Superstructure Optimization of Naphtha Processing System with Environmental Considerations

by

Mohd Ros Asmawi bin Muhammad
8600

Dissertation submitted in partial fulfillment of
the requirement for the
Bachelor of Engineering (Hons)
(Chemical Engineering)

JAN 2010

Universiti Teknologi PETRONAS
Bandar Seri Iskandar
31750 Tronoh
Perak Darul Ridzuan

CERTIFICATION OF APPROVAL

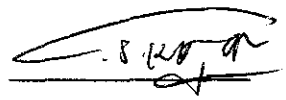
Superstructure Optimization of Naphtha Processing System with Environmental Considerations

by

Mohd Ros Asmawi Bin Muhammad
8600

A project dissertation submitted to the
Chemical Engineering Programme
Universiti Teknologi PETRONAS
in partial fulfillment of the requirements for the
BACHELOR ENGINEERING (Hons)
(CHEMICAL ENGINEERING)

Approved by,



(Mr. Khor Cheng Seong)

UNIVERSITI TEKNOLOGI PETRONAS
TRONOH, PERAK
JAN 2010

CERTIFICATION OF ORIGINALITY

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

_____

(MOHD ROS ASMAWI BIN MUHAMMAD)

ABSTRACT

The objective of this research project is to develop an optimization-based mathematical model in the form of a mixed-integer linear program (MILP) for determining the optimal configuration of a petroleum refinery. The scope for this project is to formulate the superstructure representation model for a refinery focusing on the subsystem of naphtha hydroprocessing in order to select the most economical and cost efficient process route. The alternatives for all streams are evaluated and the optimal configuration is proposed based on market demand by incorporating logical constraints and mass balance using the GAMS modeling language platform. Based on the information and knowledge about the physics of the problem of naphtha processing unit, we represent all these possible processing alternatives on a superstructure. **Carbon dioxide** emission factors have also been considered in which relevant data is obtained using the carbon weighting tonne (CWT) method. Computational studies are conducted on a representative numerical example to illustrate the proposed modeling approach.

ACKNOWLEDGEMENT

بِسْمِ ٱللَّهِ ٱلرَّحْمَٰنِ ٱلرَّحِيمِ

In the name of Allah, The Beneficent, The Merciful.

First and foremost I would like to express appreciation and gratefulness to Allah, for His blessing and giving the golden opportunity to complete this Final Year Project.

I also would like to express my sincere gratitude to Mr. Khor Cheng Seong for this valuable guidance, constructive comments and support as my supervisors. The encouragement throughout these 2 semesters has been very important for the successful completion of my Final Year Project.

Last but not least, the appreciation goes to my parents and mates, for their constant supports and ideas of this project.

TABLE OF CONTENT

CERTIFICATION OF APPROVAL . . . . . **i**

CERTIFICATION OF ORIGINATLITY . . . . . **ii**

ABSTRACT . . . . . **iii**

ACKNOWLEDGEMENT . . . . . **vi**

CHAPTER 1: INTRODUCTION **1**

1.1 Background Study 1

1.2 Problem Statement 4

1.3 Objective and Scope of Study 5

CHAPTER 2: LITERATURE REVIEW **7**

2.1 Petroleum Refinery Optimization: An Overview 7

2.2 Superstructure Representation of Design Alternative 11

2.3 Environmental Concern: Global Warming 12

2.4 Environmental Performance Assessment for Risk Evaluation of Flow sheets 14

2.5 Type of Pollutants Emitted from Each Unit in Superstructure 16

2.6 Emission Factor for EFRAT Method 20

2.7 Objective Function 23

2.8 GAMS Modeling 24

CHAPTER 3: METHODOLOGY/PROJECT WORK **25**

3.1 Procedure Identification 25

3.2 Superstructure Representation of Alternatives 27

3.3 Mathematical Model Formulation 30

3.4 CO_2 Emission Factor Calculation 32

3.5 Constraints 33

3.6 GAMS Modeling 39

CHAPTER 4: COMPUTATIONAL EXPERIENCE AND NUMERICAL RESULT.....40

4.1 Introduction.....40

4.2 Model Data.....41

4.3 Remarks on Computational Experience.....45

CHAPTER 5: CONCLUSION AND RECOMMENDATION.....46

5.1 Conclusion.....46

5.2 Recommendations.....47

REFERENCES.....48

LIST OF TABLE

Table 2.5.1: Summary of Emissions, Effluents, Residuals and Waste Streams for Topping/Separation Processes 16

Table 2.5.2: Summary of Emissions, Effluents, Residuals and Waste Streams for Thermal and Catalytic Cracking Processes.....17

Table 2.5.3: Summary of Emissions, Effluents, Residuals and Waste Streams for Combination/Rearrangement Processes.....18

Table 2.5.4: Summary of Emissions, Effluents, Residuals, By-Products and Waste Streams for Treatment Process.....19

Table 2.5.5: Summary of Emissions, Effluents, Residuals, By-Products and Waste Streams for Specialty Products Manufacture.....19

Table 2.6.1: Air Emission Factor for Petroleum Process.....20

Table 2.6.2: Basis Throughput and CWT Factor for CWT Process Unit.....22

Table 3.2: Legend for STN Superstructure Representation in Figure 3.2.....28

Table 3.5.2: Market Demand for Product.....35

Table 4.1: Model and Computational Statistic in Model Formulation.....40

Table 4.2.1: Assumption Data for Model Formulation.....41
Table 4.2.2: Computational Result Model with Selection of Material Stream.....42

LIST OF FIGURES

Figure 3.1: Major steps in the mathematical programming approach to Synthesis and design problems.....26
Figure 3.2: Superstructure Representation for Naphtha Processing Unit from ADU.....29
Figure 3.6: GAMS Modeling.....39
Figure 4.2.1: Selected Process Route for the naphtha Produced from ADU.....43

LIST OF APPENDIX

Appendix A: Objective Function (DESCRIPTION).....50
Appendix B: Emission Factors for Petroleum Refineries.....51
Appendix C: Downstream capital cost index 52
Appendix D: The Instrument Record of Global Average Temperature.....53
Appendix E: Schematic of an example integrated petroleum refinery..... 54
Appendix F: GAMS Modeling Result.....55

CHAPTER 1

INTRODUCTION

1.1 Background of Study

Crude oil is the main source of energy for the world. Apart from being used as a fuel, it is also essential feedstock for petrochemical industries [5]. All these factors demand an increase in petroleum capacity. However, designing a refinery topology that adheres to environmental regulations, operational constraints and economical needs is not an easy task.

