged with the hydrogen network, where the tail stream is sent to the fuel system in the refinery, see Appendix C. The overall balance of the PSA unit (*m*) is:

$$F_{in,m} = F_{\mathrm{Pr},m} + F_{Tl,m} \qquad \forall\, \boldsymbol{m = 1,2,...,M} \qquad (4.5)$$

where $F_{in,m}$, $F_{Pr,m}$, and $F_{Tl,m}$ represent the feed, product, and tail gas flow rates of new purification unit (m), respectively. The sources (i), existing compressors (k), processing units (u), and new compressors (n) can send streams to the new purification unit (m):

$$F_{in,m} = \sum_{i}^{I} F_{i,m} + \sum_{k}^{K} F_{k,m} + \sum_{u}^{U} F_{u,m} + \sum_{n}^{N} F_{n,m} \qquad \forall\, \boldsymbol{m = 1,2,...,M} \qquad (4.6)$$

The feed purity represented by $y_{in,m}$ is calculated by:

$$F_{in,m}\, y_{in,m} = \sum_{i}^{I} F_{i,m} y_i + \sum_{k}^{K} F_{k,m} y_k + \sum_{u}^{U} F_{u,m} y_u + \sum_{n}^{N} F_{n,m} y_n \quad \forall\, \boldsymbol{m = 1,2,..,M} \; (4.7)$$

The amount of hydrogen recovered in the product stream is calculated by:

$$F_{\mathrm{Pr},m}\, y_{\mathrm{Pr},m} = F_{in,m}\, y_{in,m}\, RCOV_m \qquad \forall\, \boldsymbol{m = 1,2,...,M} \qquad (4.8)$$

The purity of the tail gas, which is represented by $y_{Tl,m}$, is calculated by:

$$F_{Tl,m}\, y_{Tl,m} = F_{in,m}\, y_{in,m} (1 - RCOV_m) \qquad \forall\, \boldsymbol{m = 1,2,...,M} \qquad (4.9)$$

The new purification unit (m) can send the product stream to the processing units (u), existing compressors (k), and new compressors (n):

$$F_{\mathrm{Pr},m} = \sum_{k}^{K} F_{m,k} + \sum_{u}^{U} F_{m,u} + \sum_{n}^{N} F_{m,n} \qquad \forall\, \boldsymbol{m = 1,2,...,M} \qquad (4.10)$$

Where the tail gas stream is sent to the fuel gas system in the refinery:

$$F_{Tl,m} = \sum_{j \in Fuel}^{J} F_{m,j} \qquad \forall\, \boldsymbol{m = 1,2,\ldots,M} \qquad (4.11)$$

- Sources

The total amount of gas sent to the network must equal the amount available from the source:

$$F_{\mathbf{source,i}} = \sum_{u}^{U} a_{iu} F_{i,u} + \sum_{k}^{K} a_{ik} F_{i,k} + \sum_{j}^{J} a_{ij} F_{i,j} + \sum_{n}^{N} F_{i,n} + \sum_{m}^{M} F_{i,m} \qquad \forall\, \boldsymbol{i = 1,2,\ldots,I} \quad (4.12)$$

where $F_{i,u}$, $F_{i,k}$, $F_{i,j}$, $F_{i,n}$ and $F_{i,m}$ represent the streams flow rate from source (i) to processing units (u), compressors (k), sinks (j), new compressors (n) and new purification units (m), respectively. Summation of these variables gives the flow rate out of source (i), which is represented by $F_{source,i}$.

- Sinks

The sinks, mainly in the fuel gas system, are the final destinations of the unused hydrogen in the hydrogen network. The amount of gas entering the sink (j) is calculated by:

$$F_{\mathbf{sink,j}} = \sum_{i}^{I} a_{ij} F_{i,j} + \sum_{u}^{U} a_{uj} F_{u,j} + \sum_{k}^{K} a_{kj} F_{k,j} + \sum_{n}^{N} F_{n,j} + \sum_{m \in Tl}^{M} F_{m,j} \qquad \forall\, \boldsymbol{j = 1,2,\ldots,J} \quad (4.13)$$

where $F_{i,j}$, $F_{k,j}$, $F_{k,j}$, $F_{n,j}$ and $F_{m,j}$ represent the flow rates from sources (i), consumer units (u), existing compressors (k), new compressors (n) and new purification units tail gas (m), respectively, to sink (j). Summation of these variables gives the flow rate to sink (j), represented by $F_{sink,j}$. The hydrogen purity of the sink (j) is defined by:

$$F_{\mathbf{sink,j}}\, y_{\mathbf{sink,j}} = \begin{array}{l} \sum_{i}^{I} a_{ij} F_{i,j} y_i + \sum_{u}^{U} a_{uj} F_{u,j} y_{uo} + \\ \sum_{k}^{K} a_{kj} F_{k,j} y_k + \sum_{n}^{N} F_{n,j} y_n + \sum_{m \in Tl}^{M} F_{m,j} y_{Tl,m} \end{array} \qquad \forall\, \boldsymbol{j = 1,2,\ldots,J} \quad (4.14)$$

where $y_{Tl,m}$ and $y_{sink,j}$ represent the stream purity of the tail gas from the new purification unit (m), and the stream purity of sink (j), respectively.

- Processing Units

The processing units, hydrotreaters or hydrocrackers, are the only consumer of hydrogen in the hydrogen network, see Appendix C. The amount of hydrogen entering and leaving the processing units is equal to the amount consumed:

$$F_{out,u}\, y_{u} = F_{in,u}\, y_{in,u} - Cons_{u} \qquad \forall\, \boldsymbol{u = 1,2,...,U} \qquad (4.15)$$

where $Cons_u$ represents the amount of hydrogen consumed by the processing unit (u). The amount of hydrogen consumed in the processing unit is the link between the planning model and the hydrogen management model. $F_{out,u}$ and $y_{,u}$ represent the flow rates and stream purity leaving the processing unit (u), respectively. The terms $F_{in,u}$ and $y_{in,u}$ represent the flow rates and stream purity entering the processing unit (u), respectively. The feed purity and product purity of the processing unit are constant parameters.

Processing units behave as both sinks and sources. In order to maintain the operating conditions of the processing units, the amount of gas entering these units will be kept constant at the inlet:

$$F_{in,u} = R_{u} + MU_{u} \qquad \forall\, \boldsymbol{u = 1,2,...,U} \ (4.16)$$

$$MU_{u} = \sum_{i}^{I} a_{iu} F_{i,u} + \sum_{k}^{K} a_{ku} F_{k,u} + \sum_{u'}^{U'} a_{u'u} F_{u',u} + \sum_{n}^{N} F_{n,u} + \sum_{m}^{M} F_{m,u} \qquad \forall\, \boldsymbol{u = 1,2,...,U} \ (4.17)$$

where R_u *is* the recycle flow rate of the processing unit (u); MU_u is the makeup stream entering to the consumer (u); and $F_{i,u}$, $F_{k,u}$, $F_{u',u}$, $F_{n,u}$ and $F_{m,u}$ represent the flow rates from sources (i), existing compressors (k), another processing unit (u'), new compressors (n) and new purification units (m) to processing unit (u), respectively. Summation of these variables with the recycle stream from the processing unit gives the flow rate at the inlet of the processing unit (u). The hydrogen purity (partial pressure) must also be kept constant at the inlet of the processing unit:

$$F_{\boldsymbol{in,u}} y_{\boldsymbol{in,u}} = R_{\boldsymbol{u}} y_{\boldsymbol{u}} + MU_{\boldsymbol{u}}\, y_{\boldsymbol{M,u}} \qquad \forall\, \boldsymbol{u = 1,2,...,U} \quad (4.18)$$

$$MU_{\boldsymbol{u}}\, y_{\boldsymbol{M,u}} = \begin{matrix} \sum_{i}^{I} a_{iu} F_{i,u} y_{\boldsymbol{i}} + \sum_{k}^{K} a_{ku} F_{k,u} y_{\boldsymbol{k}} + \\ \sum_{u'}^{U'} a_{u'u} F_{u',u} y_{u'} + \sum_{n}^{N} F_{n,u} y_{\boldsymbol{n}} + \sum_{m}^{M} F_{m,u} y_{\boldsymbol{Pr,m}} \end{matrix} \qquad \forall\, \boldsymbol{u = 1,2,...,U} \quad (4.19)$$

where $y_{M,u}$ represents the purity of the makeup stream fed to the processing unit (u), and it is defined by multiplying the flow rates of the streams that feed the processing unit by the purities of those streams. The streams purity of the source (i), existing compressors (k), and processing unit (u'), new compressors (n) and new purification unit (m) product stream are represented by y_i, y_k, $y_{u'}$, y_n and $y_{Pr,m}$, respectively.

The amount of gas leaving the outlet of the processing unit (u) must equal the amount of gas available at the inlet side of this unit:

$$F_{\boldsymbol{out,u}} = R_{\boldsymbol{u}} + PG_{\boldsymbol{u}} \qquad \forall\, \boldsymbol{u = 1,2,...,U} \quad (4.20)$$

$$PG_{\boldsymbol{u}} = \sum_{j}^{J} a_{uj} F_{u,j} + \sum_{k}^{K} a_{uk} F_{u,k} + \sum_{u'}^{U'} a_{uu'} F_{u,u'} + \sum_{n}^{N} F_{u,n} + \sum_{m}^{M} F_{u,m} \qquad \forall\, \boldsymbol{u = 1,2,...,U} \quad (4.21)$$

where PG_u represents the purge stream of the processing unit (u) and $F_{u,j}$, $F_{u,k}$, $F_{u,u'}$, $F_{u,n}$ and $F_{u,m}$ represent the flow rates from the processing unit (u) to sinks (j), compressors (k), other processing units (u'), new compressors (n) and new purification units (m), respectively. Summation of these variables with the recycle stream gives the flow rate out of processing unit (u), which is represented by $F_{out,u}$.

- Existing Compressors

Existing compressors have known, fixed suction and discharge pressures, which allow the determination of the flow parameters between the compressors and other units. Compressors behave as both sinks and sources, where the flow rate and the stream purity are not constant, see Appendix C. The compressor constraints are mainly that the flow rates of the gases entering the compressors must be equal to the flow rates that are leaving the compressor:

$$F_{in,k} \; = \; F_{out,k} \qquad \forall\, \boldsymbol{k = 1,2,...,K} \qquad (4.22)$$

$$F_{in,k} = \sum_{i}^{I} a_{ik} F_{i,k} \; + \sum_{u}^{U} a_{uk} F_{u,k} + \sum_{n}^{N} F_{n,k} \; + \sum_{m}^{M} F_{m,k} \qquad \forall\, \boldsymbol{k = 1,2,...,K} \qquad (4.23)$$

$$F_{out,k} = \sum_{j}^{J} a_{kj} F_{k,j} \; + \sum_{u}^{U} a_{ku} F_{k,u} + \sum_{n}^{N} F_{k,n} \; + \sum_{m}^{M} F_{k,m} \qquad \forall\, \boldsymbol{k = 1,2,...,K} \qquad (4.24)$$

where $F_{i,k}$, $F_{u,k}$, $F_{n,k}$, $F_{m,k}$, $F_{k,j}$, $F_{k,u}$, $F_{k,n}$ and $F_{k,m}$ represent the flow rates from/to sources (i), processing units (u), new compressors (n) and new purification units (m) to/from existing compressor (k)., Summation of these variables gives the flow rate to compressor (k), which is defined by $F_{in,k}$. In addition, the amount of hydrogen entering the compressor must be equal to the amount leaving the compressor:

$$F_{in,k}\, y_k = \sum_{i}^{I} a_{ik} F_{i,k} y_i + \sum_{u}^{U} a_{uk} F_{u,k}\, y_u + \sum_{n}^{N} F_{n,k} y_n + \sum_{m}^{M} F_{m,k} y_{\mathrm{Pr},m} \qquad \forall\, \boldsymbol{k = 1,2,...,K} \; (4.25)$$

where y_k represents the purity of streams leaving compressor (k). All existing compressors have limited power. Therefore, the compressor flow rate is less than or equal to a maximum capacity flow (FC_k^U):

$$F_{in,k} \; \leq \; FC_k^U \qquad \forall\, \boldsymbol{k = 1,2,...,K} \qquad (4.26)$$

Finally, the power of the compressors is calculated as following:

$$Pwr_k = a_{COM}\left(\left(\frac{P_{out,k}}{P_{in,k}}\right)^{b_{COM}} - 1\right)F_{in,k} \qquad \forall\, \boldsymbol{k = 1,2,..,K} \qquad (4.27)$$

- New Compressors

The same equations for the existing compressors are valid for the new compressors, except for the capacities, Equation 4.26, which are unlimited for the new compressors. The power for the new compressor, if exists, can be calculated as follows:

$$Pwr_n - a_{COM}\left(\left(\frac{PO_n}{PI_n}\right)^{b_{COM}} - 1\right)F_{in,n} \le (1 - X_n)UPwr \qquad \forall\, \boldsymbol{n = 1,2,..,N}\ (4.28)$$

$$Pwr_n - a_{COM}\left(\left(\frac{PO_n}{PI_n}\right)^{b_{COM}} - 1\right)F_{in,n} \ge (X_n - 1)UPwr \qquad \forall\, \boldsymbol{n = 1,2,..,N}\ (4.29)$$

$$Pwr_n - X_n UPwr \le 0 \qquad \forall\, \boldsymbol{n = 1,2,..,N}\ (4.30)$$

where *UPwr* is the upper bound of the power of the new compressor (*n*).

- Cost Calculation

The objective function of the mathematical programming model can be defined as to maximize the refinery profit with the minimal hydrogen strategies cost. The hydrogen strategies cost will be defined as the total annual cost (TAC) of the hydrogen network, which is function of both capital and operating costs. The main operating cost variables that affect the economics of the model (hydrogen network) are hydrogen production, electricity (the compressor's power), and fuel credit.

- Hydrogen Cost: direct calculation through hydrogen plant production:

$$OC_{H_2} = OCH * F_{HP} \tag{4.31}$$

OC_{H2} represents the hydrogen production cost, which is function of the F_{HP}, hydrogen plant flow rate, multiplied by the unit cost of production, *OCH*.

- Electricity Cost: is evaluated by calculating the power required to operate the compressors:

$$OC_{Elc} = OCE \left(\sum_k Pwr_k + \sum_n Pwr_n \right) \tag{4.32}$$

OC_{Elc} represents the electricity cost, which is a function of the *Pwr*, compressor's power, multiplied by the unit cost of electricity, *OCE*.

- Fuel Cost: through calculating the heating value of the gas component sent to the fuel system. The fuel gas is assumed to be a binary mixture of hydrogen and methane, and both are functions of the fuel gas flow rate F_{Fuel} and the purity y_{Fuel}.

$$OC_{Fuel} = OCF * F_{Fuel} \left(LHV_{H_2} y_{Fuel} + LHV_{CH_4} \left(1 - y_{Fuel} \right) \right) \tag{4.33}$$

OC_{Fuel} represents the fuel gas credit gained by the refinery, which is function of the summation of fuel gas heating value *LHV* for hydrogen and methane multiplied by the unit cost of fuel gas *OCF*.

- The capital cost of the new compressor is a function of its power, and the capital cost of the PSA is a function of the feed flow rate:

$$Cap_n = a_{NC} * X_n + b_{NC} * Pwr_n \qquad \forall\, \boldsymbol{n = 1,2,..,N} \tag{4.34}$$

$$Cap_m = a_{PSA} * X_m + b_{PSA} * F_{in,m} \qquad \forall\, \boldsymbol{m = 1,2,..,M} \tag{4.35}$$

The operating cost is annualized by multiplying it by the number of working days per year (*OD*); the capital cost is annualized by multiplying the annual interest percentage by the total invested capital. Total annual cost is calculated as follows:

$$TAC = OD * \left(OC_{H_2} + OC_{Elc} - OC_{Fuel} \right) + AF \left(\sum_n Cap_n + \sum_m Cap_m \right) \tag{4.36}$$

Equations 4.1–4.36 represent the refinery hydrogen management model. This model will be integrated with the planning model proposed in Alhajri *et al*. (2008) to form the integrated refinery planning model. The objective function for the integrated model can be formulated to include the hydrogen alternative cost:

$$Maximize \qquad \sum_{i \in B} sp_i\ F_i - \sum_{i \in E} ce_i\ F_i - \sum_{i \in I} cx_i\ F_i - TAC \tag{4.37}$$

The above objective function represents the ordinary production planning objective (raw material and units operation cost subtracted from revenues), and hydrogen management strategy (hydrogen network operating cost plus new hydrogen equipments annualized capital cost).

4.4 Results and Discussions

The current refinery hydrogen distribution network, illustrated in Figure 4.2, is used as the base case study. The hydrogen sources in the refinery are the hydrogen plant, with a maximum production capacity of 80 MMSCFD, and the catalytic reformer, with a maximum production capacity of 15.5 MMSCFD. The purities of the hydrogen produced by the hydrogen plant and the catalytic reformer are 95.0% and 80.0%, respectively. The hydrogen sinks in the refinery are the processing units, which are the hydrocracker (HC), the gas oil hydrotreater (GOHT), the residue hydrotreater (RHT), the diesel hydrotreater (DHT), and the naphtha hydrotreater (NHT). The operating conditions of processing units, i.e., inlet and outlet pressures and inlet and outlet hydrogen purities, have to be met as described in Table 4.1. The outlet gas from the processing unit is split into recycle and purge streams. All the processing units have internal recycle compressors. The flow rate, purity, and pressure data of all hydrogen producers and consumers are given in Table 4.2 and Table 4.3, respectively. There are three makeup compressors to deliver the fresh hydrogen to the consumer processes, and the compressors' data are given in Table 4.4. The refinery fuel gas system operates at low pressure (200 psi), which allows receiving unused streams in the network.

Table 4.1. Operating Conditions of Processing Units

Processing Unit	Inlet Pressure Psi	Inlet Purity %	Outlet Pressure psi	Outlet Purity %
HC	2000	86.7	1200	80.0
GOHT	500	83.6	350	75.0
RHT	600	82.6	400	75.0
DHT	500	74.9	350	70.0
NHT	300	72.7	200	65.0

Table 4.2. Data for Hydrogen Sources

Processing Unit	Flow rate MMSCFD	Purity %	Pressure psi
HP	80	95.0	300
REF	14.317	80.0	300

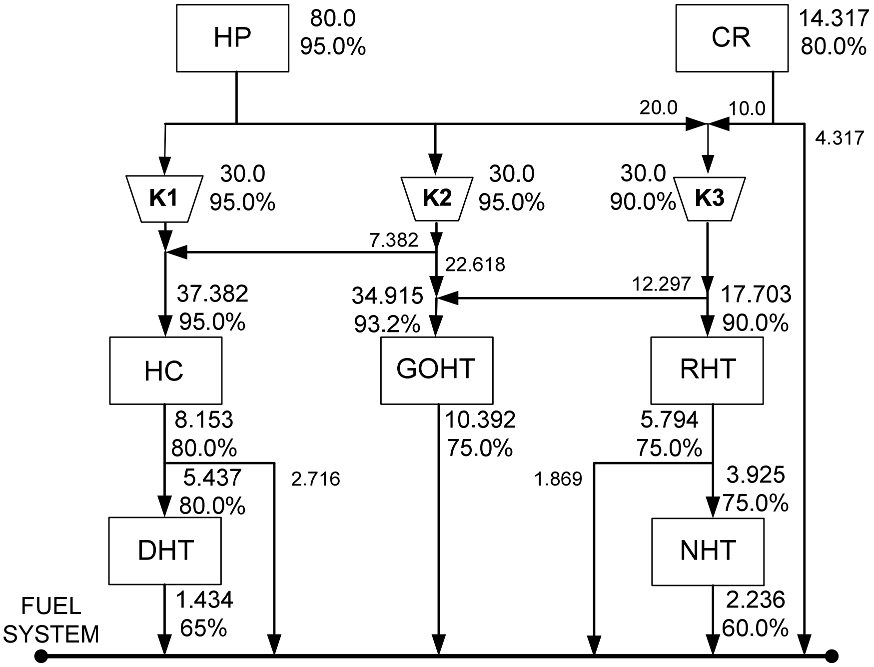

Figure 4.2. Base Case - Hydrogen Network

Table 4.3. Base Case – Data for Hydrogen Sinks

Processing Unit	**Make-up (MU)**		**Purge (PG) MMSCFD**	**Recycle (R) MMSCFD**	**F_{in} MMSCFD**	**F_{out} MMSCFD**
	Flow MMSCFD	**Purity %**				
HC	37.382	95.0	8.153	46.203	83.585	54.456
GOHT	34.915	93.2	10.392	39.130	74.045	49.522
RHT	17.703	90.0	5.794	17.381	35.084	23.175
DHT	5.437	80.0	1.434	5.736	11.173	7.170
NHT	3.925	75.0	2.236	1.204	5.129	3.440

Table 4.4. Base Case - Data for Makeup Compressors

Compressor (K)	**Section Pressure psi**	**Discharge Pressure psi**	**Flow (F_K) MMSCF**	**Max. Capacity MMSCF**
K1	300	2000	30.0	31.5
K2	300	2000	30.0	31.5
K3	300	600	30.0	31.5

The operating cost is calculated based on the following assumptions: the production cost of hydrogen (*OCH*) is 2000 \$/MMSCF; the electricity cost (*OCE*) is 0.03 \$/KWh; and the heat energy gained by burning the fuel gas (*OCF*) is 2.5 \$/MMBTU. Table 4.5 summarizes the operating cost of the base case study.

Table 4.5. Base Case - Operating Cost

Operating cost	**10^3x\$/D**
Hydrogen Production	160.00
Electricity	3.57
Fuel gas	(29.75)
Total (*TOC*)	133.82

In order to illustrate the models of the previous section, different case studies are considered. The objective is to show the importance of hydrogen in the refinery plans. Refinery planning with a properly-integrated hydrogen management plan can have a significant effect on decision made about the design and operation of the refinery. Now, the integrated model of the refinery planning and hydrogen management will be tested on the same case studies solved earlier on Chapter 3. Table 4.6 shows the result gained from the refinery planning model, which was solved without considering hydrogen limitations. Every case study will be solved twice. First, the case study will be solved with the NLP model, i.e., the binary variables of new equipments are zeros (only hydrogen requirments). Then, the case study will be solved again with the MINLP hydrogen management model.

Table 4.6. Planning Model Results

Case Study	**BASE**	**MOGAS**	**ATK**	**PROFIT**
Objective	2.0191E+6	41,416	28,613	2.0788E+6
H_2 Consumption				
HC	28.990	16.587	44.465	43.967
GOHT	24.761	24.761	23.770	24.761
RHT	11.588	11.588	11.588	11.588
DHT	3.346	4.309	3.786	2.805
NHT	1.490	1.490	1.129	0.954
Total	**70.175**	**58.735**	**84.738**	**84.074**
H_2 production				
REF	11.454	10.933	9.958	9.088

4.4.1 Base Case study

The same planning objective can be achieved, which is 2.02x10^6\$/D, by modifying the hydrogen network as shown in Figure 4.3. The new configuration reduced the operating cost by 1.5%, which is equivalent to 0.7x10^6\$/yr. Table 4.7 shows the operating cost saving in the base case study. This was achieved by reducing the hydrogen plant throughput to 78.2 MMSCF. There was no need to install any new compressors or purification units.

Table 4.7. Base Case - Operating Cost Saving

Operating cost	x **10^3\$/D**
Hydrogen Production	156.48
Electricity	3.48
Fuel gas	(28.10)
Total Operating Cost	131.86

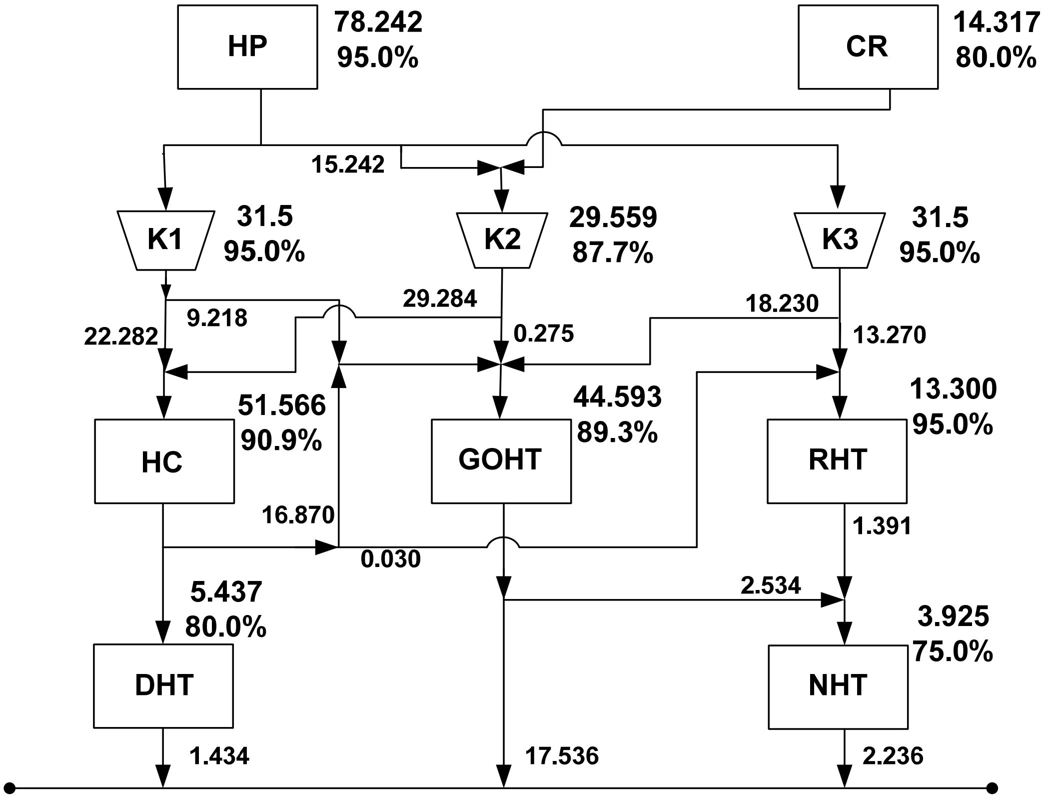

Figure 4.3: Base Case –Solution

4.4.2 Maximum Product Production Case Study

In this case, the objective is to produce the maximum quantity of the product in anticipation of increased market demand. The total hydrogen consumption required by every processing unit in each case study is shown in Table 4.6. The MOGAS case study is the lowest in its total hydrogen requirements, which means the hydrogen availability is not constraining the model. On the other hand, the hydrogen balance is critical on the ATK case study. An investigation of the hydrogen network capability to assist this objective will be studied in this section.

4.4.2.1 MOGAS Case study

A. NLP Mode

The result shows that the model is able to meet the refinery objective of MOGAS maximum production, which is equal to 41,400 BBL/D, as expected. Figure 4.4 shows the hydrogen distribution network, and Table 4.8 illustrates the operating cost.

B. MINLP Model

The need for installing new equipment is not applicable. However, the model was able to save 14.6% of the operating cost of the hydrogen network, as shown in Table 4.8. The major source of operating cost reduction was the hydrogen plant production. Figure 4.5 illustrates the hydrogen network design.

Table 4.8. MOGAS Case -Operating Cost

Operating cost	**NLP Model** x **$10^3$$/D**	**MINLP Model** x **$10^3$$/D**
Hydrogen Production	160.00	127.35
Electricity	3.57	2.74
Fuel gas	(38.37)	(23.12)
Total Operating Cost	125.20	106.97
Saving	14.6% = 6.65x**$10^6$$/yr**	

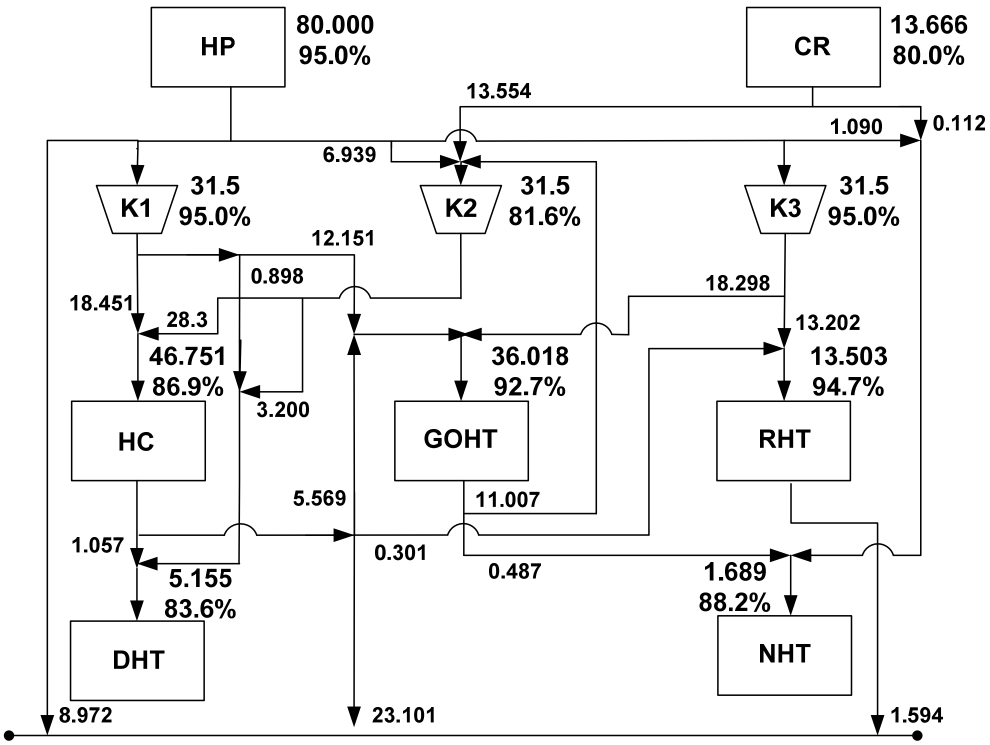

Figure 4.4 MOGAS Case – NLP Model Solution

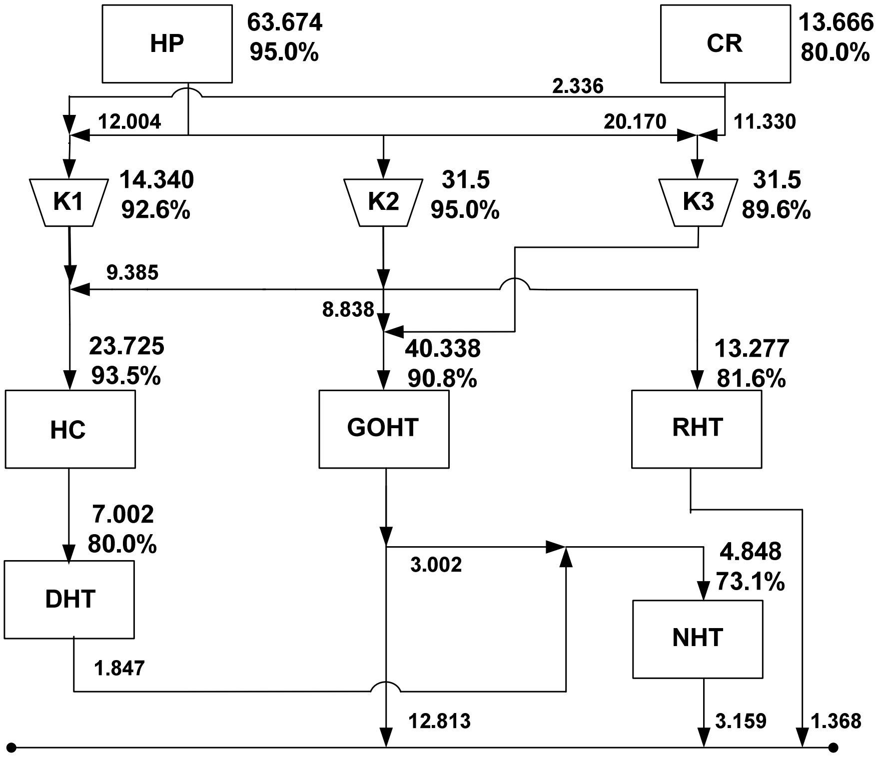

Figure 4.5. MOGAS Case - MINLP Model Solution

4.4.2.2 ATK Case Study

A. NLP Mode

This case has another critical situation for the hydrogen refinery availability, where the hydrogen requirement is 84.7 MMSCF. Figure 4.6 shows the resulting hydrogen network. The model could not achieve the planning objective of 28,600 BBL/D, since the maximum ATK production was 22,800 BBL/D. This deficiency of 5,800 BBL/d is due to hidden hydrogen availability. Table 4.9 illustrates the operating cost.

B. MINLP Model

The model result was close to the planning model objective; a maximum ATK production of 28,600 BBL/D was achieved with a negligible difference of 3 BBL/D. Two new compressors and a PSA unit are required to achieve this objective. A 23.35x10^6\$ capital cost should be invested, and the payback period will be less than four years. Figure 4.7 illustrates the hydrogen network, and Table 4.9 shows the operating cost.

Table 4.9. ATK Case - Operating Cost

Operating cost	**NLP Model** x **10^3\$/D**	**MINLP Model** x **10^3\$/D**
Hydrogen Production	160.00	160.00
Electricity	3.57	8.33
Fuel gas	(27.51)	(14.96)
Total Operating Cost	136.06	153.37
Capital Cost	Compressor (N1) = 1.30x10^6\$ Compressor (N2) = 14.96x10^6\$ PSA (1) = 7.09x10^6\$ Tot Capital Cost = 23.35x10^6\$	
Total Annual Cost (*TAC*)	59.62x10^6\$/yr = 163.34x10^3\$/D	

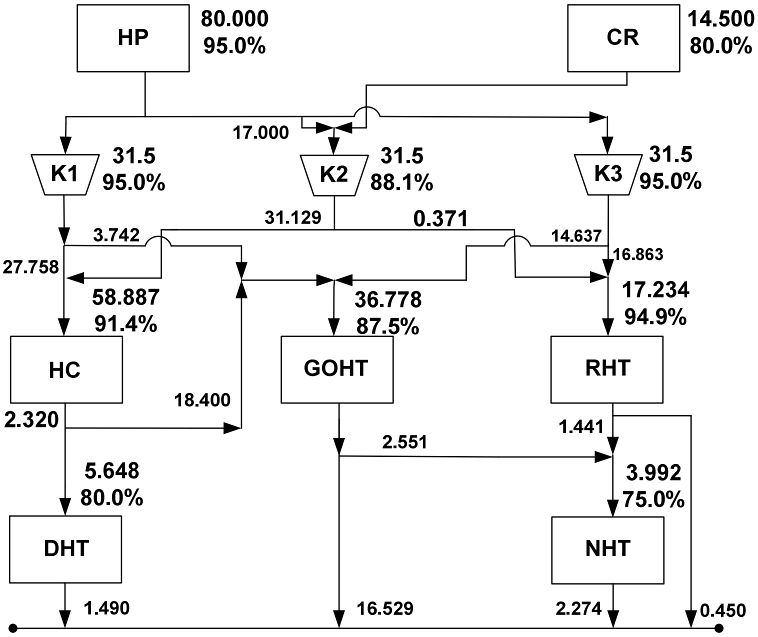

Figure 4.6. ATK Case – NLP Model Solution

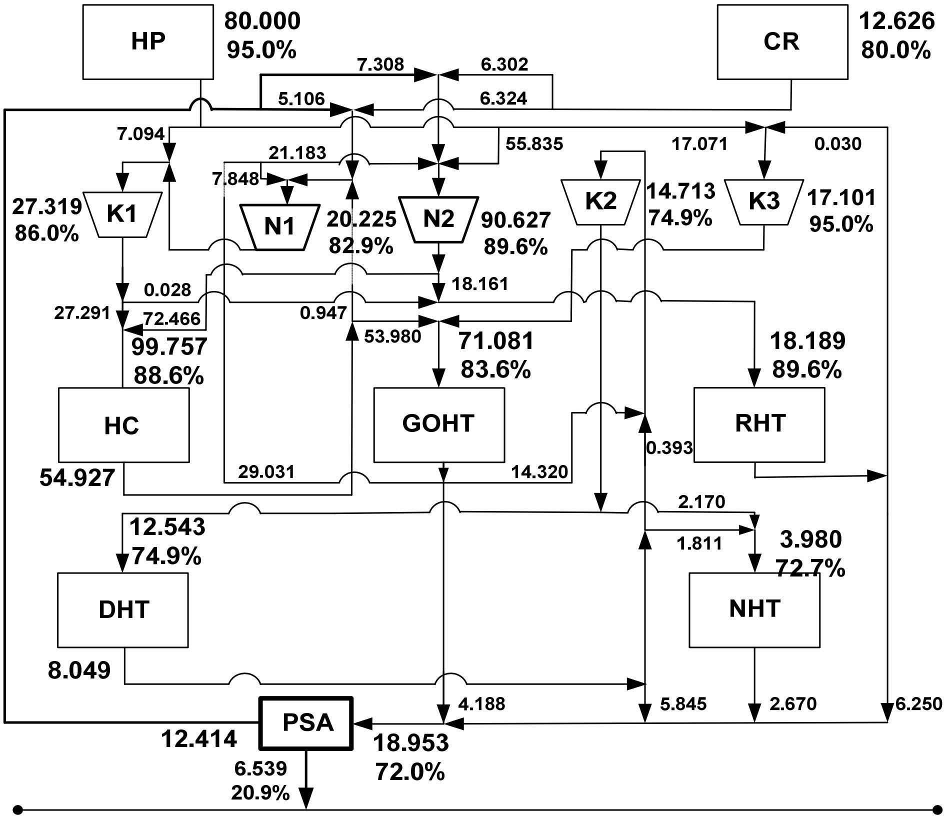

Figure 4.7. ATK Case - MINLP Model Solution

4.4.3 Maximum Profit Case Study

A. NLP Model

In this case, the net hydrogen requirement of 84.1 MMSCF was the second highest among the case studies. The NLP model result shows a maximum profit of 751.7x$10^{6}\$$/yr, which means that the model was unable to achieve the planning model objective (758.8x$10^{6}\$$/yr). The refinery profit could be increased by around 7x$10^{6}\$$/yr, if there was attention paid to the hydrogen management. Figure 4.8 shows the hydrogen distribution network, and Table 4.10 illustrates the operating cost.