Optimization will almost always be required at some stage in a process design. Process synthesis problems are typically difficult discrete optimization problems. Process synthesis or conceptual process design is concerned with the identification of the best flow sheet structure to perform a given task. The approach that have been reported in the literature to address these problems is the algorithmic approach, which utilizes optimization or mathematical programming, based on the construction of a superstructure that seeks to represent all feasible process flow sheets (Grossmann, 2002). Algorithmic methods that to a great extent can address some of the limitations of the heuristics- and physical-insights-based approach to process synthesis [10].

The complexity associated with synthesis problems in general and petroleum refinery design in particular, necessitates the development and implementation of a systematic and automated approach to efficiently and rigorously consider the elaborate interactions

and trade-offs among the design variables. In this regard, powerful formal optimization strategies potentially offer promising tools to undertake the task. The proposed optimization-based modelling approach in this project can potentially serve as a preliminary screening tool to determine the optimal topology of a refinery with environmental constraint that meets a fixed market demand of refinery products given certain types of crude oils to be processed.

The three major components of the project are as follows:

1) Superstructure representation of the alternative processing routes for an oil refinery that accounts for the complexity of the actual industrial-scale problem as much as possible;
2) Development of an optimization-based model of the above problem in the form of a mixed-integer program with environmental considerations.
3) Solution of the optimization model to obtain the desired optimal refinery topology.

The petroleum refinery flow sheet is divided to 4 main pool processing [12]:

1.1.1 Processing Pool 1: Alternatives for Atmospheric Reduced Crude (ARC)

The crude oil from the storage tank is heated in a furnace and then charged to an atmospheric crude distillation unit (ADU), which is a mainstay feature of an oil refining scheme as the primary fractionation function of the crude oil according to different boiling point ranges. ADU separates the crudes into butanes and lighter wet gases, unstabilized light naphtha, heavy naphtha, kerosene, atmospheric gas oil, and atmospheric topped or reduced crude (ARC). In older refineries especially those that typically handle low sulfur crudes, the topped crude is sent to the vacuum distillation unit (VDU) for separation into vacuum gas oil (VGO) and vacuum reduced crude (VRC) bottoms. However, modern refineries with high technology capable of processing crudes

with high sulfur content typically employ an atmospheric residuum desulfurization unit (ARDS) for sulfur removal from the crude oil.

Therefore, two design alternatives exist for ARC from ADU:

1) It is sent to the ARDS for sulfur removal to produce VRC that is then sent to the VDU.
2) It is sent directly to the VDU to produce VGO and VRC, with the VGO subsequently hydrotreated for sulfur removal in a unit denoted as GOHDT (which stands for gas oil hydrotreater).

1.1.2 Processing Pool 2: Alternatives for Naphtha Exiting Hydrotreater (HDT)/Hydrodesulfurizer (HDS)

For the full-range naphtha leaving ADU that has been treated for sulfur removal via the hydrotreater (NHDT) or hydrodesulfurizer (HDS), the following alternatives are available:

1) Its subcomponent of the light straight-run naphtha (LSRN) stream from the top of the distillation column is sent to a gasoline blending pool (BLND).
2) It is utilized as a feedstock for the catalytic reformer (CREF) and/or the isomerization unit (ISO).
3) It is directly sold (SOLD)

1.1.3 Processing Pool 3: Alternatives for Vacuum Gas Oil (VGO) Processing

The VGO stream is fed to either the fluidized catalytic cracker (FCC) or the hydrocracker (HCR) following hydrotreatment in GOHDT. Both FCC and HCR convert heavy gas oils into lighter products that are subsequently utilized as blendstocks for gasoline and diesel fuels. Hence, in general practice, both units do not coexist in a single site especially for relatively low-to-medium crude oil throughput unless the economies

of scale as dictated by a high throughput justifies the routing of the hydrotreated VGO to be split into two streams, one for FCC and the other for HCR. Nevertheless, in principle, both units can coexist, with HCR usually favored over FCC and is thus relatively more common, particularly in large-scale refineries that typically handles high crude oil throughput.

1.1.4 Processing Pool 4: Alternatives for Vacuum Residue or Vacuum Reduced Crude (VRC) Processing and Upgrading

Depending on the crude oil type and the related process economics, VRC is further processed for production of transportation fuels (i.e., gasoline, kerosene, and diesel), typically via one of the following intermediary process units: visbreaker (VIS), solvent deasphalter (SDA), or mild hydrocracker (M-HCR).

1.2 Problem Statement

The complexity associated with synthesis problems in general and petroleum refinery design in particular, necessitates the development and implementation of a systematic and automated approach to efficiently and rigorously consider the elaborate interactions and trade-offs among the design variables. In this regard, powerful formal optimization strategies potentially offer promising tools to undertake the task. The proposed optimization-based modelling approach in this project can potentially serve as a preliminary screening tool to determine the optimal topology of a refinery with environmental constraint that meets a fixed market demand of refinery products given certain types of crude oils to be processed.

It is a highly complex task to model optimal petroleum refineries topology that satisfies multiple economics, operations, and environmental constraints.
The questions that are interested to answer in this research concern the optimal design of the topology or configuration of a refinery with environmental considerations that addresses the following aspects:

1) The **selection** of the process units (tasks) and material streams (states) in terms of the types of the units as well as the number of the units and streams.
2) The **sequence** of the interconnections among the units and the streams.
3) The **levels** of production as given by the stream flow rates.

1.3 Objective and Scope of Study

The main objective of this research project is to develop a mathematical optimization model to determine the optimal configuration of a petroleum refinery. In order to achieve the main objectives, the following sub-objectives are formed:

1. To develop a superstructure representation for a refinery network topology with a suitable level of detail and abstraction by incorporating environmental features;
2. To construct an optimization model based on the superstructure representation that includes: (a) mass balances (linear), (b) energy balances, and (c) logical constraints enforcing the design specifications and the interconnectivity relationships among the units and the streams for the selection of the alternative routes;
3. To solve the mixed-integer linear programming (MILP) optimization model using the modelling language GAMS as the interface between the model and optimization solver.

CHAPTER 2

LITERATURE REVIEW

2.1 Petroleum Refinery Optimization: An Overview

The petroleum refining industry converts crude oil into more than 2500 refined products, including liquefied petroleum gas, gasoline, kerosene, aviation fuel, diesel fuel, fuel oils, lubricating oils, and feedstocks for the petrochemical industry [13]. Petroleum refinery activities start with receipt of crude for storage at the refinery, include all petroleum handling and refining operations, and they terminate with storage preparatory to shipping the refined products from the refinery. The petroleum refining industry employs a wide variety of processes [5]. A refinery's processing flow scheme is largely determined by the composition of the crude oil feedstock and the chosen slate of petroleum products. It contents 3 main part of process flow which are separation, conversion and treating process.

Optimization from practical level is defined as a system or process to find the best possible find the best possible solution to this process with respect to a certain objective and subject to within certain constraints (material and energy balances, equilibrium relationships, . minimum approach temperature, T_{min}, design equations for reactor, thermodynamic limitations on the problem) [9]. From mathematical definition of optimization it is defined as a space of alternatives that are specified through constraints in a mathematical model, select decision variables to optimize an objective function. For FYP II, the main concern of the project is being narrowed to the subsystem of naphtha hydroprocessing. Below are the main units of the naphtha processing and brief description on the every unit:

2.1.1 Fluidized-bed Catalytic Cracking (FCC)

The FCC process uses a catalyst in the form of very fine particles that act as a fluid when aerated with a vapor. Fresh feed is preheated in a process heater and introduced into the bottom of a vertical transfer line or riser with hot regenerated catalyst. The hot catalyst vaporizes the feed, bringing both to the desired reaction temperature, 470 to 525°C (880 to 980°F) The high activity of modern catalysts causes most of the cracking reactions to take place in the riser as the catalyst and oil mixture flows upward into the reactor. The hydrocarbon vapors are separated from the catalyst particles by cyclones in the reactor. The reaction products are sent to a fractionators for separation [13] .

The spent catalyst falls to the bottom of the reactor and is steam stripped as it exits the reactor bottom to remove absorbed hydrocarbons. The spent catalyst is then conveyed to a regenerator. In the regenerator, coke deposited on the catalyst as a result of the cracking reactions is burned off in a controlled combustion process with preheated air. Regenerator temperature is usually 590 to 675°C (1100 to 1250°F). The catalyst is then recycled to be mixed with fresh hydrocarbon feed.

2.1.2 Thermal Cracking

Thermal cracking processes include visbreaking and coking, which break heavy oil molecules by exposing them to high temperatures. For visbreaking, topped crude or vacuum residuals are heated and thermally cracked (455 to 480°C, 3.5 to 17.6 kg/cm2 [850 to 900°F, 50 to 250 pounds per square inch gauge (psig)]) in the visbreaker furnace to reduce the viscosity, or pour point, of the charge. The cracked products are quenched with gas oil and flashed into a fractionator. The vapor overhead from the fractionator is separated into light distillate products. A heavy distillate recovered from the fractionator liquid can be used as either a fuel oil blending component or catalytic cracking feed [13].

Coking is a thermal cracking process used to convert low value residual fuel oil to higher value gas oil and petroleum coke. Vacuum residuals and thermal tars are cracked in the coking process at high temperature and low pressure. Products are petroleum coke, gas oils, and lighter petroleum stocks. Delayed coking is the most widely used process today, but fluid coking is expected to become an important process in the future. In the delayed coking process, heated charge stock is fed into the bottom of a fractionator, where light ends are stripped from the feed.

The stripped feed is then combined with recycle products from the coke drum and rapidly heated in the coking heater to a temperature of 480 to 590°C (900 to 1100°F). Steam injection is used to control the residence time in the heater. The vapor-liquid feed leaves the heater, passing to a coke drum where, with controlled residence time, pressure (1.8 to 2.1 kg/cm2 [25 to 30 psig]), and temperature (400°C [750°F]), it is cracked to form coke and vapors. Vapors from the drum return to the fractionator, where the thermal cracking products are recovered.

2.1.3 Naphtha Hydrotreating

Hydrotreating, often referred to hydroprocessing, is used to remove impurities (e.g., sulfur, nitrogen, oxygen, halides, and trace metals) from petroleum fractions. When the process is employed specifically for sulfur removal, it is usually called hydrodesulphurization. Hydrotreating further "upgrades" heavy feeds by converting olefins and diolefins to paraffins, which reduces gum formation in fuels. Hydroprocessing also cracks heavier products to lighter, more saleable products. The severity of the hydrotreating process determines the final result. Mild hydrotreating, for example, is employed to remove sulfur and saturate olefins. More severe hydrotreating saturates aromatic rings and removes nitrogen and additional sulfur [14].

2.1.4 Hydrocracking

Hydrocracker is designed to produce high quality distillate products. It converts vacuum gas oil (MVGO and HVGO) to premium diesel, heavy diesel, kerosene and naphtha. Hydrocracking is a catalytic cracking process assisted by the presence of an elevated partial pressure of hydrogen gas. Similar to the hydrotreater, the function of hydrogen is the purification of the hydrocarbon stream from sulfur and nitrogen hetero-atoms.

The products of this process are saturated hydrocarbons; depending on the reaction conditions (temperature, pressure, and catalyst activity) these products range from ethane, LPG to heavier hydrocarbons comprising mostly of isoparaffins. Hydrocracking is normally facilitated by a bifunctional catalyst that is capable of rearranging and breaking hydrocarbon chains as well as adding hydrogen to aromatics and olefins to produce naphthenes and alkanes. Major products from hydrocracking are jet fuel and diesel, while also high octane rating gasoline fractions and LPG are produced. All these products have a very low content of sulfur and other contaminants.