B. MINLP Model

The model result indicates that an investment of 1.3x$10^{6}\$$ in one new compressor will make the refinery capable of achieving a profit of 752.4x$10^{6}\$$/yr. This is an increment of 0.7x$10^{6}\$$/yr over the NLP model result, which means that refinery can pay back this investment in less than two years. However, the model still could not reach the unconstrained planning objective. Figure 4.9 illustrates the resulting hydrogen network, and the operating cost is shown in Table 4.10.

Table 4.10. PROFIT Case - Operating Cost

Operating cost	**NLP Model** x **$10^{3}\$$/D**	**MINLP Model** x **$10^{3}\$$/D**
Hydrogen Production	160.00	160.00
Electricity	3.57	4.01
Fuel gas	(24.81)	(23.50)
Total Operating Cost	138.76	140.51
Capital Cost	Compressor (1) = 1.32x$10^{6}\$$	
Total Annual Cost (*TAC*)	51.49x$10^{6}\$$/yr = 141.07x$10^{3}\$$/D	

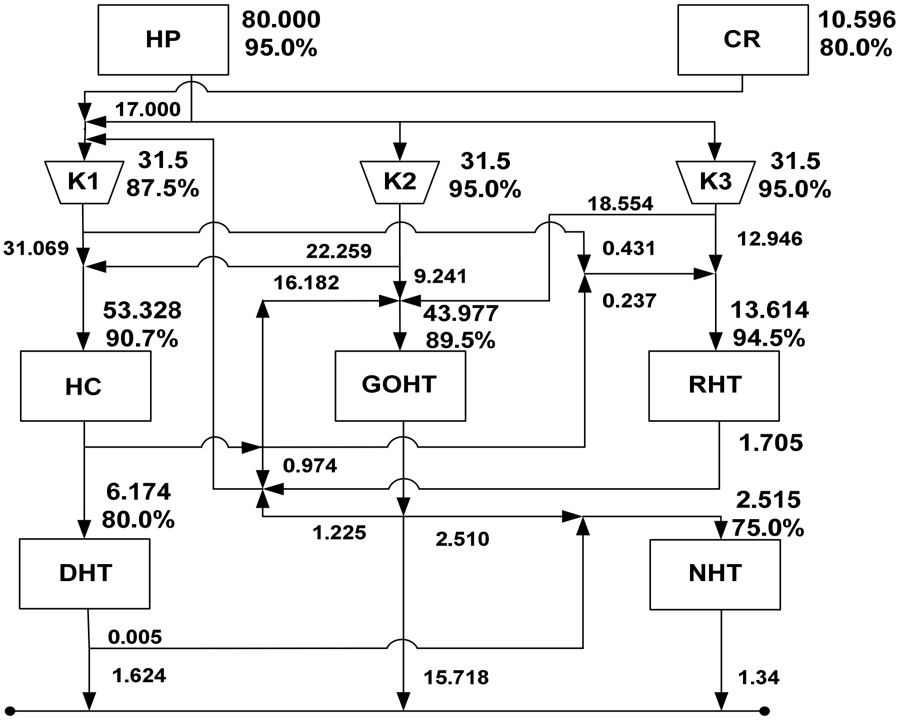

Figure 4.8. PROFIT Case - NLP Model Solution

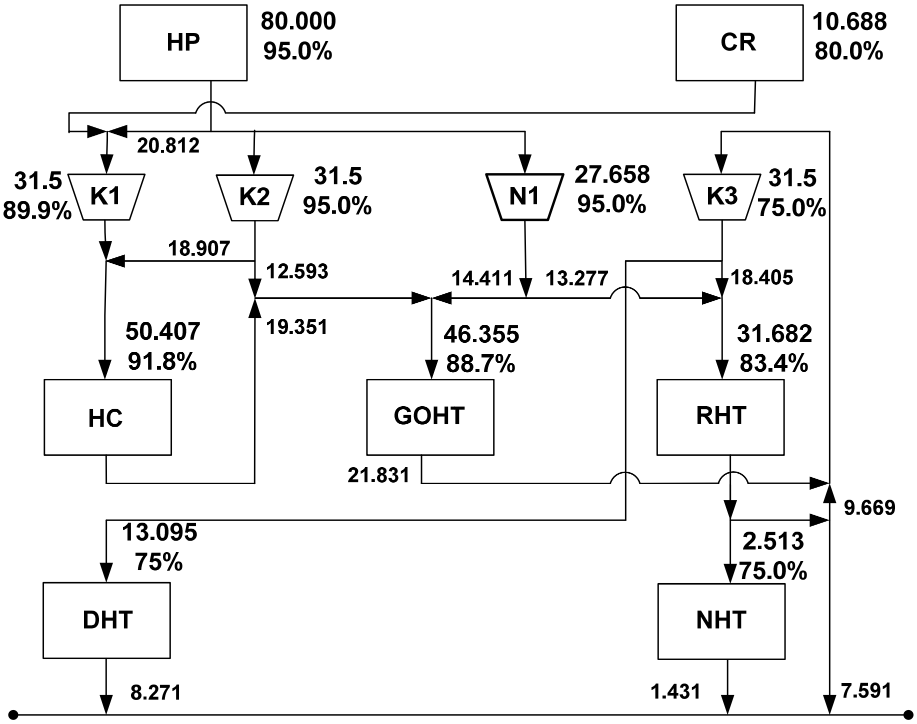

Figure 4.9. PROFIT Case - MINLP Model Solution

4.4.4 Hydrogen Shortage Case Study

In the last case, maximum profit, there was a difference in the result between the objective function for the integrated model (752.4x10^6\$/yr), and the planning model (758.8x10^6\$/yr). This is due to the shortage in hydrogen availability, although hydrogen plant was running at its maximum production capacity. This case study was undertaken in order to investigate the ability of the integrated model to overcome this problem. The model will be allowed to import hydrogen "over the fence." The purity of the hydrogen was the same as the 95.0% purity of hydrogen produced by the hydrogen plant.

The integrated model with the new modification achieved the planning objective of 758.7x10^6\$/yr, as shown in Figure 4.10. In order to do so, the refinery must import 2.2 MMSCFD of hydrogen, which would cost 7.6x10^3\$/D, and invest \$13 million in purchasing new PSA unit. However, the refinery profit increases around 7x10^6\$/yr. The new result proves that hydrogen is an important commodity, a significant asset in a refinery. Table 4.11 shows the operating costs for this case.

Table 4.11. Maximum Profit Case Study - Operating Cost

Operating cost	**MINLP** x **10^3\$/D**	**External** x **10^3\$/D**
Hydrogen Production	160.00	160 + 7.59
Electricity	4.01	3.57
Fuel gas	(23.50)	(16.62)
Total Operating Cost	140.51	154.54
Capital Cost	NC (1) = 1.32x10^6\$	PSA (1) = 13.11x10^6\$
Total Annual Cost (*TAC*)	51.49x10^6\$/yr = 141.07x10^3\$/D	58.45x10^6\$/yr = 160.14x10^3\$/D

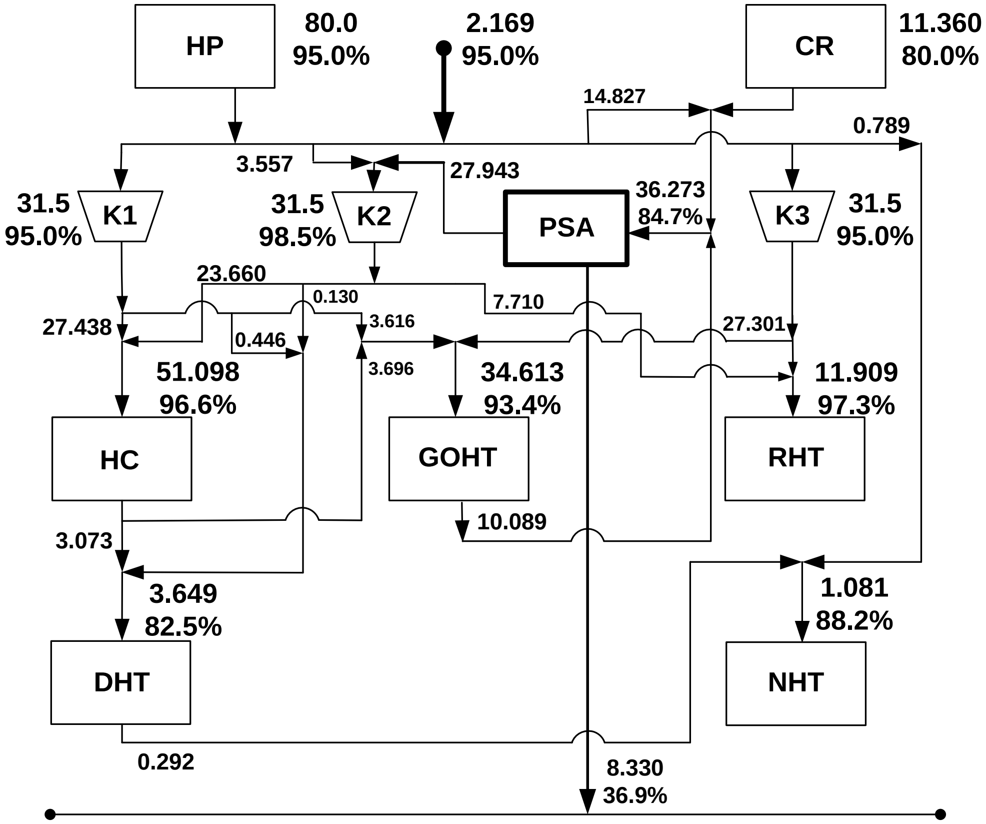

Figure 4.10. Hydrogen Shortage Case- Profit

4.5 Summary

In this chapter, an integrated refinery planning model was proposed to simultaneously solve for the optimal refinery hydrogen management strategy and operational planning. The model incorporates processing unit models, a compressor model, a purification unit model, and detailed economic models. The integrated model was then analyzed through different case studies, and important characteristics of the results were discussed. According to the presented results, different strategies must be adopted, depending on the objectives of the decision makers of the refinery.

The optimization results show that for gasoline case, there was no need for running the hydrogen plant with its maximum capacity, and that can save for refinery more than $6.5x10^6$\$/yr. In the maximum ATK production case, hydrogen availability proves to be a constraint that prevents the achievement of the planning objective for the refinery. In the maximum profit case, there was a hidden annual profit equivalent to more than \$7 million. Moreover, the necessity of having an integrated production planning model for the refinery decision maker was illustrated.

The proposed model is able to successfully integrate hydrogen management and production planning. Hydrogen should not be treated as a refinery utility as has been done in the past. Instead, it should be considered as a part of the overall refinery system, and doing so will ensure better profit margins for the refinery. The integrated model presented in this work has been demonstrated to be an efficient tool for assisting with appropriate production planning in petroleum refineries.

CHAPTER 5

OVERALL INTEGRATION OF HYDROGEN AND CO_2 MANAGEMENT WITHIN REFINERY PLANNING

5.1 Introduction

Refineries have to consider many factors when establishing the new CO_2 emission levels: a) identifying the CO_2 emission sources, b) assessing the overall allowable quantity that can be released to the atmosphere, and c) evaluating available mitigation options and their costs. In this chapter, we will accommodate the above-mentioned factors in a mathematical refinery CO_2 model that can be integrated with the overall refinery-planning model.

The objective of this chapter is to develop an integrated model, including processing planning, hydrogen network, and CO_2 emissions in refineries, that will allow assessment and maximization of overall profits by increasing the revenue of products sold and reducing the cost of hydrogen alternatives and CO_2 mitigation options. The model will be able to select the best refinery CO_2 strategy between available mitigation alternatives to achieve a given reduction target.

This chapter is organized as follows. The refinery CO_2 problem statement is presented in the next section. In section 5.3, the proposed model formulation is illustrated. Then, a computational study is carried out to evaluate the performance of the model in section 5.4. This chapter ends with concluding remarks.

5.2 Problem Statement

The CO_2 management strategy consists of three main steps. The first step is to identify the emission sources from the refinery processes. The second step is to present options and alternatives for dealing with the emissions in each particular area. The third step is to model the emissions and options of mitigation in a mathematical representation to decide on which options to implement for the refinery. Each mitigation option described will have a different impact on the refinery emissions, each will interact with each other, and each has a different capital and operating cost.

The three main areas of the refinery emissions (fuel, hydrogen and FCC) are modeled with the considered mitigation options (balancing, fuel switching and capture process) to form the CO_2 management model. The model will select the best route to meet the desired reduction target. The goal of this chapter is to develop an integrated model of processing units, hydrogen network, and CO_2 emissions in refineries, that will allow assessment and maximization of overall profits by increasing the selling products revenue, and reduce the cost for hydrogen elements and CO_2 mitigation options.

The CO_2 emissions in a refinery consist of sources i = {fuel or process derived} and mitigation options g = {balancing, fuel switching, and capturing technology}. The emissions (E) from the processing units, as well as the mitigation options cost for these emissions are optimization variables.

The refinery CO_2 problem to be addressed in this chapter can be stated as follows,
"*what is the best CO_2 strategy a refinery can select in order to meet a given emission reduction targets, while maximizing the overall profit and satisfying the product demand and specifications, and the hydrogen requirements quantity and purity?* "

The mathematical equivalent of the problem statement above consists of maximizing an objective function while observing equality and inequality constraints. The problem is modeled mathematically and can be written as the following Mixed Integer Non-Linear Programming (MINLP):

$$\max_{x,y} f(x,y) \qquad \text{(objective function)}$$

such that,

$$h(x,y) = 0 \qquad \text{(equality constraints)}$$

$$g(x,y) \leq 0 \qquad \text{(inequality constraints)}$$

$$x \in X \leq R^n \qquad (x \text{ is a vector of continuous variables})$$

$$y \in Y = \{0,1\} \qquad (y \text{ is a vector of binary variables})$$

Variables

- Continuous variables, x, are real numbers that may represent CO_2 emissions from processing units.
- Binary variables, y, are assigned (0-1) to represent the selection of the potential mitigation options, such as fuel switching or installment of new MAE process.

Objective Function

The objective is to maximize the overall refinery profit. In this chapter, $f(x,y)$ is the same objective function of Chapter 4, adding on it the retrofitting cost associated with CO_2 strategy, and capital and operating cost of the new equipments installed.

Constraints

- $h(x,y) = 0$
    a) CO_2 emissions constraints: the emissions from a processing unit.
- $g(x,y) \leq 0$
    a) Target emission constraint: the maximum CO_2 emissions allowed.
    b) Assignment constraints: the upper and lower constraints to assign value to a variable, such as emissions quantity or mitigation option cost.

5.3 Model Formulation

In this research, we will consider three different mitigation alternatives for CO_2 emission reduction:

1. Balancing or load shifting that considers the adjustment of production throughput across the refinery units to reduce CO_2 emissions.
2. Fuel switching in which we reduce emissions by selecting to switch from one type of fuel to another, (essentially switching from fuel oil to natural gas).
3. Capture technology, which considers installment of capture process to reach high levels of CO_2 reduction.

CO_2 emissions in petroleum refinery are emitted either from burning fuel on processing unit furnace or from the process itself as a by-product. In this research, all but two processing units are using fuel oil as the current furnace fuel; two units (hydrogen plant and FCC) are using natural gas. The proposed model will be incorporated with our previous model presented in Chapter 4. We will adopt the same refinery configuration as described in Chapter 3, see Figure 3.1. First, each emission source will be mathematically developed. Then, the CO_2 model will be formulated to include the emissions sources and the mitigation options cost. The objective function of the overall integrated refinery model will be updated to include the CO2 strategies cost.

5.3.1 CO_2 Emissions Sources

CO_2 emissions sources, as described earlier, are identified to be from fuel combustion or with the process as a by-product. Fuel-derived emissions of each unit $i \in I$ are calculated by multiplying the emission factor of each fuel EF_{fuel} by the unit fuel consumption FC_i, which is a function of the inlet flowrate:

$$E_i = EF_{fuel}\ FC_i \qquad \forall i \in I \qquad (5.1)$$

For the process-derived emissions, a hydrogen plant and FCC units are the two major sources in the refinery. The CO_2 emissions from the hydrogen plant and FCC are a function of processing unit variables.

The hydrogen plant produces significant CO_2 emissions that may be vented to the atmosphere. The amount of CO_2 emitted depends on the carbon content of the feedstock. Different approaches are available for estimating CO_2 emissions from a hydrogen plant. For natural gas feed, which is the case for this study, and based on hydrogen production rate and stoichiometric ratio of H_2 produced to CO_2 produced, the CO_2 emissions can the be calculated from the following equation:

$$EP_{HP} = HPR \times \frac{1\,CO_2}{4\,H_2} \times \frac{MW_{CO_2}}{MVC} \tag{5.2}$$

Where,

EP_{HP} = HP emissions of CO_2 in units of mass per year

HPR = rate of hydrogen production in scf per year

MW_{CO_2} = molecular weight of CO_2

MVC = molar volume conversion

The FCC unit strips off the coke deposits on the catalyst by continuously burning in the regenerator section of the unit. The coke burned is assumed to proceed completely to CO_2. The CO_2 emissions can be expressed as:

$$EP_{FCC} = RC \times CFC \times \frac{MW_{CO_2}}{MW_C} \tag{5.3}$$

Where,

EP_{FCC} = FCC emissions of CO_2 in units of mass per year

RC = rate of coke burn in units of mass per year

CFC = carbon fraction in the coke burned

MW_{CO_2} = molecular weight of CO_2

MW_C = molecular weight of carbon

5.3.2 CO_2 Mitigation Options

The three mitigation options included in this research are balancing, fuel switching, and capture processes. The CO_2 emissions can be reduced by applying the balancing option through reducing the feed to the highest CO_2 emitter-processing unit. For further reduction of the emissions from the furnace, a switching option is a good alternative. The fuel used in the furnace can be switched to lower CO_2 emission fuel such as natural gas, which means lower emission factor EF_{fuel}':

$$E_{i,\,Switch} = EF_{fuel'}\ FC_i + EP_i \qquad \forall i \in I \qquad (5.4)$$

For high level targets of CO_2 reduction, it can be achieved by applying capture technology to the emissions from processing unit:

$$E_{i,\,Capture} = \left(EF_{fuel}\ FC_i + EP_i\right) \times \left(1 - \varepsilon_{Capture}\right) \qquad \forall i \in I \qquad (5.5)$$

where ε_{Cap} represents the efficiency of a given capture process.