2.1.5 Sulfur Recovery Plant

Sulfur recovery plants are used in petroleum refineries to convert the hydrogen sulfide (H2S) separated from refinery gas streams into the more disposable byproduct, elemental sulfur [13]. The **Claus process** is the most significant gas desulfurizing process, recovering elemental sulfur from gaseous hydrogen sulfide. First patented in 1883 by the scientist *Carl Friedrich Claus*, the Claus process has become the industry standard. The multi-step Claus process recovers sulfur from the gaseous hydrogen sulfide found in raw natural gas and from the by-product gases containing hydrogen sulfide derived from refining crude oil and other industrial processes.

2.2 Superstructure Representation of Design Alternative

A general flow sheet contains 3 main elements which are state, task and equipment. State refers to the physical, chemical properties and also composition of a stream in the process. This can represent by quantitative information such as mass flow, temperature, pressure and composition. Task is defined as physical and chemical transformation that can occur between two sates or simply process. Equipments are physical devices that execute a given task. The two fundamental superstructure representations are State-task Network (STN) and State-Equipment Network (SEN) [9].

State-Task Network (STN) representations require state and task to be defined while the equipment assignment is unknown. State-Equipment Network (SEN) requires state and equipment to be defined while the task to the equipment is to be defined. In this project, State-task Network (STN) is used because of:

1. Most straight forward representation from which are clear optimization model can best be formulated to establish a systematic approach for determining the optimum configuration of a refinery.
2. Can handles the assignment of equipment implicitly and then reduce the combinatorial complexity of the mathematical model.

In this project, mathematical modeling is done by mixed integer linear programming (MILP). MILP is a commonly occurring type of optimization problem involves both integer and continuous variables. These are very useful to many engineering applications especially the various requirements of process design optimization. It is simply to optimize the continuous variable for the various integer variable combinations (i.e., optimize continuous variable for each set of values of possible integers values then compare and select the best values) [11].

2.3 Environmental Concern

2.3.1 Global Warming

Global Warming is defined as the increase of the average temperature on Earth. As the Earth is getting hotter, disasters like hurricanes, droughts and floods are getting more frequent. Global warming is the term extensively used to portray a potentially dramatic increase in the annual average global surface temperature of the Earth. Estimates of how big that temperature increase will be range from 1.5 °C to 4 °C (Houghton *et al.*, 1996). The vivid temperature increased and the profound alterations towards the climate change are believed to be caused by CO_2 emission and other greenhouse gases in Earth's atmosphere.

Drake (2000) says that "These greenhouse gases act to trap outgoing thermal radiation which then warms the earth" (p.1). With the onset of the industrial revolution in the 1700s, increasing use has been made of fossil fuels which release large amount of CO_2 when burnt (Weyant and Yanisagawa, 1998). The industrial and domestic energy demands of our modern society mean that approximately 7 gigatonnes (Gt) of carbon dioxide being released every year (Houghton et al., 1996). When it comes to the upstream activities, over 13 TSCF of net hydrocarbon gas remained undeveloped due to the high CO_2 contents ranging from 28% to 87% [7].

At present, all CO_2 from producing fields and excess CO_2 from gas plants in Malaysia are being vented out to the atmosphere. Effective and optimal disposal of CO_2 is required if the high CO_2 gas fields are to be developed.

2.4 Environmental Performance Assessment for Risk Evaluation of Flow sheets

2.4.1 Life cycle analysis (LCA) by Allen and Shonnard (2002) [1]

To incorporate environmental considerations in the proposed modeling framework, the life cycle analysis (LCA) approach is utilize proposed by Allen and Shonnard (2002) that uses certain performance assessment metrics for the environmental risk evaluation of process flowsheets. The methodology aims to rank the available design alternatives through performing their relative environmental risk assessment by integrating the following aspects into the design:

a) Emissions estimation
b) Environmental fate and transport calculations
c) Environmental impact data and indicators.

In this work, the refinery air emissions is represent with a set of relative environmental risk indices that measure the potential of global warming (GWP), stratospheric ozone depletion (ODP), acid rain deposition/acidification (ARP), and smog formation (SFP). To estimate the index for a particular impact category, the contributions of each chemical released from a process weighted by their emission rate is being sum up, yielding:

$$I_{\{\overline{\text{GWP}},\overline{\text{ODP}},\overline{\text{ARP}},\overline{\text{SFP}}\}\in\overline{\text{DPRI}}} = \sum_{i\in I}\left(\text{Dimensionless Potential Risk Index DPRI}\right)_i \times m_i$$

$$I_{\{\text{GWP},\text{ODP},\text{ARP},\text{SFP}\}\in\text{DPRI}} = \sum_{i\in I}\left(\text{Dimensionless Potential Risk Index DPRI}\right)_i \times m_i$$
$$= I^{*}_{\text{DPRI},i} \times m_i$$

But in our case especially for global warming,

$$I_{\mathrm{GWP}} = \sum_{i \in I} \mathrm{GWP}_i \times (\text{emission factor} \times f_i)$$
$$= (\mathrm{GWP}_{\mathrm{CO_2}} \times m_{\mathrm{CO_2}}) + (\mathrm{GWP}_{\mathrm{CO}} \times m_{\mathrm{CO}}) + (\mathrm{GWP}_{\mathrm{SOx}} \times m_{\mathrm{SOx}}) + (\mathrm{GWP}_{\mathrm{NOx}} \times m_{\mathrm{NOx}})$$

In which the emission rate m_i is given by the multiplication of the emission factor and mass flowrate. The greenhouse chemicals or pollutants i considered in this work are CO_2, CO, SO_x, and NO_x. To illustrate an example, the sum for the product of the GWP and the mass emission rate of a pollutant over all pollutants considered, results in I_{GW} for the entire process, which in other words, is the sum of the emissions-weighted GWPs for each pollutant. It provides the equivalent process emissions of greenhouse chemicals in the form of the benchmark compound CO_2. The summation of the indices, as given by the following expression, is appended to the objective function for minimization:

$$I_{\mathrm{PC}} = \sum_{i \in I} \sum_{p \in P} (I_{\mathrm{GWP},i} + I_{\mathrm{ODP},i} + I_{\mathrm{ARP},i} + I_{\mathrm{SFP},i})$$

2.5 Type Of Pollutants Emitted from Each Unit In Superstructure. [13]

During the refining of crude oil into various petroleum products, petroleum refineries use and generate an enormous amount of chemicals, some of which are present in air emissions, wastewater, or solid wastes. Emissions are also created through the combustion of fuels and as by-products of chemical reactions occurring when petroleum fractions are upgraded. Process heaters and boilers are a large source of air emissions. In addition to CO, SOx, and NOx, some processes create considerable amounts of particulates and other emissions from catalyst regeneration or decoking processes. Volatile chemicals and hydrocarbons are also released from equipment leaks, storage tanks, and wastewaters.