5.3.3 CO_2 Management Model

Equations 1-5 can be gathered in general formulation of emission flowrate of a processing unit $i \in I$ over multiple mitigation alternatives $g \in G$ by:

$$E_i = \sum_g E_{i,g}\ XC_{i,g} \qquad \forall i \in I \qquad (5.6)$$

where $XC_{i,g}$ is a binary variable representing the selection of different mitigation alternatives. In order to represent Equation 5.6, we first will redefine the binary variable $XC_{i,g}$ in terms of either fuel switching $XC_{i,Switch}$ or capture processes $XC_{i,Capture}$. Using appropriate upper bounds on different emissions, Equation 5.6 can be written as a set of inequality constraints. Furthermore, for the three mitigation alternatives (balancing, fuel switching, and capture technology) a set of inequality constraints will be derived. For the balancing alternative, the constraints can be written as:

$$E_i \le \left(EF_{fuel}\ FC_i + EP_i\right) + UE_i\left(\sum_{g\in Switch} XC_{i,g} + \sum_{g\in Capture} XC_{i,g}\right) \qquad \forall i \in I \qquad (5.7)$$

$$E_i \ge \left(EF_{fuel}\ FC_i + EP_i\right) - UE_i\left(\sum_{g\in Switch} XC_{i,g} + \sum_{g\in Capture} XC_{i,g}\right) \qquad \forall i \in I \qquad (5.8)$$

where UE_i is an upper limit on CO_2 emission. On the other hand, fuel switching alternative from $fuel$ to $fuel'$ constraints can be written as:

$$E_i \le \left(EF_{fuel'}\ FC_i + EP_i\right) + UE_i\left(1 - \sum_{g\in Switch} XC_{i,g} + \sum_{g\in Capture} XC_{i,g}\right) \qquad \forall i \in I \qquad (5.9)$$

$$E_i \ge \left(EF_{fuel'}\ FC_i + EP_i\right) - UE_i\left(1 - \sum_{g\in Switch} XC_{i,g} + \sum_{g\in Capture} XC_{i,g}\right) \qquad \forall i \in I \qquad (5.10)$$

Similarly, applying a capture process to a given processing unit $i \in I$ can be expressed as:

$$E_i \le \left(EF_{fuel}\ FC_i + EP_i\right) \times \left(1 - \varepsilon_{Capture}\right) + UE_i \left(1 + \sum_{g \in Switch} XC_{i,g} - \sum_{g \in Capture} XC_{i,g}\right) \qquad \forall i \in I \qquad (5.11)$$

$$E_i \ge \left(EF_{fuel}\ FC_i + EP_i\right) \times \left(1 - \varepsilon_{Capture}\right) - UE_i \left(1 + \sum_{g \in Switch} XC_{i,g} - \sum_{g \in Capture} XC_{i,g}\right) \qquad \forall i \in I \qquad (5.12)$$

In addition, for a given processing unit $i \in I$ only one fuel, one capture process and a single mitigation alternative is applied. Respectively, this can be expressed as:

$$\sum_{g \in Switch} XC_{i,g} \le 1 \qquad \forall i \in I \qquad (5.13)$$

$$\sum_{g \in Capture} XC_{i,g} \le 1 \qquad \forall i \in I \qquad (5.14)$$

$$\sum_{g \in Switch} XC_{i,g} + \sum_{g \in Capture} XC_{i,g} \le 1 \qquad \forall i \in I \qquad (5.15)$$

The total CO_2 emission is controlled by specifying a reduction target:

$$\sum_i E_i \le (1 - ERT\ )\ TE \qquad (5.16)$$

where ERT and TE represent the CO_2 emission reduction target and the current total emission, respectively. Total emission is obtained from the base case (no mitigation alternatives) of a given refinery.

The best CO_2 strategy for refineries can be selected as a function of the cost of the mitigation options and the desired level of reduction. To avoid nonlinearity in the objective function, the cost will be defined by introducing new variables and an additional set of bounding constraints. Let us introduce new variables $SWAC_i$ representing the annualized cost of fuel switching and CAC_i representing the annualized capture process cost. We then can add the following set of bounding constraints on both costs.

For switching cost $SWAC_i$:

$$SWAC_i \le UCS_i \sum_{g \in Switch} XC_{i,g} \qquad i \in I \tag{5.17}$$

$$SWAC_i \ge Cost_{switch} E_i - UCS_i \left(1 - \sum_{g \in Switch} XC_{i,g}\right) \qquad i \in I \tag{5.18}$$

$$SWAC_i \le Cost_{switch} E_i + UCS_i \left(1 - \sum_{g \in Switch} XC_{i,g}\right) \qquad i \in I \tag{5.19}$$

where UCS_i is properly selected to provide upper bound on switching cost for each processing unit $i \in I$, and $Cost_{switch}$ represents the cost of switching furnace fuel for each unit of flowrate. Similarly, another set of bounding constraints is derived for the capture process cost CAC_i:

$$CAC_i \le UCC_i \sum_{g \in Capture} XC_{i,g} \qquad i \in I \tag{5.20}$$

$$CAC_i \ge Cost_{Capture} E_i - UCC_i \left(1 - \sum_{g \in Capture} XC_{i,g}\right) \qquad i \in I \tag{5.21}$$

$$CAC_i \le Cost_{Capture} E_i + UCC_i \left(1 - \sum_{g \in Capture} XC_{i,g} \right) \qquad i \in I \qquad (5.22)$$

where UCC_i is properly selected to provide upper bound on capturing cost for each processing unit $i \in I$, and $Cost_{Capture}$ represents the cost of installing a capture process for each unit of flowrate.

Equations 5.7–5.22 represent the refinery CO2 management model. This model will be integrated with the planning and hydrogen model proposed in Chapter 4 to form the integrated refinery-wide planning model. The objective function for the integrated model can be formulated to include the CO2 mitigation options cost:

$$\begin{aligned} Maximize \quad & \sum_{i \in B} sp_i\, F_i - \sum_{i \in E} ce_i\, F_i - \sum_{i \in I} cx_i\, F_i \\ & - \left[OD \sum_h OC_h + AF \left(\sum_n CCC_n + \sum_m CCP_m \right) \right] \qquad (5.23) \\ & - \sum_i \left(SWAC_i + CAC_i \right) \end{aligned}$$

The above objective function represents the ordinary production planning objective (raw material and units operation cost subtracted from revenues), hydrogen management strategy (hydrogen network operating cost plus new hydrogen equipments annualized capital cost), and CO_2 management strategy (CO_2 mitigation annualized capital cost), respectively.

5.4 Results and Discussions

In order to illustrate the proposed model performance, different case studies have been developed on the same refinery used in Chapter 3, see Figure 3.1. The model objective function is to maximize the refinery's overall profit while maintaining the hydrogen requirements and satisfying the CO_2 reduction target levels. The model solved different CO_2 reduction targets. In addition to the base case study, the other studies are categorized as follows:

- Base case: Solve the model without any CO_2 mitigation option.
- Balancing case: Solve the model considering only flow rate balancing as the CO_2 mitigation option. This is just to show that balancing can affect the results.
- Switching case: Solve the model considering two mitigation options (flow rate balancing and fuel switching) to meet certain CO_2 reduction targets.
- Capturing case: Solve the model considering all the mitigation options (flow rate balancing, fuel switching, and CO_2 capture technology) to meet certain CO_2 reduction targets.

5.4.1 Base case:

The objective of this case is to identify the CO_2 emissions sources and the contribution of each processing unit in refinery. This goal can be achieved through solving the integration model (processing unit planning model and hydrogen management model) without any CO_2 reduction target.

Figure 5.1 shows that the major source of the refinery CO_2 emission is the emission from the fuel used in the combustion furnace, which represents 67% of total refinery CO_2 emission. Also, it can be seen that accounting for hydrogen plant in both refinery planning problem and CO_2 management problem has a great impact in the final result, see Figure 5.2.

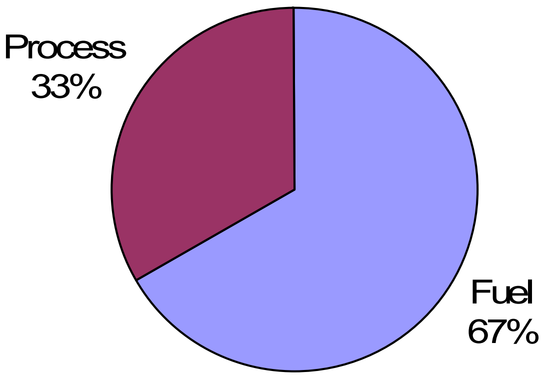

Figure 5.1. CO_2 Emission Categories

Figure 5.3 illustrates the CO_2 emissions from each unit, process and combustion, without any mitigation options. Fuel oil is used in combustion for seven units (CDU, GOHT, HC, CR, RHT, DHT, and NHT), where natural gas is used for two units (HP and FCC). The emission for the HP and the FCC include all CO_2 emissions from each unit. The results show a total CO_2 emission of 1650 KTon/yr and a profit of $747.9x10^6$ \$/yr.

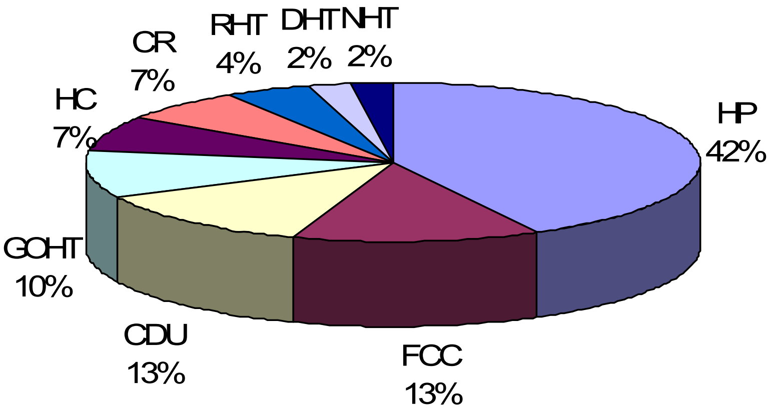

Figure 5.2. Processing units CO_2 Emission

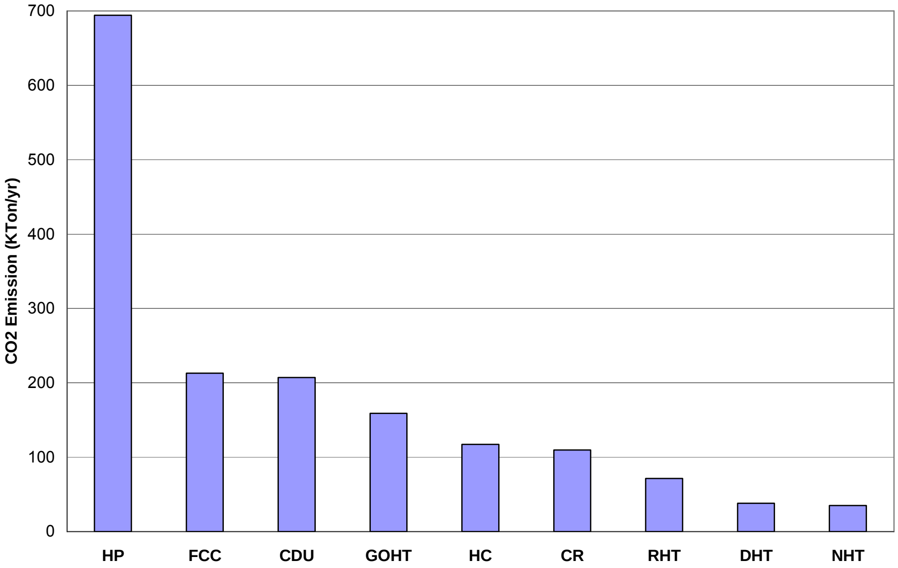

Figure 5.3. Base Case - CO_2 Emission

5.4.2 Balancing Case:

The objective of this case is to show that low CO_2 reduction targets can be achieved by shift load from one processing unit to another. In this case, it is found that CO_2 balancing is a good option only when the CO_2 reduction targets are less than 5%. This reduction can be achieved by simply decreasing the flow rate for the units that emit more CO_2 such as the HP and the FCC and increase production from units that emit less CO_2 such as the NHT and the DHT.

For the 3% CO_2 reduction target (Figure 5.4), the production from HP, the largest CO_2 emission source, is reduced by 4.5% (remove 31 KTon/yr). It can be notice that FCC unit production has increased by 14%. However, HC unit has reduced by similar amount. In addition, CR unit has significant reduction emission, which is around 32 KTon/yr. The profit for the 3% CO_2 reduction is 747.1×10^6 \$/yr with a decrease by 0.1% from the base case. The base case is shown in each figure for comparison.

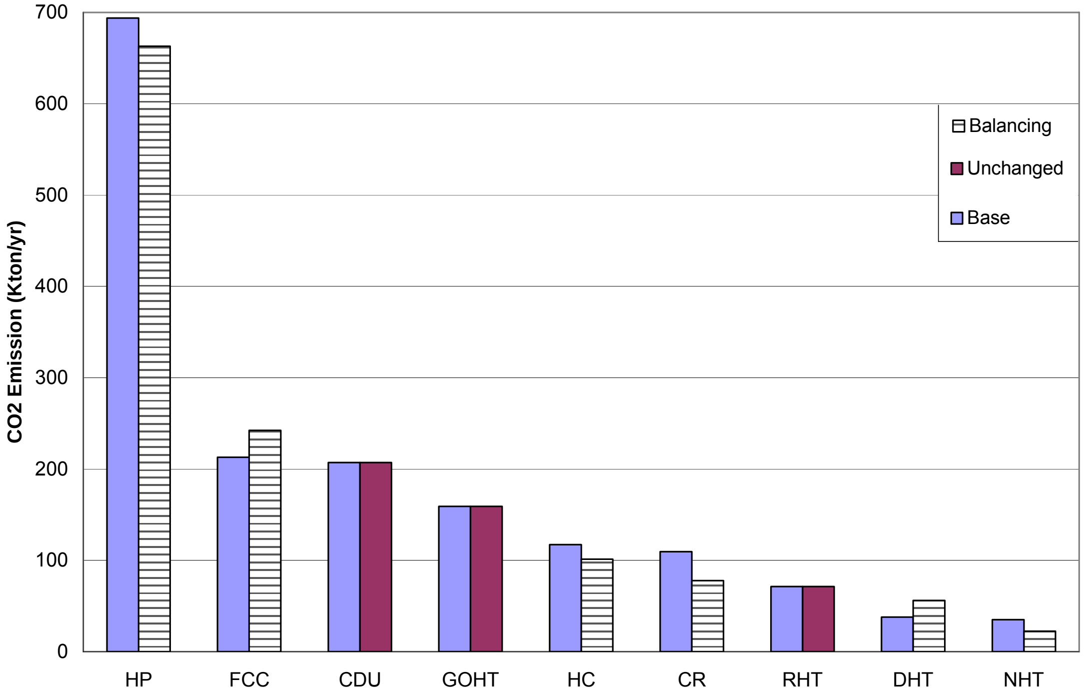

Figure 5.4. 3% CO_2 Reduction

Table 5.1 shows the results for different CO_2 reduction targets, where the only CO_2 mitigation option is forced to be balancing. The HP production is included in each reduction target to show the important of integrating both hydrogen and CO_2 managements within the refinery-planning model. Figure 5.5 illustrates that profit reduction is increased as the CO_2 reduction target increased. Nevertheless, when the model solved without forcing any CO_2 mitigation option, the maximum CO_2 reduction can be achieved is 3%.

Table 5.1. CO_2 reduction Targets for Balancing Case

CO_2 Reduction Target (%)	Total Emission (KTon/yr)	Profit (10^6 \$/yr)	Reduction in Profit (%)	HP (MMSCFD)
Base	1650.0	747.9	0.00	80.0
1	1633.5	747.7	0.03	80.0
3	1600.5	747.1	0.11	76.4
5	1567.5	746.2	0.23	69.7
10	1485.0	733.0	2.00	60.8

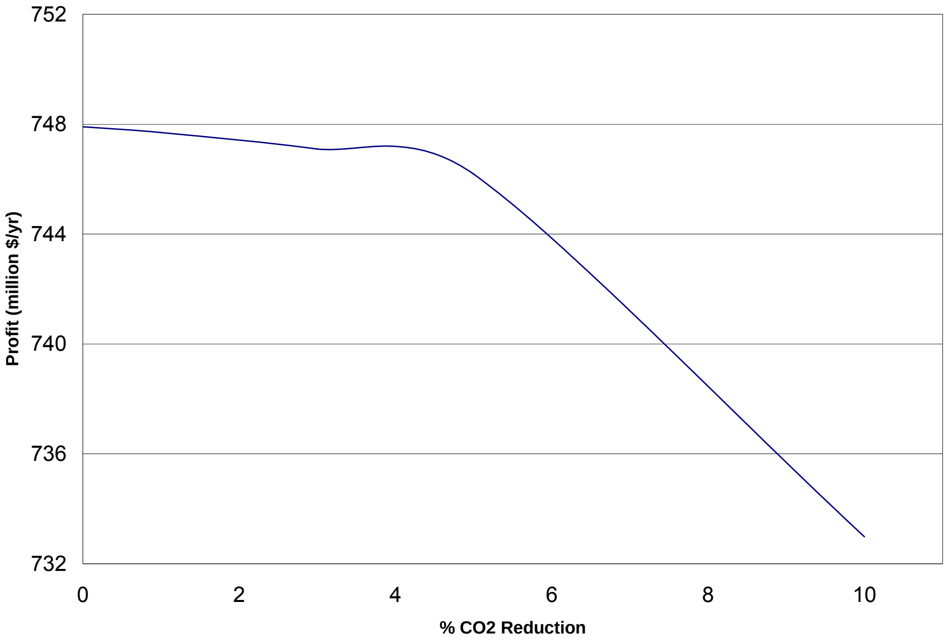

Figure 5.5. Balancing Case: Profit for Different CO_2 Reduction Target

From the results above, more CO_2 mitigation options need to be considered for higher reduction targets. These include fuel switching and CO_2 capture.

5.4.3 Switching Case:

In this case, fuel switching to natural gas from the current used fuel oil is considered. The cases included here are those with balancing and fuel switching are the only CO_2 mitigation options. As indicated in the previous case, Table 5.1, up to 10% CO_2 reduction can be achieved by balancing only. In this case, switching proves it is a better choice for low and medium reduction targets level.

Figure 5.6 shows the results for 5% CO_2 reduction target. Similarly, it is observable that a reduction by 5.5 MMSCFD on the HP production is significant to reduce CO_2 emissions. This led to reduce the HC unit production and increase the FCC unit production. More diesels are produced and DHT unit runs with the maximum capacity and model chose to switch DHT unit to run with natural gas. The profit (746.6×10^6 \$/yr) decreases with higher CO_2 reduction target due to the retrofit cost for switching. The natural gas cost and economic data are given in Appendix D.

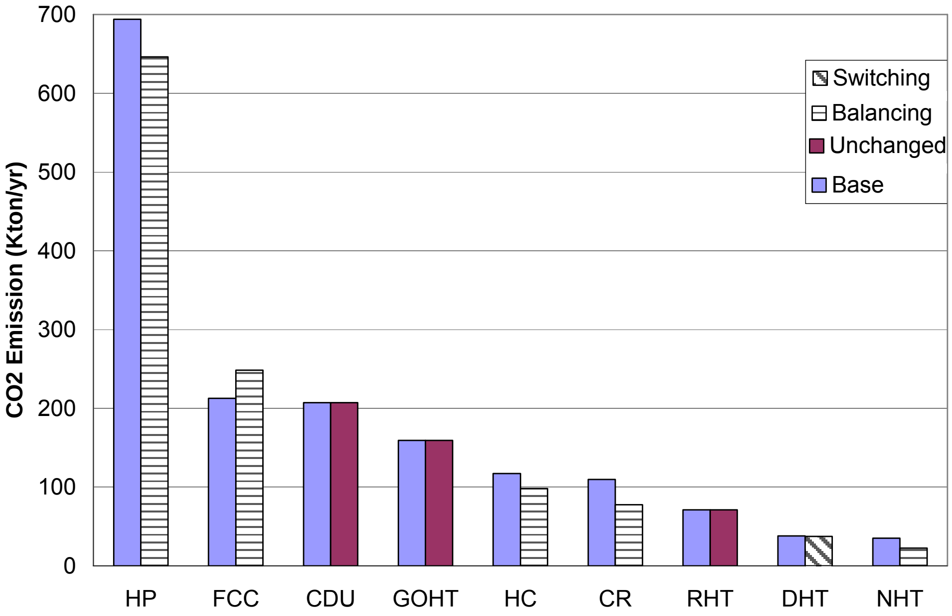

Figure 5.6. 5% CO_2 Reduction

For 10% reduction target, see Figure 5.7. The model tends to switch more units to natural gas (CR, RHT, and NHT). HP production was the lowest among all other reduction targets (68 MMSCFD). The profit decreased by $2.7x10^6$ \$/yr with a total CO_2 mitigation cost of $1.1x10^6$ \$/yr.

As expected for 20% reduction target, even more units will be switched to natural gas. Figure 5.8 shows that all units (CDU, GOHT, HC, CR, RHT, and DHT) expect NHT unit are chosen to be switched to natural gas. The profit with a $741x10^6$ \$/yr is reduced by almost 1% (around $6x10^6$ \$/yr).

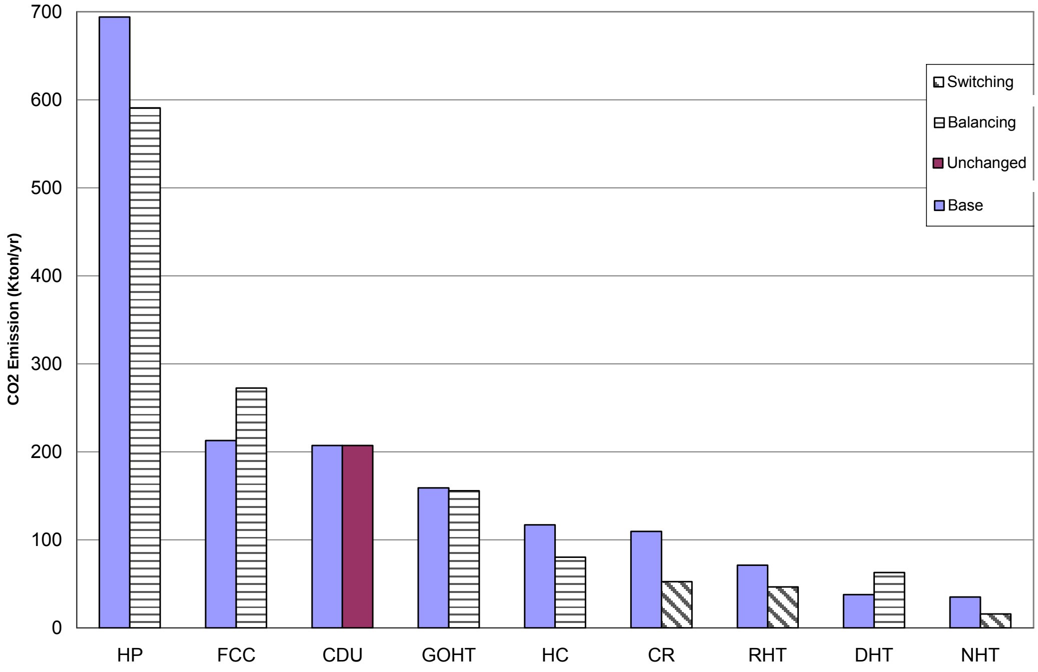

Figure 5.7. 10% CO_2 Reduction

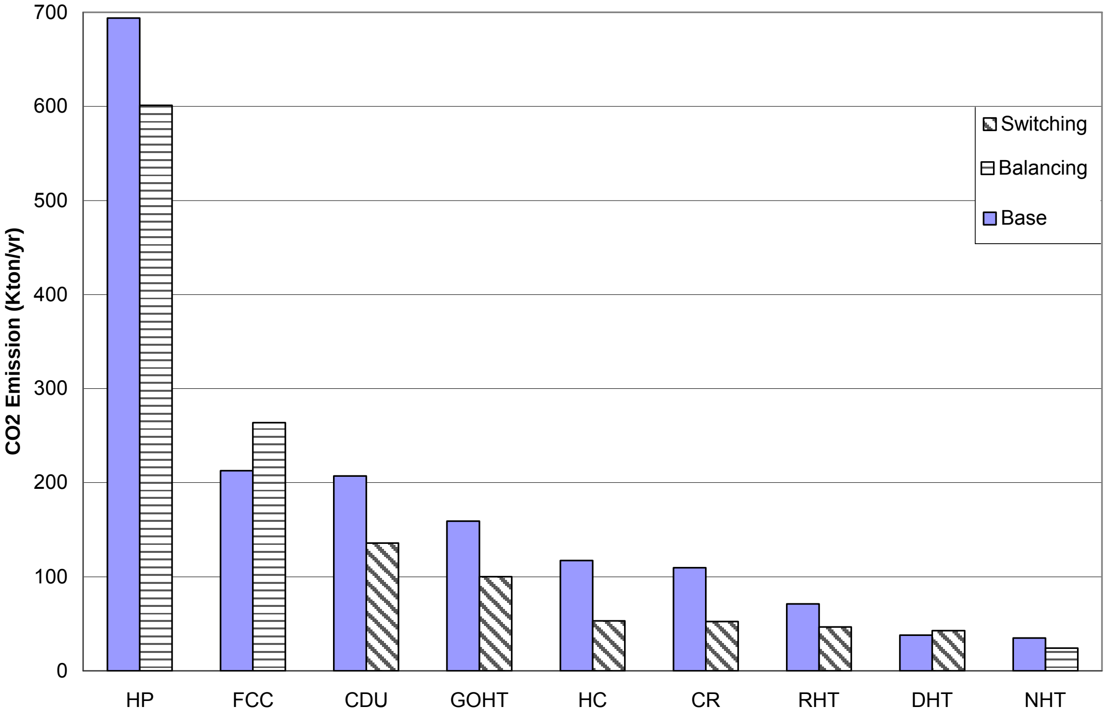

Figure 5.8. 20% CO_2 Reduction

Table 5.2 gives a summary of the results for the switching case. It shows the total CO_2 emissions, profit, profit reduction%, and HP production for each reduction target. The mitigation cost and action are listed for every CO_2 reduction target. For 10% reduction, the profit decreases by only 0.4% since only three units are switched to natural gas. This case shows that including fuel switching to the mitigation options led to a better result, which improves the profit by 13.6×10^6 \$/yr over the balancing option only. As more units are switched to run with natural gas, the profit decreases by a noticeable percent. For higher reduction targets, more than 20%, fuel switching still can be a valid CO_2 mitigation option. However, this lead to a sharp decline in the profit, which indicates that other mitigation options (such as capturing technology) must be considered. Figure 5.9 illustrates the overall refinery profit as a function of CO_2 reduction target.

Table 5.2. CO_2 Reduction Targets for Switching Case

Reduction Target (%)	Total Emission (KTon/yr)	Profit (10^6 \$/yr)	Profit Reduction (%)	HP (MMSCFD)	Mitigation Cost (10^6 \$/yr)	Mitigation Action (Unit Switched)
Base	1650.0	747.9	0.00	80.0	0.0	-
5	1567.5	746.6	0.17	74.5	0.1	DHT
10	1485.0	745.0	0.39	68.1	0.4	RHT-NHT-CR
15	1402.5	743.2	0.62	68.0	0.8	CDU-DHT-CR
20	1320.0	741.1	0.91	69.3	1.5	CDU-GOHT-RHT-DHT-HC-CR
25	1237.5	686.1	8.27	68.0	1.6	CDU-GOHT-RHT-DHT-NHT-HC-CR
30	1155.0	646.0	13.63	66.0	1.6	CDU-GOHT-RHT-DHT-NHT-HC-CR

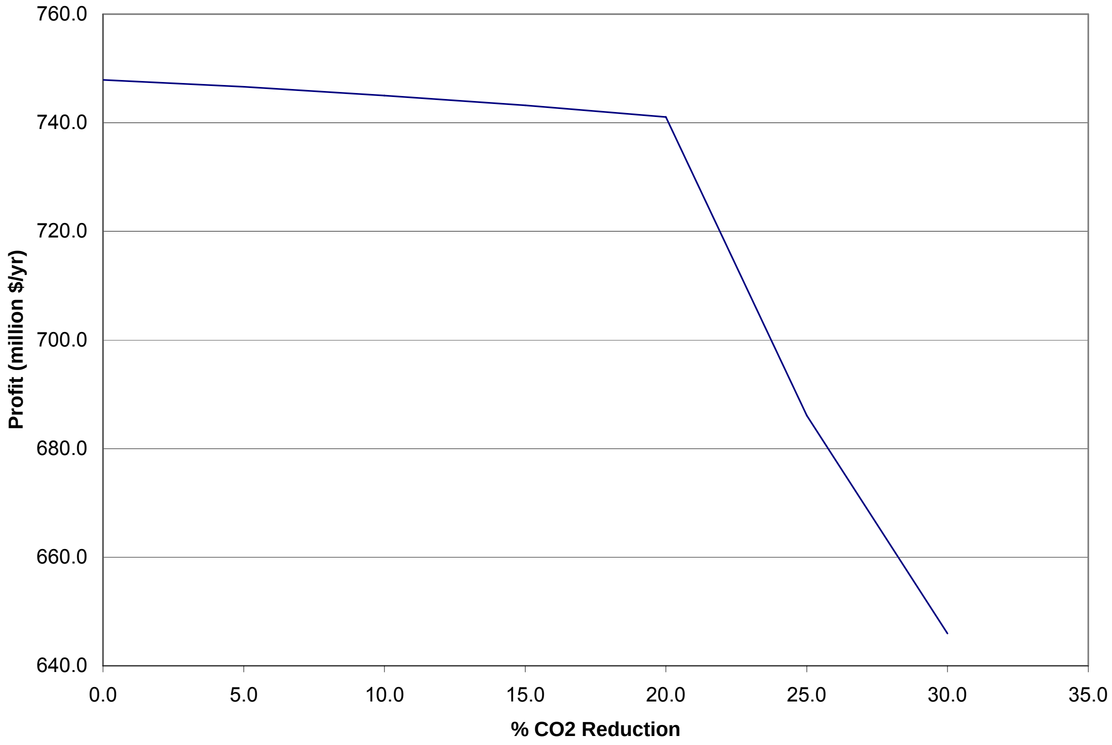

Figure 5.9. Switching Case: Profit for Different CO_2 Reduction Target

5.4.4 Capturing Case:

In this case, all the CO_2 mitigation options (balancing, fuel switching and CO_2 capture process) are considered in solving the integrated model to achieve higher level of CO_2 reduction targets. The capture process under consideration is MEA process since it is the only commercially available at this scale.

Although 30% CO_2 reduction can be achieved by switching, as shown in previous case, this case shows that capturing option is a better alternative to achieve the same and high percentage of CO_2 reduction. Figure 5.10 shows the results for 30% CO_2 reduction. Capture process is selected to be installed for the FCC and HC units, and fuel switching is selected to natural gas for all other processing units. The profit is $730x10^6$ \$/yr, which is higher than the switching case (without considering capturing) with an $84x10^6$ \$/yr.

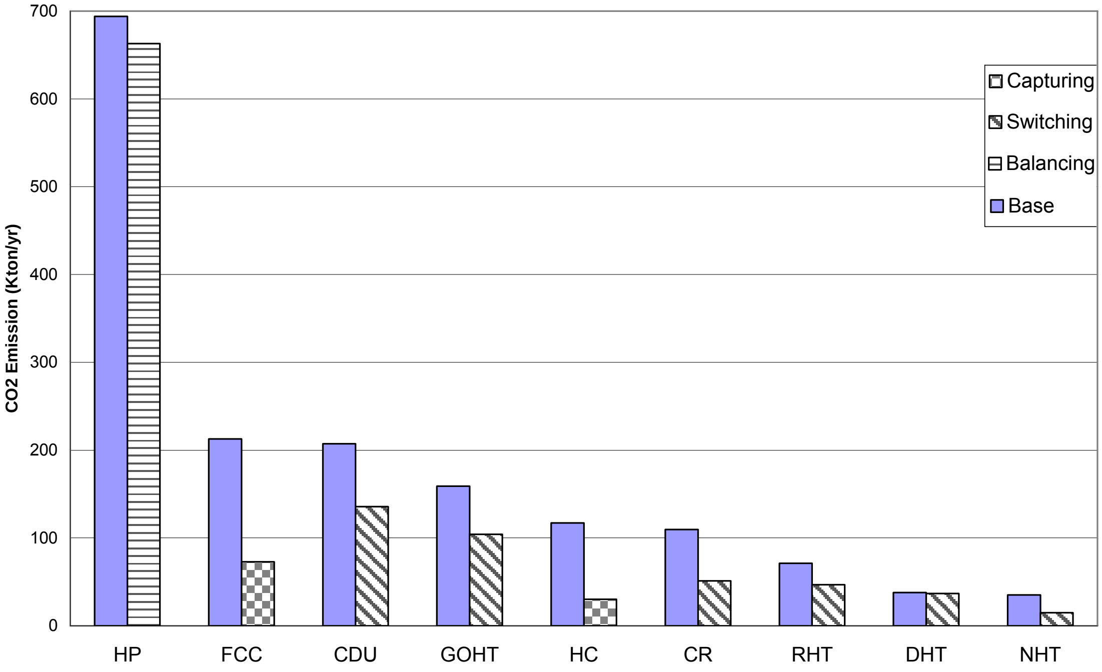

Figure 5.10. 30% CO_2 Reduction

It becomes necessary to capture the CO_2 emissions from the HP to achieve higher reduction targets, since HP is the major source of CO_2 emissions in refinery. Figure 5.11 illustrates the 50% CO_2 reduction target results. It shows that four units (HP, HC, CR, and NHT) are chosen to install the capture process, and other four units (CDU, GOHT, RHT, and DHT) are chosen to switched fuels to natural gas. The CO_2 reduction cost is 36.5x10^6 \$/yr which reduce the refinery profit to 710x10^6 \$/yr.

The maximum CO_2 reduction target was around 70%, see Figure 5.12. The results show that CO_2 emissions should be captured from six units and only NHT has to be switched fuel to natural gas. A summary of results for capturing case is given in

Table 5.3. It shows that the profit decreases by about 2.4% at 30% CO_2 reduction target. About 8% drop in profit is noticed at 70% CO_2 reduction when CO_2 emissions from all units are captured.