2.5.1 Separation/Topping Process

Table 2.5.1: Summary of Emissions, Effluents, Residuals and Waste Streams for Topping/Separation Processes

Process	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Crude Oil Desalting	Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)	Hot salty process water (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids). Water flow = 2.1 gal/bbl of oil	Crude oil/desalter sludge (iron rust, clay, and, water, emulsified oil sand wax, heavy metals)
Crude Distillation (atmospheric and vacuum)	Heater stack gas (CO, SOx, NOx, ydrocarbons and particulates and steam injector emissions (hydrocarbons)	Oily sour water from the fractionators (hydrogen sulfide, ammonia, suspended solids, chlorides, mercaptans, phenol). Water flow = 26.0 gal/bbl oil	Little or no residual, wastes or by-products

2.5.2 Thermal and Catalytic Cracking Processes

Table 2.5.2: Summary of Emissions, Effluents, Residuals and Waste Streams for Thermal and Catalytic Cracking Processes

Process	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Visbreaking	Fugitive emissions from process vents	Sour wastewater from the fractionator (hydrogen sulfide, ammonia, phenol, suspended solids, dissolved solids). Water flow = 2.0 gal/bbl feed	Little or no residuals, waste or by-products generated
Coking	Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates) Particulate emissions from decoking can also be considerabl	Coke-laden water from decoking operations in delayed cokers (hydrogen sulfide, ammonia, suspended solids) [Fluid coking produces little or no effluents]. Water flow = 1.0 gal/bbl feed	Coke dust (carbon particles and hydrocarbons) may not be a waste; coke fines may be a produc
Fluid Catalytic Cracking	Catalyst regeneration and CO boilers (hydrocarbons, CO, NOx, SOx and particulates	Sour wastewater from the fractionator/gas concentration units and steam strippers (high levels of oil, suspended solids, phenols, cyanides, H2S, NH3).). Water Flow = 15 gal/bbl feed	Spent catalysts (metals from crude oil and hydrocarbons), spent catalyst fines from electrostatic precipitators (aluminum silicate and metals).
Catalytic Hydrocracking	Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)	Sour wastewater from the fractionator and hydrogen separator (suspended solids, H2S). Water Flow = 2 gal/bbl feed	Spent catalysts (metals from crude oil, and hydrocarbons).

2.5.3 Combination/Rearrangement Process

Table 2.5.3: Summary of Emissions, Effluents, Residuals and Waste Streams for Combination/Rearrangement Processes

Process	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Alkylation	Process vents, fugitive emissions	Wastewater from water-wash of reactor hydrocarbon products (suspended solids, dissolved solids, hydrogen sulfide), spent sulfuric acid Water flow = ~2.6 gal/bbl feed Spent Sulfuric Acid = 13-30 lbs/bbl alkylate	Neutralized alkylation sludge (sulfuric acid, hydrocarbons
Catalytic Reforming	Heater stack gas (CO, SOx, NOx), hydrocarbons and particulates), fugitive emissions, and catalyst regeneration	Process wastewater (high levels of oil, suspended solids, low hydrogen sulfide) Water flow = 6.0 gal/bbl feed	Spent catalyst and hydrogen gas Hydrogen Gas production: 1100 - 1700 scf/bbl:
Isomerization	(CO, SOx, NOx, hydrocarbons and particulates), HCl (possible in fuel gas), vents and fugitive emissions (hydrocarbons	Sour water (low hydrogen sulfide, ammonia), chloride salts, and caustic wash water	Calcium chloride sludge from neutralized HCl gas
Ethers Manufacture	Boiler stack gas (CO, SOx, NOx, hydrocarbons and particulates)	Pretreatment wash-water (nitrogen contaminants); cooling and alcohol wash water are recycled	Spent catalysts

2.5.4 Treatment Process

Table 2.5.4: Summary of Emissions, Effluents, Residuals, By-Products and Waste Streams for Specialty Products Manufacture

Process	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Catalytic Hydrotreating	Heater stack gas (CO, SOx, NOx, hydrocarbons and particulates)	Sour wastewater from the fractionator and hydrogen separator (suspended solids, H2S, NH3, phenols) Water Flow = 1 gal/bbl feed	Spent catalyst fines (aluminum silicate and metals)
Sweetening/ Merox Process	Vents and fugitive emission	Little or no wastewater generated	Spent caustic solution, residual oil-disulfide mixture
Sulfur Removal/ Claus Process	Process tail gas (NOx, SOx, hydrogen sulfide), fugitive emissions	Process wastewater (hydrogen sulfide, ammonia)	Hazardous air emissions - hydrogen sulfide, carbonyl sulfide (COS) and carbon disulfide (CS2); fugitive solvent emissions may be toxic (e.g., diethanolamine)

2.5.5 Specialty Product Manufacture Process

Table 2.5.5: Summary of Emissions, Effluents, Residuals, By-Products and Waste Streams for Specialty Products Manufacture

Process	Largest Sources of Air Emissions	Largest Sources of Process Wastewater	Waste, Residuals, or By-Products
Lubricating Oil Manufacture (deasphalting, solvent extraction, dewaxing	Heater stack gas (CO, NOx, SOx, hydrocarbons, particulates), fugitive propane, and fugitive solvents)	Steam stripping wastewater (oil and solvents), solvent recovery wastewater (oil and propane	Little or no residuals, wastes or by-products Fugitive solvent emissions may be toxic

2.6 Emission Factor for EFRAT Method

2.6.1 Process Unit emission factor

An **emission factor** can be defined as the average emission rate of a given pollutant for a given source, relative to the intensity of a specific activity. Emission factors are used to derive estimates of air pollutant or greenhouse gas emissions based on the amount of fuel combusted, the number of animals in animal husbandry, on industrial production levels, distances traveled or similar activity data [14].