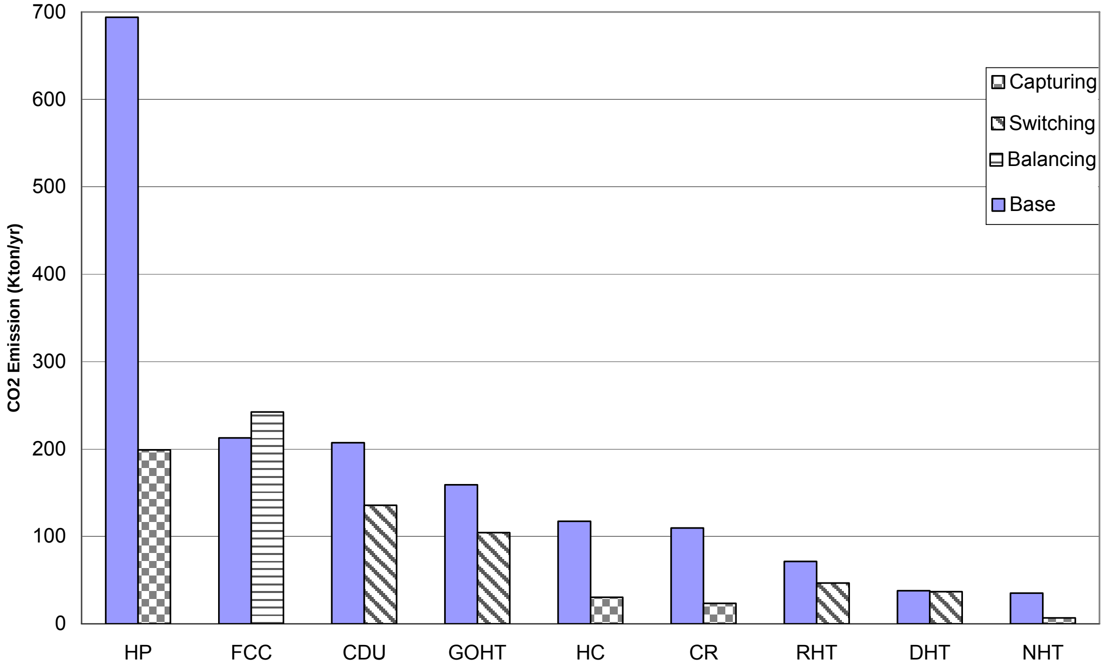

Figure 5.11. 50% CO_2 Reduction

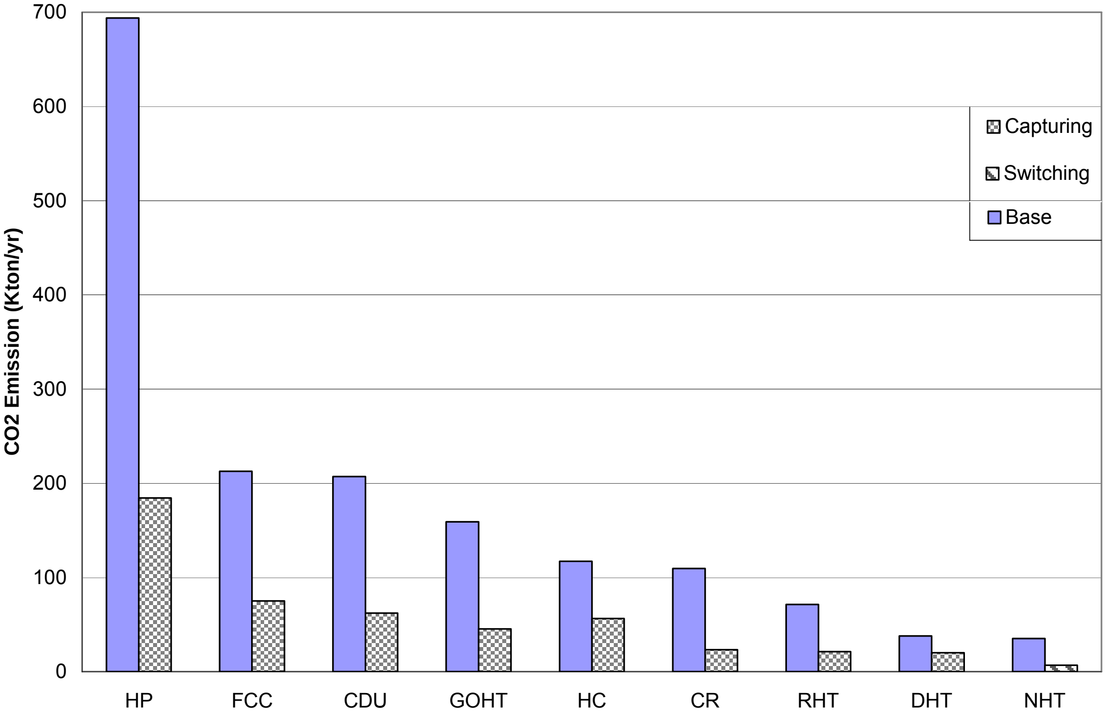

Figure 5.12. 70% CO_2 Reduction

Table 5.3. CO_2 Reduction Targets for Capturing Case

Reduction Target (%)	Total Emission (KTon/yr)	Profit (10^6 \$/yr)	Profit Reduction (%)	HP (MMSCFD)	Mitigation Cost (10^6 \$/yr)	Mitigation Action
Base	1650.0	747.9	0.00	80.0	0.0	-
30	1155.0	730.0	2.39	74.6	17.06	SW: CDU-GOHT-CR-RHT-DHT-NHT CAP: FCC-HC
40	990.0	719.8	3.75	69.5	25.93	SW: CDU-CR-RHT-DHT CAP: HP
50	823.0	710.6	4.98	76.4	36.47	SW: CDU-GOHT-RHT-DHT CAP: HP-HC-CR-NHT
60	660.0	701.3	6.23	76.4	45.80	SW: CDU-GOHT-RHT-DHT CAP: HP-FCC-HC-CR-NHT
70	495.0	688.4	7.95	70.9	56.83	SW: NHT CAP:HP-FCC- CDU-HC-GOHT-CR-RHT-DHT

Figure 5.13 shows the profit for each reduction target for capturing case study. Only higher reduction target is shown since no capture process is chosen to be applied for less than 30% reduction target. The profit decreases as more CO_2 emissions are captured from more units.

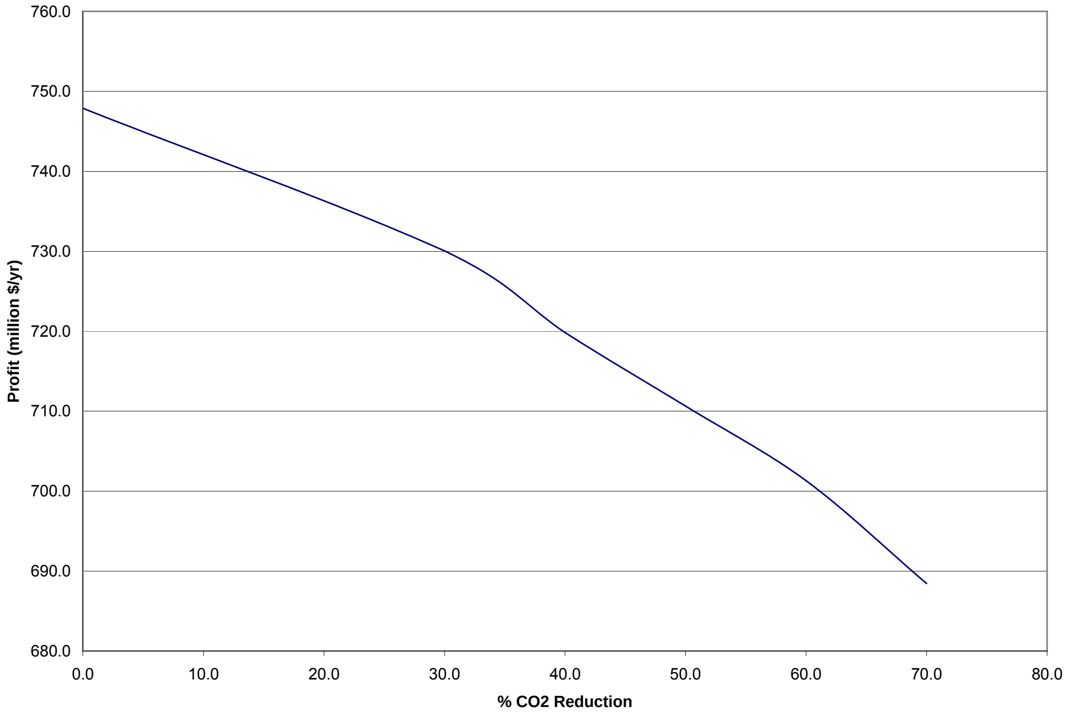

Figure 5.13. Capturing Case: Profit for Different CO_2 Reduction Target

5.5 Summary

In this chapter, the optimization problem of CO_2 emissions from a petroleum refinery was addressed. A MINLP model was developed to support the refinery decision in selecting the optimal CO_2 reduction strategies. The refinery CO_2 emission major sources are fuel system, hydrogen plant, and FCC unit, were formulated, as well as the CO_2 mitigation options. In this study, three mitigation options were considered: balancing, fuel switching, and capturing technology. The model was able to solve for the refinery processing planning model and the CO_2 management model simultaneously, since the model objective was to maximize the overall refinery profit, considering the capital and operating cost of the mitigation options, while meeting a certain CO_2 emissions reduction target.

Case studies with various reduction targets were carried out to test the model performance. It was shown that the balancing option can reach up to 10% reduction, but from an economical point of view, this option works well up to 3% reduction with a reduction in refinery profit of less than 0.2%. For the fuel switching option, it can achieve a maximum 30% reduction. However, the optimal reduction level for this option was 20%, with a reduction in the refinery profit of only 0.9%. The capacity of the unit was the controlling factor for this option; for example, for a higher reduction target CDU unit, which is the largest capacity unit in the refinery, the preferred choice was fuel switching. Finally, for the capturing option, it was found that any reduction target higher than 30% percent could never be reached by any option except capturing processes. Nevertheless, for 20% reduction, it was found that the capturing option works better that switching and saves $84x10^6$\$/yr for the refinery. Also, the maximum reduction target that the refinery can reach was 70%, with a great impact on the refinery profit (8% profit reduction).

The proposed model has been shown to integrate hydrogen management, CO_2 management, and production planning successfully. The integrated model presented in this chapter has been demonstrated to be an efficient tool for assisting production planning in refineries.

CHAPTER 6

CONCLUSIONS AND RECOMMENDATIONS

This chapter presents the major findings and conclusions from this dissertation. The petroleum refining industry was extensively studied and challenged in three areas: production planning, hydrogen network and, CO_2 emissions. At first, we will cover the significant outcome and highlight the novel contributions. Recommendations for further work will be stated and discussed at the end of this Chapter.

6.1 Conclusions

The three major challenging issues were identified, and solutions were provided for each problem. Starting with the nonlinear refinery planning model, which solves the production planning problem. Then, the refinery hydrogen management model, which solves the hydrogen network problem. Finally, the refinery CO_2 management model, which solve the CO_2 emissions problem. The conclusions of each area are as follows:

6.1.1 The Refinery Planning

The objective was to formulate a mathematical model that aims at maximizing the profit of selling final products with meeting properties specifications and market demands. Therefore, an accurate and efficient nonlinear refinery-planning model has been presented to satisfy this objective (Chapter 3). The following conclusions were drawn for this part of the research:

1. Rigorous NLP processing units' models offered the accuracy needed to represent the refinery processes. For example, the CDU unit model, through optimizing the CDU fractions cut-point temperature, determines the fractions

quantity and properties and show the greatest effect on other units' capacity and operation, and on the final products flow rates and quality.

2. The independency of modeling each processing unit enables the refiner to model any refinery configuration and to integrate new processing units or replace the existing units with new ones without major modifications.

3. The NLP planning model proved to minimize the quality give-away through embedding the blending correlations and manipulating the processing units operating variables resulting in large savings for the refinery.

4. In the maximum profit case study, the NLP planning model showed that optimizing the operating variables of the processing unit could increase the refinery profit.

5. The NLP planning model showed more reliable results and explored more viable potential from product blending by employing better planning strategy rather than the traditional linear models.

6.1.2 The Refinery Hydrogen Management

The objective was to offer a model that is able to attain maximum overall refinery profit and meet the hydrogen requirements with least cost. An integrated MINLP hydrogen management model with the planning model was presented to satisfy this objective (Chapter 4). The following conclusions were drawn for this part of the research:

1. In the hydrogen surplus case, maximum gasoline case, the model chose to reduce the hydrogen plant production and not to install any new equipments and this action saves the refinery more than $6.5x10^6$\$/yr.

2. In the hydrogen shortage case, maximum ATK case, the model chose to invest a $23.35x10^6$\$ on installing two new compressors and a PSA unit. This

investment allowed the refinery to achieve its objective with a payback period less than four years.

3. In the external hydrogen supplier case, the model was able to achieve a hidden annual profit equivalent to more than $7x10^6$\$. This case proves that hydrogen availability is a constraint that prevents the refinery from achieving maximum profit.

4. The MINLP model was able to successfully integrate hydrogen management and production planning and simultaneously solve for the optimal refinery strategy. Depending on the objectives of the refinery decision makers, different strategies must be adopted. In addition, the general format allows the model to be adapted in other chemical industries.

6.1.3 The Refinery CO_2 Management

The objective was to formulate a model that is able to find the best CO_2 management strategies for the refinery while achieving the maximum refinery profit. An integrated MINLP CO_2 management model with the integrated hydrogen management model was presented to satisfy this objective (Chapter 5). The following conclusions were drawn for this part of the research:

1. The balancing option showed to be the best option for low emissions reduction targets, although it can reach up to 10% reduction. For 3% emissions reduction, which is the optimal reduction level for this option, hydrogen plant was the big contributor in this reduction and this reduced the refinery profit by less than 0.2%.

2. For the fuel switching option, the optimal reduction level was 20%, with a reduction in the refinery profit by only 0.9%. As the reduction target increased, the large CO_2 emitter units were the target for fuel switching (like CDU unit).

3. The capture technology option is necessary for any reduction target above 30%. Although switching option can reach up to 30% reduction, it was found that the capturing option works better than the switching and save $84x10^6$\$/yr for refinery. The maximum reduction target refinery can reach was 70%, with a great impact on the refinery profit (i.e. 8% profit reduction).

4. The MINLP model proved to be supporting the refinery decision in selecting the optimal CO_2 reduction strategies. The model demonstrated to be an efficient tool in developing appropriate production plans in petroleum refineries.

6.2 Recommendations

An important goal of any thesis is to open new avenues for future research and identify areas where further development is required. The recommendations proposed by this thesis are as follows:

1. In the planning problem, thinking of integration and coordination between multi-site refineries would improve the overall result for each refinery. Exchange the light and heavy products between the refineries would enhance the processing unit conversion and the final products. The overall profit of the refinery should improve as well.

2. In the hydrogen network problem, the hydrogen inlet flowrate and purity and the purge streams purity were specified in advance as a constant parameter. However, in real situations, these values are changing frequently. Consequently, modeling the hydrogen network under conditions of uncertainty should provide a more robust design and better optimal result.

3. In the CO_2 emissions problem, the maximum CO_2 reduction target was bounded by the capture process efficiency. This study assumed capturing process efficiency as a

constant (70%). Therefore, it might be attractive to do more research on the capturing efficiency as an optimization variable or to include different types of capturing technology.

4. In the CO_2 emissions problem, this research did not include the emissions trading scheme (ETS) for CO_2 emissions, which has been introduced to comply with the Kyoto commitments. However, including ETS factor in the optimization model might change the CO_2 strategies selection in the refinery.

5. The size of the problem solved in this thesis is considered to be a large-scale. The number of continuous and integer variables are high and the difficulty of solving this problem is tremendous. This in addition to the nonlinearity nature of the problem. Since, the current commercial solvers, such as DICOPT or SSP, are consuming long solution time or sometimes fail to find any solution. Thus, more studies are required to develop efficient algorithms that allow for solving the problem in less time or to find the global solution.

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APPENDIX A

REFINERY PROCESSING UNIT MODELS

A.1 CDU Model

The crude oil should be characterized before being fed to the CDU. One of the key attributes for characterizing the hydrocarbons composing crude oils is by boiling point. This attribute is determined through laboratory test methods by measuring the temperature at which the components of the crude oil will evaporate at a given pressure (typically atmospheric pressure unless stated to be a different pressure basis). A true boiling point (TBP) curve is developed as a part of the crude assay in order to determine the liquid volume percent of the crude oil that evaporates relative to temperature at atmospheric pressure (Watkins, 1979; Maples, 1993; Gary, 1994). Figure A.1 shows the TBP curve for the crude assay (Alaska) used in this study. The cuts produced in the CDU are shown in Table A.1.

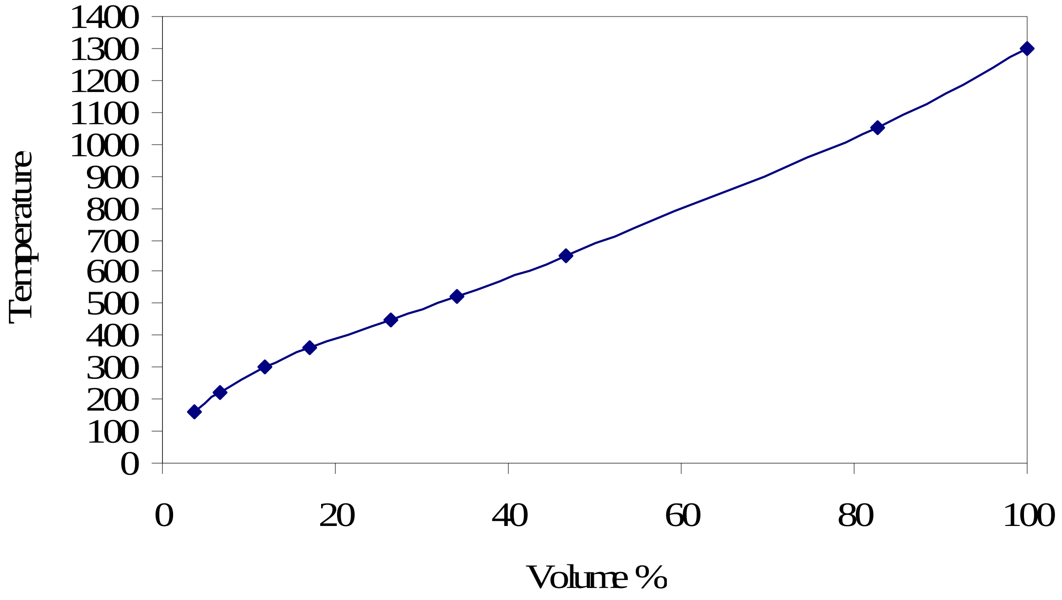

Figure A.1. TBP Distillation Curve (Crude: Alaska)

Table A.01. Boiling Range of Typical Crude Oil Fractions

Fraction	**TBP – Boiling range (^{0}F)**
SRLN	90 – 220
SRHN	180 – 380
Kerosene	330 – 520
Diesel	420 – 630
VGO	610 – 1050
Residue	950 +

The mathematical model for the crude distillation unit is expressed by constraints similar to the general constraints (3.2)-(3.7) discussed earlier. The same notation will be used here, where the unit (*i*) for this case will be the CDU unit. The operating variable of the CDU unit is the cut-point temperature for fraction (*s*), $x = TE_{CDU}$. Also, the products stream for the CDU unit are fractions (*s*) ($s \in S_{CDU}$ = *LPG*, *SRLN*, *SRHN*, *Kero*, *Diesel*, *VGO*, and *Rsd*). The CDU model is described as follows:

$$Cut_s = \sum_{k=0}^{4} a_k \, (TE_{CDU,s})^k \qquad \forall\ s \in S_{CDU} - \{Rsd\} \qquad \text{(A.1)}$$

Cut_s represents the volume percent vaporized of all fractions (*s*), except the residue product, of CDU unit. The cuts are usually represented as a polynomial function in $TE_{CDU,s}$ which is equivalent to the end point temperatures (EP). For every product from the CDU the $TE_{CDU,s}$ has an upper and a lower bound which called the swing cut. Figure A.2 shows an illustration of the CDU cuts volume as a function of the fractions temperature $TE_{CDU,s}$. The coefficients of the polynomial of the CDU equation are listed in Table A.2. The residual cut volume percent is expressed as:

$$Cut_{CDU,s=Rsd} = 100 \tag{A.2}$$

Since the last cut is the residue of the crude, so it will be assumed that the accumulative vaporized percent will be 100%.

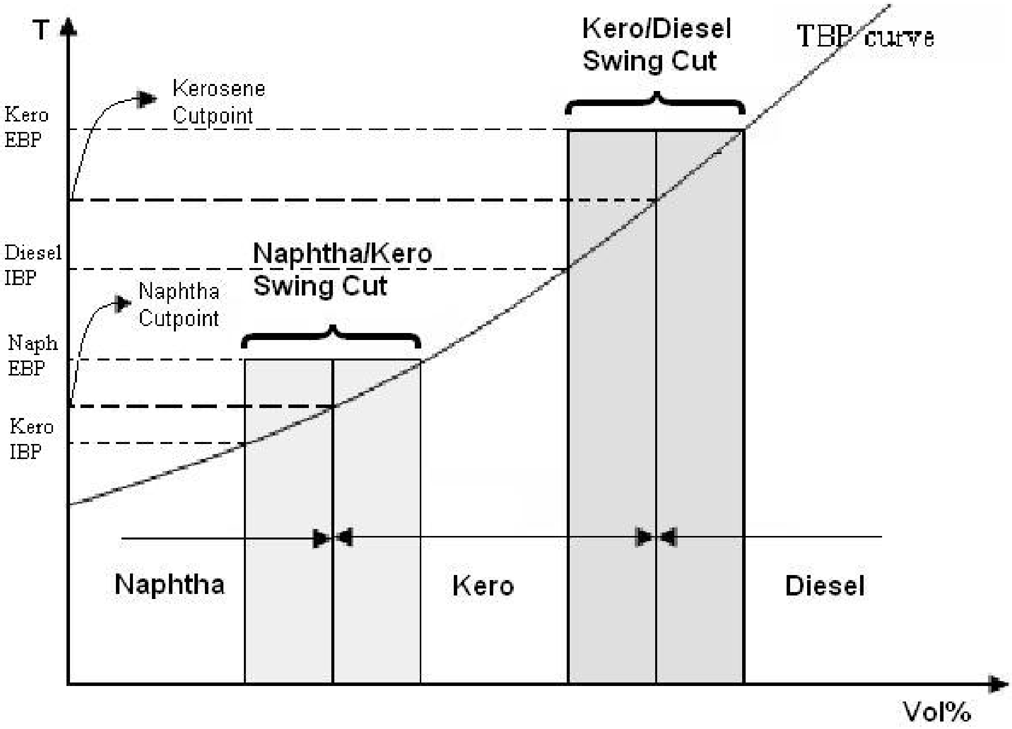

Figure A.2. Swing Cut of CDU Fractions

Table A.2. CDU Unit Model Equations coefficients

Parameter	Cut % (Vol.) Eq. A.8	API Eq. A.12	SUL% Eq. A.12	N% Eq. A.12
a_0	4.040637061	81.848	50.579 E-03	-8.829E-4
a_1	-47.272E-03	-3.778	-20.363 E-03	3.044E-4
a_2	3.25 E-04	113.288E-03	18.494 E-04	-2.297E-05
a_3	-2.843E-07	-15.436E-04	-3.257E-05	4.589E-07
a_4	8.153E-11	7.19E-06	2.03E-07	6.77E-09

Each product volumetric flow rate is calculated by subtracting its accumulated volume percent vaporized from the previous cut volume and multiply the result with crude oil feed to the CDU, i.e.

$$V_{CDU,s} = F_{CDU} * \left(\frac{Cut_s - Cut_{s-1}}{100} \right) \qquad \forall\ s \in S_{CDU} \qquad \text{(A.3)}$$

$V_{CDU,s}$ represents the volume flow rate of all the products (s) from the CDU unit, and F_{CDU} is the crude oil to the CDU unit.

Properties of each product from the CDU (API, sulfur… etc) are expressed as polynomial functions in each product mid-volume percent vaporized, $MidV_{CDU,s}$. The mid-volume for any product can be calculated from averaging the accumulative current cut volume percent with the previous cut volume percent vaporized:

$$MidV_{CDU,s} = \frac{Cut_s + Cut_{s-1}}{2} \qquad \forall\ s \in S_{CDU} \qquad \text{(A.4)}$$

$$PV_{CDU,s,p} = \sum_{k=0}^{4} a_k \ MidV_s^{\ k} \qquad \forall s \in S_{CDU}, p \in P_s \qquad \text{(A.5)}$$

$PV_{CDU,s,p}$ represents different properties (p) for each product (s) from the CDU unit. P_s is the set of all the properties calculated for the specified stream (s).

$$V_{CDU,s} = \sum_{m \in M} VS_{CDU,s,m} \qquad \forall\ s \in S_{CDU} \qquad \text{(A.6)}$$

$VS_{CDU,s,m}$ represents the volume flow rate of all the streams split from the CDU products (s) to different destinations (m), as explained in equation (3.6).

All fractions for the CDU, except residue, have an upper and a lower limit for their cut-point, i.e.

$$TE^{L}_{CDU,s} \leq TE_{CDU,s} \leq TE^{U}_{CDU,s} \qquad \forall\ s \in S_{CDU} - \{Rsd\} \qquad (A.7)$$

Also, the crude feed to the unit cannot exceed its throughput capacity:

$$F_{CDU} \leq Umax_{CDU} \qquad (A.8)$$

A.2 NHT Unit Model

The operating variable of the NHT unit is the conversion %, $x = Conv_{NHT}$. Also, the products stream for the NHT unit are fractions (s) ($s \in S_{NHT} = TLN$ and THN). The model consists of the following equations, where all the parameters values are listed in Table A.3.

Products yield:

$$V_{NHT,s} = F_{NHT} * \left(a_s + b_s * FP_{NHT,SG}\right) * \left(c_s - d_s * XU_{NHT,Conv\%}\right) \qquad s \in S_{NHT} \qquad (A.9)$$

$V_{NHT,s}$ represents the yield for NHT unit products, where FP_{SG} is the specific gravity of the NHT feed and the operating variable XU is the conversion of the NHT unit. The NHT unit consumes hydrogen to carry out the desulfurization reactions. The amount of hydrogen required can be predicted from Equation A.10.

$$V_{NHT,H_2} = F_{NHT} * \left(6.639 \times 10^{-3} + 4.409 \times 10^{-4} * FP_{NHT,OLE}\right) * XU_{NHT,Conv\%} \qquad (A.10)$$

$FP_{NHT,OLE}$ represents the olefin content on the feed.

Products properties:

The products specific gravity is a function of both the specific gravity of the feed and conversion of the unit.

$$PV_{NHT,s,SG} = \frac{a_s + b_s * FP_{NHT,SG} + c_s * XU_{NHT,Conv\%} + d_s * XU^{2}_{NHT,Conv\%}}{\left(1 - e_s * XU_{NHT,Conv\%}\right)} \qquad s \in S_{NHT} \qquad \text{(A.11)}$$

The aromatic and naphthene contents are function of unit conversion and the olefin aromatic and naphthene content on the feed, respectively.

$$PV_{NHT,s,ARO} = \sum_{h=0}^{1} \left(a_s * FP_{NHT,OLE} + b_s * FP_{NHT,ARO}\right) * XU^{h}_{NHT,Conv\%} \qquad s \in S_{NHT} \qquad \text{(A.12)}$$

$$PV_{NHT,s,NAPH} = \sum_{h=0}^{1} \left(a_s * FP_{NHT,OLE} + b_s * FP_{NHT,NAPH}\right) * XU^{h}_{NHT,Conv\%} \qquad s \in S_{NHT} \qquad \text{(A.13)}$$

Table A.3. NHT Unit Model Equations coeffecients

Equation	Parameter	TLN	THN
Product Yield	a	665.274E-6	665.274E-6
	b	349.15E-3	349.15E-3
	c	0.0	1.0
	d	0.88	- 0.88
SG	a	0.67	0.0
	b	0	1.0
	c	179.641E-3	- 0.67
	d	0.0	- 179.641E-3
	e	0.0	1.0
NAPH	ao	0.0	0.1
	b0	0.0	0.1
	a1	149.7E-3	0.0
	b1	1.497	0.0
ARO	ao	0.0	0.1
	b0	0.0	0.1
	a1	0.0	0.0
	b1	1.497	0.0

A.3 DHT Unit Model

The operating variable of the DHT unit is the conversion %, $x = Conv_{DHT}$. Also, the products stream for the DHT unit are fractions (s) ($s \in S_{DHT} = N$, *Kero*, and *TDiesel*). The model consists of the following equations, where all the parameters values are listed in Table A.4.

Products yield:

$$V_{DHT,s} = F_{DHT} * \left(\sum_{h=0}^{2} \left(a_{s,h} - b_{s,h} * FP_{DHT,SG} - c_{s,h} * FP_{DHT,S\%} \right) * XU_{DHT,Conv\%}^{h} \right) \quad s \in S_{DHT} \qquad \text{(A.14)}$$

$V_{DHT,s}$ represents the yield for DHT unit products, where FP_{SG} is the specific gravity of the DHT feed and the operating variable XU is the conversion of the DHT unit. Hydrogen is consumed to carry out the desulfurization reactions. The amount of hydrogen required can be predicted as following:

$$V_{DHT,H_2} = F_{DHT} * \left(\begin{array}{c} \left(2.28\times10^{-3} + 8.207\times10^{-4} * FP_{DHT,S\%} \right) + \\ \left(4.012\times10^{-5} + 9.119\times10^{-7} * FP_{DHT,S\%} \right) * XU_{DHT,Conv\%} \end{array} \right) \qquad \text{(A.15)}$$

Products properties:

Equation A.16 represents the products *API* and cetane number, where they are a function of both the specific gravity and sulfur content of the feed and conversion of the unit.

$$PV_{DHT,s,p} = \sum_{h=O}^{1} \left(a_s + b_s * FP_{DHT,API} + \frac{\left(c_s + d_s * FP_{DHT,S\%} \right)}{FP_{DHT,SG}} \right) * XU_{DHT,Conv\%}^{h} \quad \begin{array}{c} p = API; s \in S_{DHT} \\ p = CET; s = Kero, Diesel \end{array} \qquad \text{(A.16)}$$

The product sulfur content is expressed as a function of both the sulfur content of the feed and conversion of the unit.

$$PV_{DHT,s,S\%} = a_s * \left(b_s + c_s * XU_{DHT,Conv\%} \right) * FP_{DHT,S\%} \qquad s \in S_{DHT} \qquad \text{(A.17)}$$

Table A.4. DHT Unit Model Equations coeffecients

Equation	Parameter	N	Kero	TDiesel
Product Yield	a0	0.0	429E-6	1.851E-3
	b0	1.0E-3	186.872E-3	807.128E-3
	c0	0.0	154E-6	0.666E-3
	a1	0.0	7.543E-6	32.577E-6
	b1	0.40E-3	- 75.2E-6	- 324.8E-6
	c1	0.0	0.171E-6	0.74E-6
	a2	0.0	0.0	0.0
	b2	0.0	- 0.94E-6	- 4.06E-6
	c2	0.0	0.0	0.0
SG	a0	55	7.2	- 1.8
	b0	0.0	1	1
	c0	12.3E-3	11.4E-6	11.4E-6
	d0	3.26E-6	4.104E-6	4.104E-6
	a1	0.0	0.04	0.04
	b1	0.0	0.0	0.0
	c1	0.0	0.2E-6	0.2E-6
	d1	0.0	4.56E-9	4.56E-9
CET	a0	0.0	- 3.592	- 29.2
	b0	0.0	1.64	2
	c0	0.0	18.696E-6	22.8E-6
	d0	0.0	6.731E-6	8.208E-6
	a1	0.0	65.6E-3	0.08
	b1	0.0	0.0	0.0
	c1	0.0	0.328E-6	0.4E-6
	d1	0.0	7.478E-9	9.12E-9
S%	a	609.8E-3	1.0976	8.25E-6
	b	0.1	0.1	1.02E-3
	c	0.9E-3	0.9E-3	0.9E-3

A.4 GOHT Unit Model

The operating variable of the GOHT unit is the conversion %, $x = Conv_{GOHT}$. Also, the products stream for the GOHT unit are fractions (s) ($s \in S_{GOHT} = N$, $Dist$, and TGO). The model consists of the following equations, where all the parameters values are listed in Table A.5.

Products yield:

$$V_{GOHT,s} = F_{GOHT} * \left(\sum_{h=0}^{1} \left(a_{s,h} + b_{s,h} * FP_{GOHT,SG} + c_{s,h} * FP_{GOHT,VABP} \right) * XU_{GOHT,Conv\%}^{h} \right) \quad s \in S_{GOHT} \qquad \text{(A.18)}$$

$V_{GOHT,s}$ represents the yield for GOHT unit products, where FP_{SG} is the specific gravity of the DHT feed and the operating variable XU is the conversion of the GOHT unit. Hydrogen is consumed to carry out the desulfurization reactions. The amount of hydrogen required, IC_4, and NC_4 gases produced can be predicted from Equation. A.19. Table A.6 shows all the parameters values.

$$V_{GOHT,s} = F_{GOHT} * \left(a_s + b_s * FP_{GOHT,SG} \right) * \left(c_s + d_s * FP_{GOHT,VABP} + e_s * XU_{GOHT,Conv\%} \right) \quad s = H_2, IC_4, NC_4 \qquad \text{(A.19)}$$

Products properties:

The API of the products is a function of both the API and volume average boiling point of the feed and conversion of the unit.

$$PV_{GOHT,s,API} = a_s + b_s * FP_{GOHT,API} + c_s * FP_{GOHT,VABP} + d_s * XU_{GOHT,Conv\%} \quad s \in S_{GOHT} \qquad \text{(A.20)}$$

The products sulfur content and the Conradson carbon residue (CCR) are expressed as a function of conversion of the unit.

$$PV_{GOHT,s,p} = FP_{GOHT,p} * \left(a_s + b_s * XU_{GOHT,Conv\%} \right) \quad \begin{array}{c} s = Dist; p = S\% \\ s = TGO; p = S\%, CCR \end{array} \qquad \text{(A.21)}$$

Another important property of the treated gas oil (*TGO*) product is the volume average boiling point (*VABP*).

$$PV_{TGO,VABP} = \left(PV_{TGO,SG} * \left(FP_{GOHT,K} + 0.01 * XU_{GOHT,Com\%}\right)\right)^3 - 460 \tag{A.22}$$

Table A.5. GOHT Unit Model Equations coeffecients

Equation	Parameter	N	Dist	TGO
Product Yield	a0	0.0	- 1.292E-3	0.0
	b0	0.02	78.3E-3	0.913
	c0	0.0	7.599E-6	0.666E-3
	a1	0.0	- 277.51E-6	0.0
	b1	10.0E-3	1.255E-3	- 9.0E-3
	c1	0.0	0.0	0.0
SG	a	29.17	12.69	0.34
	b	1.23	1.11	1.0
	c	0.0	0.0	2.0E-3
	d	0.0	0.0	73.04E-3
S%	a		1.03E-3	10.0E-6
	b		1.777E-3	26.667E-3
CCR	a			12.1E-6
	b			66.665E-3

Table A.6. Coeffecients of Equation A.19

Parameter	H_2	IC_4	NC_4
a	1	0.0	0.0
b	0.0	1	1
c	1.292E-3	1.0E-3	700.0E-6
d	7.599E-6	0.0	0.0
e	277.51E-6	150.0E-6	105.0E-6

A.5 RHT Unit Model

The operating variable of the RHT unit is the conversion %, x = $Conv_{RHT}$. Also, the products stream for the RHT unit are fractions (s) ($s \in S_{RHT} = N, Dist, LSFO$). The model consists of the following equations, where all the parameters values are listed in Table A.7.

Products yield:

$$V_{RHT,s} = F_{RHT} * FP_{RHT,SG} * \begin{bmatrix} \left(a1_s + a2_s * FP_{RHT,N\%} + a3_s * \dfrac{FP_{RHT,N\%}}{FP_{RHT,SG}} \right) + \\ \left(b1_s + b2_s * FP_{RHT,SG} + \dfrac{b3_s}{FP_{RHT,SG}} \right) * XU_{RHT,Conv\%} + \\ \left(c1_s + c2_s * FP_{RHT,SG} + c3_s * FP^2_{RHT,SG} \right) * XU^2_{RHT,Conv\%} \\ \end{bmatrix} \qquad s \in S_{RHT} \qquad \text{(A.23)}$$

$V_{RHT,s}$ represents the yield for RHT unit products, where FP_{SG} and $FP_{N\%}$ are the specific gravity and the nitrogen content of the RHT feed and the operating variable XU is the conversion of the RHT unit. The RHT unit consumes a large amount of hydrogen to carry out the desulfurization reactions. The amount of hydrogen required, IC_4, and NC_4 gases produced can be predicted from Equation. A.24. Table A.8 shows all the parameters values.

$$V_{RHT,s} = \begin{matrix} F_{RHT} * \left(a_s + b_s * FP_{RHT,SG} + c_s * FP^2_{RHT,SG} \right) * \\ \left(d_s * FP_{RHT,N\%} + e_s * FP_{RHT,Metal} + z_s * XU_{RHT,Conv\%} \right) \end{matrix} \qquad s = H_2, IC_4, NC_4 \qquad \text{(A.24)}$$

Products properties:

The products API and sulfur content are a function of both the specific gravity of the feed and conversion of the unit.

$$PV_{RHT,s,SG} = a_s * FP_{RHT,SG} + \left(b_s - \frac{c_s}{FP_{RHT,SG}} \right) * V_{RHT,H_2} \qquad s \in S_{RHT} \qquad \text{(A.25)}$$

and

$$PV_{RHT,s,SUL\%} = \left(a_s + b_s * FP_{RHT,S\%} \right) * XU_{RHT,Conv\%} \qquad s \in S_{RHT} \qquad \text{(A.26)}$$

Viscosity is one of the important properties of the LSFO product from the RDH unit. A blending index method is used to predict the value of the LSFO viscosity, which will be explained in the coming section. Viscosity is a function of both the specific gravity and the viscosity of the RHT feed:

$$VisFct = \frac{FP_{RHT,SG} - 0.1244 * \log\left(4.664 * FP_{RHT,Vis} - 31\right)}{0.9255 - 0.098 * \log\left(4.664 * FP_{RHT,Vis} - 31\right)} + 0.56 * \left(PV_{LSFO,SG} - FP_{RHT,SG} \right) - 0.084 \qquad \text{(A.27)}$$

$$PV_{LSFO,Vis} = \frac{1}{4.664} * \log^{-1} \left(\frac{0.9255 * VisFct - PV_{LSFO,SG} + 0.078}{0.098 * VisFct - 0.116} \right) + 6.6466 \qquad \text{(A.28)}$$

PV_{Vis} represents the LSFO viscosity, where FP_{SG} and FP_{Vis} are the specific gravity and the viscosity of the RHT feed. A new variable *VisFct* is introduced to simplify the viscosity calculation.

Table A.7. RHT Unit Model Equations coeffecients

Equation	Parameter	N	Dist	LSFO
Product Yield	a1	0.0	0.0	1
	a2	0.0	0.0	4.197E-3
	a3	0.0	0.0	-2.484E-3
	b1	- 9.50E-3	- 3.382	3.45
	b2	20.350E-3	7.245	- 7.279
	b3	0.0	0.0	- 30.590E-3
	c1	0.0	- 144.4E-3	144.4E-3
	c2	0.0	618.6E-3	- 618.6E-3
	c3	0.0	- 662.6E-3	662.6E-3
SG	a	751.505E-3	823.506E-3	1.0
	b	0.0	0.0	103.737E-9
	c	1.35E-6	1.35E-6	63.838E-9
S%	a	70.83E-3	166.67E-3	1.667
	b	-4.853E-6	19.414E-6	71.832E-3
VISC	a	0.0	11.75	0.0
	b	0.0	- 0.6	0.0

Table A.8. Coeffecients of Equation A.24

Parameter	H_2	IC_4	NC_4
a	- 0.564	0.0	0.0
b	0.953	- 0.333	- 0.218
c	0.0	0.713	0.468
D	1.543E-3	0.0	0.0
E	6.231E-6	0.05	0.3502
Z	2.28E-3	315E-6	2.206E-3

A.6 CR Unit Model

The operating variable of the CR unit is the severity, $x = Sevr_{CR}$. Severity of the CR unit is defined as reformate product research octane number (RON). Also, reformate stream will be the only product stream of the CR (s) ($s \in S_{CR} = Reformate$). The model consists of the following equations, where all the parameters values are listed in Table A.9.