Table 2.6.1: Air Emission Factor for Petroleum Process

Table 2-8. Air Emission Factors for Petroleum Refining Processes (lbs/1000 barrels of fresh feed)

Process	SOx	NOx	CO	Hydrocarbons	Aldehydes	Ammonia	Particulates
Fluid Catalytic Cracking Units							
- Uncontrolled	493	71	13,700	220	19	54	242
- Electrostatic Precipator and CO Boiler	493	71	Neg	Neg	Neg	Neg	45
Moving Bed Catalytic Crackers	60	5	3,800	87	12	6	17
Fluid Cokers							
- Uncontrolled	ND	ND	ND	ND	ND	ND	523
- Electrostatic Precipator and CO Boiler	ND	ND	Neg	Neg	Neg	Neg	6.8
Vacuum Distillation Column Condensers							
- Uncontrolled	Neg	Neg	Neg	50	Neg	Neg	Neg
- Controlled (vented to heater or incinerator)	Neg	Neg	Neg		Neg	Neg	Neg
Claus Plant and Tail Gas Treatment							
- SCOT Absorber and Incinerator	5.66	Neg	Neg	Neg	Neg	Neg	Neg
- Incinerator Exhaust Stack (2 Catalytic Stages)	85.9	Neg	Neg	Neg	Neg	Neg	Neg
Blowdown Systems							
- Uncontrolled	Neg	Neg	Neg	560	Neg	Neg	Neg
- Vapor Recovery System and Flaring	26.9	18.9	Neg	0.8	Neg	Neg	Neg

2.6.2 Emission Factor based on CWT method

The sector organizations CONCAWE and European have investigated and further developed the Solomon CWB approach, which resulted in the Solomon "CO2 weighted tonne" (CWT) approach. This approach is owned by CONCAWE who is free to promote it and apply it within Europe. When using the CWT approach, the single "product" of the refinery is the CWT. To develop the factors, Solomon used an extensive database on some 200 worldwide refineries which have for many years, supplied energy consumption data, as well as consulted process licensors. The present set of values has been in use since 2006. It is important to note that the CWT factors are only used as weighing factors between individual units within the refinery [15].

The actual benchmarking (i.e. measuring difference in performance) is done when comparing the actual emissions to total CWT of the refinery. Since the CWT factors serve as weighting factors for different process units, changing a factor would only change the relative impact of that process unit. Lowering CWT factors as such would thus not automatically result in a steeper benchmark curve and/or a higher level of free allocation to refineries [15].

Each of the generic process unit was assigned an emission factor relative to crude distillation, which is denoted as the CWT factor (see **Table 2.6.2**). The CWT factor of the crude distillation unit is taken as 1, and factors of other units are representative of their CO2 emission intensity at an average level of energy efficiency, for the same standard fuel type for each process units for combustion, and for average process emissions of the process unit [15].

Since we tend to have some problem regarding the emission factor before this, so by applying this approach this problem is being solved. As a result of that, the CWT value has been used as the emission factor throughout the modeling section.

Table 2.6.2: Basis for throughput and CWT factors for CWT process units

CWT process unit	Basis for throughput[1]	CWT factor[2]
Atmospheric Crude Distillation	F	1.00
Vacuum Distillation	F	0.85
Visbreaker	F	1.40
Delayed Coker	F	2.20
Fluid Coker	F	7.60
Flexicoker	F	16.60
Fluid Catalytic Cracking	F	5.50
Other Catalytic Cracking	F	4.10
Thermal Cracking	F	2.70
Distillate/Gas oil hydrocracker	F	2.85
Residual Hydrocracker	F	3.75
Naphtha Hydrotreater	F	1.10
Kerosene/Diesel Hydrotreater	F	0.90
Residual Hydrotreater	F	1.55
VGO Hydrotreater	F	0.90
Reformer (inc. AROMAX)	F	4.95
Solvent Deasphalter	F	2.45
Alky/Poly/Dimersol	P	7.25
C4 Isom	R	3.25
C5/C6 isom	R	2.85
Coke Calciner	P	12.75
Hydrogen production, gas feed	P	296.00
Hydrogen production, liquid feed	P	348.00
Special fractionation for purchased NGL	F	1.00
Propylene	F	3.45
Asphalt	P	2.10
Polymer Modified Asphalt	P	0.55
Sulphur	P	18.60
Oxygenates	P	5.60

2.7 Objective Function

The goal of this research project is to determine the flow sheet of the optimal refinery network topology with the minimum annualized cost and environmental impacts. *Capital cost* is defined as the investment required to construct the plant and serve to identify and better characterized the project. *Operating cost* is the annual cost required to operate the plant. This consists of *variable cost* and *fixed cost. Fixed cost* is immobile and means that the money, once spent, cannot be quickly converted in to cash or other asset [11].

The objective function involves a combination of the following:

1. Minimizing the cost components that consist of the capital investment cost for equipment (CC_i), installation cost (IC_i), raw material cost (RMC_i), and operating cost (OC_i) associated with utility consumption (electricity, cooling water, and steam);

2. Maximizing revenues from the sales of the refined products (S_i); and

3. Minimizing environmental risk in our case is CO_2 emission rate cost. Thus, the objective function is expressed as:

$$\min z = \underbrace{\sum_{i \in I} \left(CC_i + IC_i + RMC_i + OC_i - S_i \right)}_{\text{economic-based costs}} + \underbrace{\sum_{i \in I} \sum_{p \in P} CO_2 EmissionRate \times CO_2 Cost}_{\text{environmental risk indices}}$$

2.8 GAMS Modeling

The General Algebraic Modeling System (GAMS) is specifically designed for modeling linear, nonlinear and mixed integer optimization problems. The system is especially useful with large, complex problems. GAM is available for use on personal computers, workstations, mainframes and supercomputers. GAMS allow the user to concentrate on the modeling problem by making the setup simple. The system takes care of the time-consuming details of the specific machine and system software implementation. GAMS is especially useful for handling large, complex, one-of-a-kind problems which may require many revisions to establish an accurate model. The system models problems in a highly compact and natural way. The user can change the formulation quickly and easily, can change from one solver to another, and can even convert from linear to nonlinear with little trouble [2].

Using GAMS, data are entered only once in familiar list and table form. Models are described in concise algebraic statements which are easy for both humans and machines to read. Whole sets of closely related constraints are entered in one statement. GAMS automatically generate each constraint equation, and let the user make exceptions in cases where generality is not desired. Statements in models can be reused without having to change the algebra when other instances of the same or related problems arise. The location and type of errors are pinpointed before a solution is attempted [2].

GAMS handles dynamic models involving time sequences, lags and leads and treatment of temporal endpoints. GAMS is flexible and powerful. Models are fully portable from one computer platform to another when GAMS is loaded to each platform. GAMS facilitates sensitivity analysis. The user can easily program a model to solve for different values of an element and then generate an output report listing the solution characteristics for each case. [2]

CHAPTER 3

METHODOLOGY/PLANNED PROJECT WORK

3.1 Procedure Identification

In order to determine the optimal topology or configuration of a petroleum refinery superstructure representation, the optimal operating conditions for the process unit and the optimal flow rates of the material streams; a tradeoff between some factors need to be considered intensely. These factors are process operability, raw material utilization and energy management [9].

In this work, the mathematical model programming approach is utilized to determine the optimal design routes of design alternatives of refinery processing. In general, the mathematical programming approach to process synthesis and design activities and problems consists of the following four major steps (Grossmann, 1990; Floudas, 1995, pp. 233.234; Novak et al., 1996) as in Figure 3.1 with the following descriptions:

1. Development of the superstructure to represent the space of topological alternatives of the naphtha flow to petrochemical plant configuration;
2. Establishment of the general solution strategy to determine the optimal topology from the superstructure representation of candidates;
3. Formulation or modeling of the postulated superstructure in a mathematical form that involves discrete and continuous variables for the selection of the configuration and operating levels, respectively; and
4. Solution of the corresponding mathematical form, i.e., the optimization model from which the optimal topology is determined.

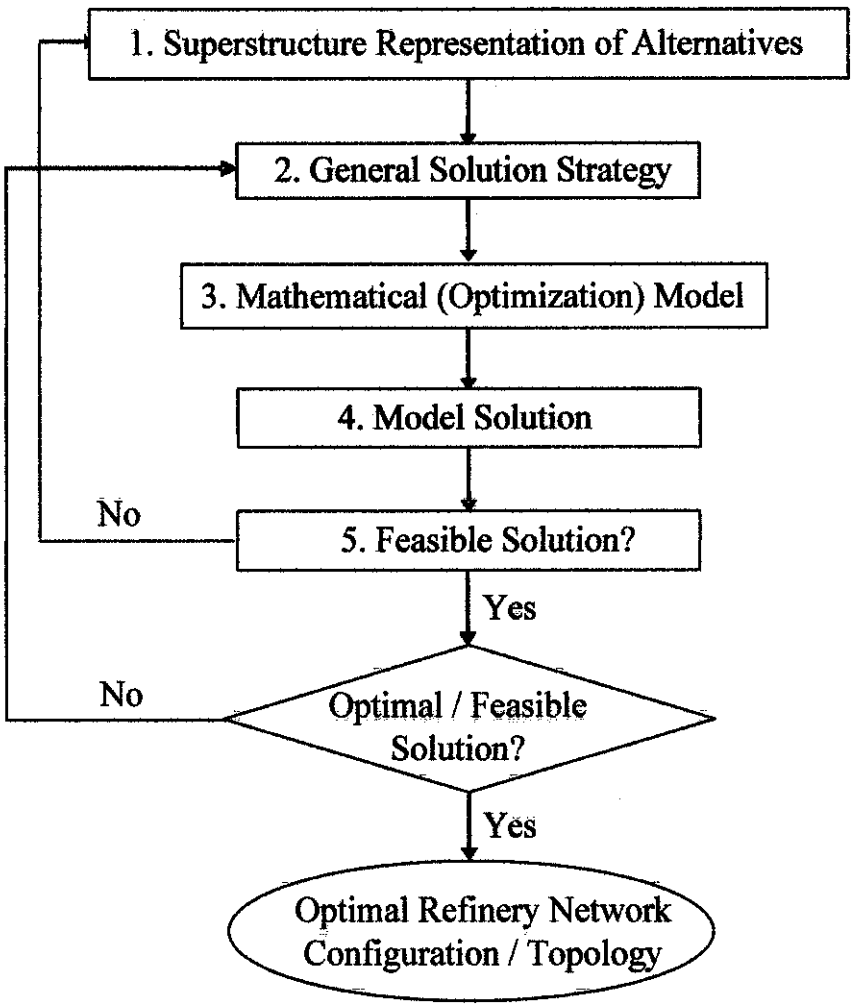


Figure 3.1 Major steps in the mathematical programming approach to Synthesis and design problems

3.2 Superstructure Representation of Alternatives

Figure 1 shows a State–Task Network (STN)-based superstructure representation that is sufficiently rich to embed all feasible alternative topologies for a refinery. We begin with the development of a state–task network (STN)-based superstructure representation that is sufficiently rich to encompass all possible topology alternatives of a conventional oil refinery. Subsequently, a bi-objective mixed-integer linear program (MILP) of profit maximization and environmental impacts minimization is formulated according to the constructed superstructure. Then, based on a given set of fixed amounts of desired products, the model is solved to generate an optimal topology. The proposed optimization framework also incorporates principles from life cycle analysis (LCA) to account for potential environmental impacts [1]. As being state before, to facilitate development of the superstructure, a typical refinery network is considered to be decomposed into four processing pools:

1) Naphtha exiting the atmospheric distillation unit (ADU);
2) Reduced crude from the ADU and the vacuum distillation unit (VDU);
3) Vacuum gas oil from VDU;
4) Heavy oil processing and upgrading.