Products yield:

$$V_{CR,s} = F_{CR} * FP_{CR,SG} * \left(a_s + b_s * FP_{CR,NAPH} + c_s * FP_{CR,ARO} + d_s * XU_{CR,Sevr}\right) \quad s \in S_{CR} \tag{A.29}$$

$V_{CR,s}$ represents the yield for CR unit products, where FP_{SG}, FP_{NAPH}, and FP_{ARO} are the specific gravity, naphthene, and aromatic content of the CR feed and the operating variable XU is the severity of the CR unit. Hydrogen and LPG gases (H_2, C_3, IC_4, and NC_4) produced from the CR unit can be predicted from Equation. A.29 as well, Table A.9 lists all the parameters values.

Products properties:

The reformate specific gravity is a function of: the specific gravity, naphthene, aromatic of the feed; and severity of the unit.

$$PV_{CR,Rformate,SG} = FP_{CR,SG} * \left(0.72 - \frac{67.3}{100.3 + 0.2 * FP_{CR,NAPH} + 0.4 * FP_{CR,ARO} - XU_{CR,Sevr}}\right) \tag{A.30}$$

The RON, aromatic, and benzene contents are function of unit severity and the RON, aromatic, and benzene content of the feed, respectively. The properties parameters values are listed in Table A.10.

$$PV_{CR,Rformate,p} = \left(a + b * XU_{CR,Sevr}\right) * \left(c * FP_{CR,p}\right) \qquad p = RON, ARO, BNZ \tag{A.31}$$

Table A.9. CR Unit Model Equation A.29 coeffecients

Parameter	a	b	c	D
Reformate	50.185E-3	1.442E-3	2.884E-3	-7.210E-3
H_2	-16.800E-3	-0.400E-3	-0.800E-3	0.200E-3
C_3	2.825E-3	-0.110E-3	-0.220E-3	0.550E-3
IC_4	3.901E-3	-0.152E-3	-0.304E-3	0.760E-3
NC_4	-17.000E-3	-0.400E-3	-0.800E-3	0.200E-3

Table A.10. Reformate Product Properties - Coeffecients of Equation A.31

Parameter	A	b	C
RON	0.000	1.000	$1/RON_{CR}$
ARO	-92.000	1.500	1.000
BNZ	-49.773	0.543	$1/BNZ_{CR}$

A.7 FCC Unit Model

FCC is the most widely used catalytic cracking process. Many refiners call the FCC the heart of the refinery (Maples, 1993). The products stream are light naphtha gasoline (LN), Heavy naphtha gasoline (HN), light catalytic gas oil (LGO) and heavy catalytic gas oil (HGO). There have been several efforts at modeling the FCC unit and other refinery processing units. Various correlations in the literature for predicting the FCC product yields and properties have been published. Al-Enezi *et al.* (1999) presented linear and nonlinear regression models for predicting yields and properties of the FCC process and tested them against refinery data. The feedstock properties and the conversion were used as the correlation parameters. Li et al. (2005) proposed a nonlinear correlation for predicting the yields without considering the properties correlations. The FCC model we employed is similar of Al-Enezi *et al.* (1999). The operating variable of the FCC unit is the conversion %., $x = Conv_{FCC}$. Also, the products stream for the FCC unit are fractions (s) ($s \in S_{FCC} = LN$, HN, LCO and HCO). The model consists of the following equations, where all the parameters values are listed in Table A.11.

Products yield:

$$V_{FCC,s} = F_{FCC} * FP_{FCC,SG} * \left(\sum_{h=0}^{4} \left(a_{s,h} + b_{s,h} * FP_{FCC,K} \right) * XU_{FCC,Conv\%}^{h} \right) \quad s \in S_{FCC} \qquad \text{(A.32)}$$

$V_{FCC,s}$ represents the yield for FCC unit products, where FP_K is the characterization factor of the FCC feed and the operating variable XU is the conversion of the FCC unit.

Products properties:

The products API_s and sulfur content are a function of both the characterization factor of the feed and conversion of the unit.

$$PV_{FCC,s,API} = \frac{\left(\sum_{h=0}^{1} \left(a_{s,h} + b_{s,h} * FP_{FCC,K} \right) * XU_{FCC,Conv\%}^{h} \right)}{\left(c_s + d_s * XU_{FCC,Conv\%} \right)} \qquad s \in S_{FCC} \qquad \text{(A.33)}$$

and

$$PV_{FCC,s,SUL\%} = FP_{FCC,SUL\%} * \left(\frac{\left(a_s + b_s * XU_{FCC,Conv\%} \right)}{\left(c_s + d_s * XU_{FCC,Conv\%} \right)} \right) \qquad s \in S_{FCC} \qquad \text{(A.34)}$$

Research octane number (RON) was correlated for LN and HN as function of unit conversion:

$$PV_{FCC,s,RON} = \frac{\left(a_s + b_s * XU_{FCC,Conv\%} \right)}{\left(c_s + d_s * XU_{FCC,Conv\%} \right)} \qquad s = LN, HN \in S_{FCC} \qquad \text{(A.35)}$$

Kerosene flash point is also correlated as function of unit conversion:

$$PV_{FCC,s,FLSH} = 210 + \frac{\left(a_s + b_s * XU_{FCC,Conv\%}\right)}{\left(c_s + d_s * XU_{FCC,Conv\%} + e_s * XU^2_{FCC,Conv\%}\right)} \qquad s = Kero \in S_{FCC} \qquad \text{(A.36)}$$

Table A.11. FCC Unit Model Equations coeffecients

Equation	Parameter	LN	HN	LCO	HCO
Product Yield	a_0	-0.00308535	-0.001778704	0.0325	0.9675
	a_1	0.001337565	0.000771106	0.00175	-0.01175
	a_2	4.34839E-05	2.50685E-05	-0.00005	0.00005
	a_3	-1.29355E-07	-7.45732E-08	0	0
	a_4	-6.5E-10	-3.74725E-10	0	0
	b_0	0.02374645	0.013689828	0	0
	b_1	0.000104739	6.0382E-05	0	0
	b_2	-1.76439E-05	-1.01717E-05	0	0
	b_3	1.54805E-07	8.92451E-08	0	0
	b_4	6.5E-10	3.74725E-10	0	0
API	a_0	1672	7427	35	17
	a_1	70	-41	-0.2	-0.2
	b_0	0	654	5	6
	b_1	0	-6	0	0
	c	30.7	169.3	1	1
	d	1	-1	0	0
SUL%	a	2.215	17.745	1.3	2.5
	b	0.01	-0.12	0	0
	c	30.7	169.3	1	1
	d	1	-1	0	0
RON	a	2906.1	15417.9		
	b	90	-90		
	c	30.7	169.3		
	d	1	-1		
FLSH	a			81750	
	b			-750	
	c			650	
	d			35	
	e			-1	

APPENDIX B

REFINERY BLENDING CORELLATIONS

B.1 Density (API)

The density of petroleum oil is expressed in terms of API gravity rather than specific gravity. The blended API can be calculated by the following equation (Gary, 1994):

$$API_{blend} = \frac{141.5}{SG_{blend}} - 131.5 \tag{B.1}$$

Specific gravity (*SG*) can be averaged while API cannot. Therefore, the SG of the blend can be calculated as:

$$SG_{blend} = \frac{\sum_s V_s * SG_s}{\sum_s V_s} \tag{B.2}$$

V_s represents the volume percent of stream s and SG_s is the specific gravity of stream s.

B.2 Sulfur content (wt%)

Sulfur content is an important property which has a major influence on the value of crude oil and petroleum products. The sulfur content for a blended stream SUL_{blend} is the average sulfur content for all coming streams SUL_s and should be expressed in weight percent. It can be calculated from the following equation (Gary, 1994):

$$SUL_{blend} = \frac{\sum_s W_s \times SUL_s}{\sum W_s} \tag{B.3}$$

Where W_s is the weight flow rate for stream s being blended.

B.3 Octane number (ON)

Octane numbers are blended on a volumetric basis using the blending index of the components. True octane numbers do not blend linearly and it is necessary to use blending octane numbers in making calculations. Several blending approaches are provided in the literature and the simplest form has been converted to the following analytical relation (Riazi, 2005):

$$RONI_s = 651z^3 - 1552.9z^2 + 1272(z) - 299.5 \tag{B.4}$$

Where z = RON/100

$$RON_{blend} = \frac{\sum_s V_s * RONI_s}{\sum_s V_s} \tag{B.5}$$

B.4 Reid Vapor Pressure (RVP)

The Reid vapor pressure (RVP) is one of the important properties of gasoline and jet fuels and it is used as a criterion for blending products. RVP is the absolute pressure exerted by a mixture at 100 ^{0}F. The approach for calculation of RVP of a blend when several components with different RVP_s are blended is often to use a blending index for RVP as (Riazi, 2005):

$$RVPBI_s = RVP_s^{1.25} \tag{B.6}$$

$$RVPBI_{blend} = \frac{\sum_s V_s * RVPBI_s}{\sum_s V_s} \tag{B.7}$$

$$RVP_{blend} = \left[RVPBI_{blend} \right]^{0.8} \quad \text{(B.8)}$$

Where $RVPBI_s$ is the blending index for RVP_s. RVP can be calculated in bar or psia in the above equation. This relation was originally developed by Chevron and is also recommended in other industrial manuals under Chevron blending number.

B.5 Flash point

Flash point is an important characterization of light petroleum fractions and products under a high temperature environment and is directly related to the safe storage and handling of such petroleum products. The flash point of the blend should be determined from the flash point indexes of the components as given by (Riazi, 2005):

$$\log_{10} FLSHI_S = -6.1188 + \frac{2414}{FLSH_S - 42.6} \quad \text{(B.9)}$$

$FLSHI_S$ is the flash point blending index of stream *s* and $FLSH_s$ is the flash point in degrees Kelvin. The blend flash point index can be determined from the general equation 3.9 with a volume averaging.

B.6 Cetane Index

For diesel engines, the fuel must have a characteristic that favors auto-ignition. The ignition delay period can be evaluated by a fuel characterization factor called cetane number (CN). The cetane index (CI) is empirically correlated to the API gravity and aniline point (AP) in ^{0}C. CI is expressed as follows (Riazi, 2005):

$$CI_s = 0.72 * \left(\frac{(API_s)(1.8AP_s + 32)}{100} \right) + 10 \quad \text{(B.10)}$$

The blending index is calculated with volume fraction as in equation 3.9.

B.7 Freezing point

Freezing point is one of the important characterizations of aviation fuels. The equation to calculate the freezing point index is (Baid, 1987):

$$FRZI_S = Exp\left(13.333 \ln \frac{FRZ_S + 460}{600}\right) \tag{B.11}$$

where FRZ_s represents the freezing point of stream s in (^{0}F). The blending index is calculated with volume fraction as in equation 3.9.

APPENDIX C

HYDROGEN NETWROK UNITS' MODELS

C.1 Processing unit Model

Figure C.1 shows a hydrogen consumer unit in a refinery, and the sinks and sources of hydrogen are clearly identified.

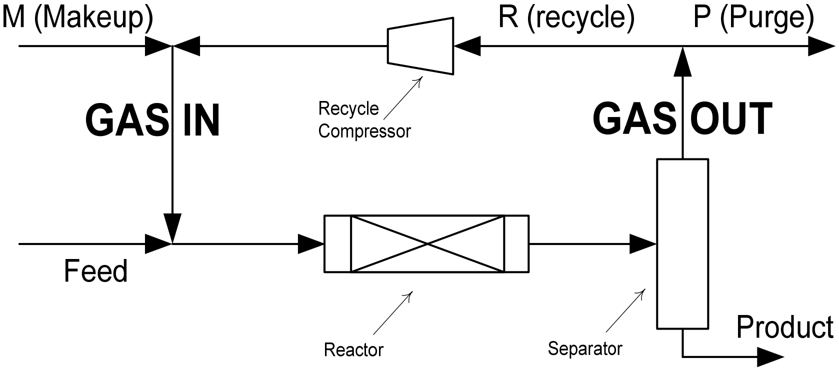

Figure C.1. Simplified Processing Unit Hydrogen Balance

The sink for any consumer unit is defined by the make-up and the recycle gas as follows:

$$F_{\boldsymbol{sink}} = F_M + F_R \tag{C.1}$$

The term F_{sink} represents the feed flow rate to a sink unit, and it is equal to the sum of F_{M} and F_{R}, which are make-up and recycle flow rates, respectively. The purity of the streams fed to a sink unit is the volume average of these flows:

$$y_{sink} = \frac{F_M y_M + F_R y_R}{F_M + F_R} \tag{C.2}$$

where y_{sink}, y_M, and y_R are the sink feed, makeup stream purity, and recycle stream purity, respectively. Source flow rate streams from unit can be shown as:

$$F_{source} = F_P + F_R\,, \tag{C.3}$$

where F_{source} represents the source flow rate from the unit and is equal to the sum of F_P and F_R, which are purge and recycle flow rates, respectively. On other hand, the purities of the recycle streams are always equal to its source unit:

$$y_{source} = y_P = y_R\,, \tag{C.4}$$

where y_{source} and y_P are the source stream purity and purge stream purity, respectively.

C.2 Compressor Model

The compressors are used in the hydrogen network to satisfy the pressure requirements of the consumers. Figure C.2 shows a simplified flow diagram of a compressor. Equations (C.5)-(C.8) are valid for existing and new compressors.

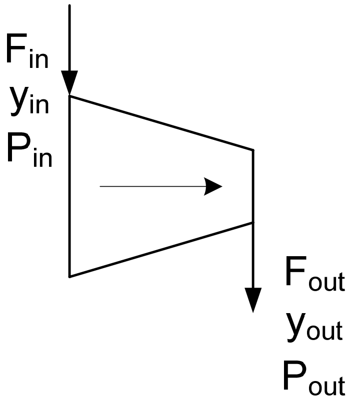

Figure C.2. Simplified Compressor Flow Diagram

The flow rate and hydrogen purity are unchanged in the compressor section (inlet) and discharge (outlet):

$$F_{in} = F_{out} \tag{C.5}$$

The amount of gas fed to the compressor is equal to the amount that leaves the compressor. Also, the amount of hydrogen gas enters the compressor is equal to the amount that exits the compressor:

$$F_{in}\, y_{in} = F_{out}\, y_{out} \tag{C.6}$$

The rate of work of the compressor is:

$$W = 0.08531Q\left(\frac{k_g}{k_g - 1}\right)T_s\left(\left(\frac{P_d}{P_s}\right)^{\frac{z(k_g-1)}{k_g}} - 1\right), \tag{C.7}$$

where: W = rate of work, horsepower

Q = flow rate into the compressor, MMSCFD

$k_g = C_p / C_v$ for gas at suction condition (assumed to be 1.26)

T_s = suction temperature, °R (assumed to be 520 °R)

z = compressibility factor of gas at suction condition (assumed to be 0.9)

P_d = discharge pressure, psi

P_s = suction pressure, psi

The effective and unfixed variables of the compressor are flow rate, suction pressure, and discharge pressure. Equation C.7 can be simplified to:

$$Pwr = a_{COM}\left(\left(\frac{P_{out}}{P_{in}}\right)^{b_{COM}} - 1\right)F_{in} \tag{C.8}$$

Power (Pwr) calculated from Equation C.8 is in KW, and the power coefficients a_{COM} and b_{COM} are constant as 160.376 and 0.1857, respectively. Finally, the capital cost of the new compressor (Cap_{NC}), which is in (10^3x\$), can be calculated as shown:

$$Cap_{NC} = a_{NC} + b_{NC} * Pwr \tag{C.9}$$

The capital cost coefficients a_{NC} and b_{NC} are constant as 150.0 and 1.91, respectively.

C.3 PSA Model

The purification unit has one inlet stream and two outlet streams. One outlet stream is the product stream and the other is the tail stream. Figure C.3 shows a simplified flow diagram of a PSA unit. The operating parameters that control the economics of the PSA are the recovery ratio of the hydrogen in the feed ($RCOV$) and the product purity (y_{Pr}). In this research, these two parameters are fixed at 90.0% and 99.0%, respectively.

Equations (C.10) and (C.11) represent the overall balance and the hydrogen balance across the PSA unit, respectively:

$$F_{in} = F_{\text{Pr}} + F_{Tl} \tag{C.10}$$

$$F_{in}\, y_{in} = F_{\text{Pr}}\, y_{\text{Pr}} + F_{Tl}\, y_{Tl} \tag{C.11}$$

F_{in}, F_{Pr}, and F_{Tl} represent the flow rates of feed, product, and tail gas in the PSA unit, respectively. Feed and tail gas purities are represented by y_{in} and y_{Tl}, respectively. The amount of hydrogen recovered in the product is calculated by:

$$F_{\text{Pr}}\, y_{\text{Pr}} = F_{in}\, y_{in} \left(RCOV\right) \tag{C.12}$$

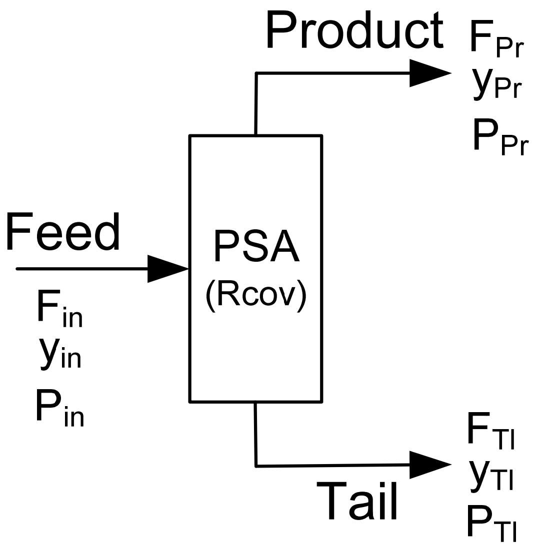

Figure C.3. Simplified PSA Flow Diagram

Important variables of the PSA unit are the product pressure and the tail-gas pressure. The product pressure is almost equal to the feed pressure, whereas the tail-gas pressure is usually low enough that the tail-gas stream can be sent to the fuel-gas system in the refinery.

$$P_{in} = P_{\mathrm{Pr}} \tag{C.13}$$

Finally, the capital cost of the PSA unit (Cap_{PSA}), which is in 10^3x$, can be calculated as shown:

$$Cap_{PSA} = a_{PSA} + b_{PSA} * F_{in} \tag{C.14}$$

The capital cost coefficients a_{PSA} and b_{PSA} are constant as 503.8 and 347.4, respectively.