For this semester, the scope of the Final Year Project 2 (FYP 2) is to formulate and modify the superstructure representation for the Naphtha exiting the distillation unit, in order to develop the logical constraints and to calculate the mass balance. This also involves getting familiarized with the modeling software GAMS and already started the modeling dot that pool. Based on the information and knowledge about the physics of the problem of Naphtha processing unit, we represent all these possible processing alternatives on a superstructure, which is a diagram that contains multiple feasible flowsheets for naphtha processing. Below are the abbreviations of the unit in the superstructure and the description for them:

Table 3.2: Legend for the STN superstructure representation in Figure 3.2

CR	Crude oil	HDT	Hydrotreater
ADU	Atmospheric distillation unit	LPG	Liquefied petroleum gas
LSRN	Light straight run naphtha	H2	Hydrogen
HSRN	Heavy straight run naphtha	ISO	Isomerization unit
NAP	Naphtha	SRU	Sulfur recovery unit
MIX	Mixer	REF	Reformer
SPLT	Splitter	S	Sulfur
VIS	Visbreaker	FG	Fuel gas
COK	Coker	BLND	Blending
FCC	Fluidized catalytic cracker	FGH	Fuel gas header
HCR	Hydrocracker	GSLN	Gasoline
PCHN	Purchased naphtha	TG	Tail gas

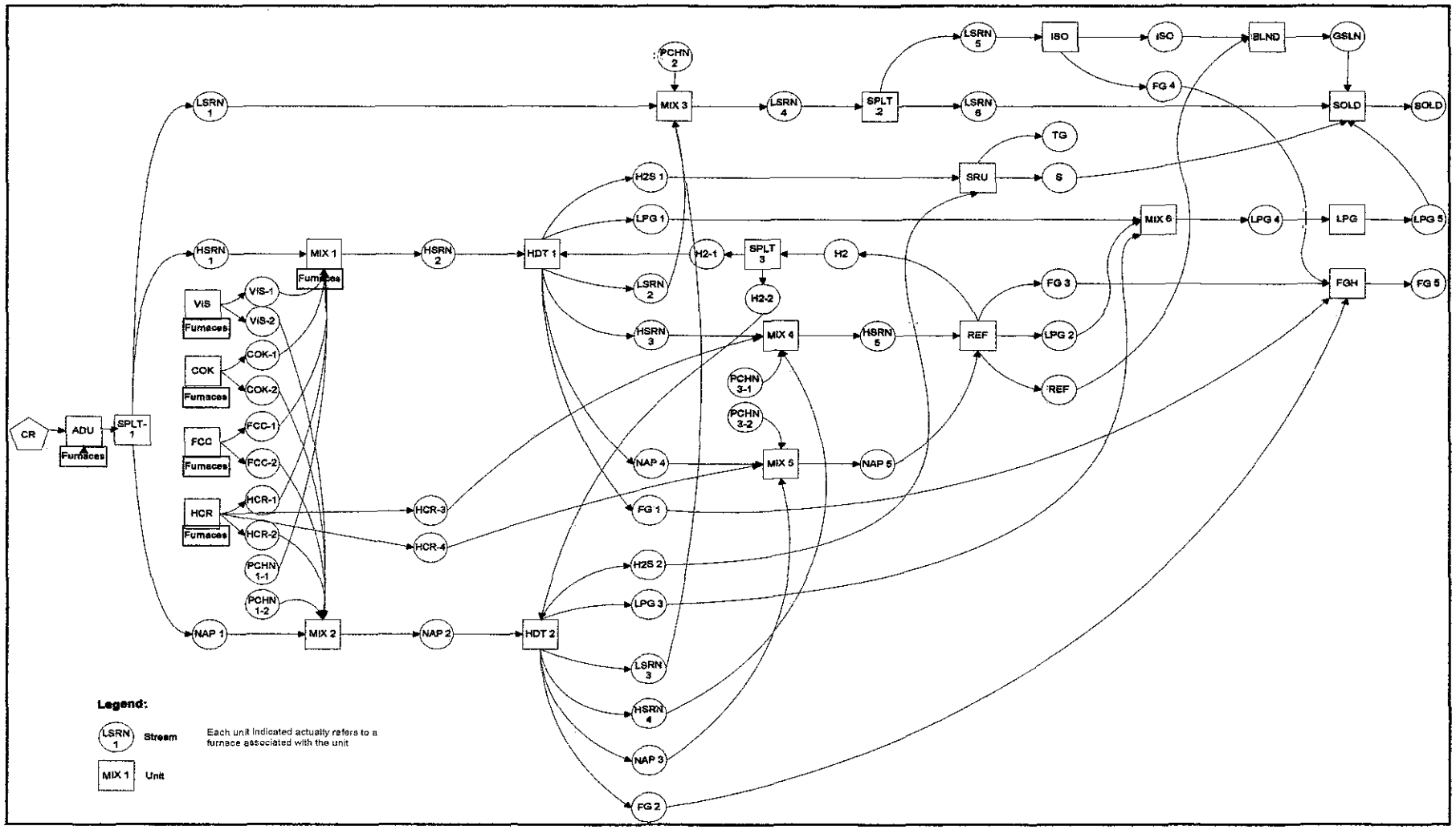


Figure 3.2: State–task network (STN) superstructure representation for the naphtha produced from the ADU

3.3 Mathematical Model Formulation

The refinery air emissions are representing with a set of relative environmental risk indices that measure the potential of global warming (GWP [1]. To estimate the index for a particular impact category, the contributions of each chemical released from a process weighted by their emission rate is being sum up, yielding:

$$I_{\{\overline{\text{GWP}},\overline{\text{ODP}},\overline{\text{ARP}},\overline{\text{SFP}}\}\in\overline{\text{DPRI}}} = \sum_{i\in I}\left(\text{Dimensionless Potential Risk Index DPRI}\right)_i \times m_i$$

$$I_{\{\text{GWP,ODP,ARP,SFP}\}\in\text{DPRI}} = \sum_{i\in I}\left(\text{Dimensionless Potential Risk Index DPRI}\right)_i \times m_i$$
$$= I^{*}_{\text{DPRI},i} \times m_i$$

But in our case especially for global warming we interested in how much CO_2 emission is being emitted from the refinery. So the environmental indices is not being together in the equation but the concept how the CO_2 emission is being calculated is being described in the equation below:

$$CO_2 Emission Rate = \sum_{i\in I}\left(\text{emission factor} \times f_i\right)$$

In which the emission rate is given by the multiplication of the emission factor and mass flowrate from each unit in the superstructure. The greenhouse chemicals or pollutants *i* considered in this work are CO_2. Then we relate the CO_2 emission rate with the economic term by multiply the CO_2 emission rate with the CO_2 emission cost and get the equation below:

$$CO_2 Emission\_Cost = \sum_{i\in I}\left(CO_2 \text{ emission rate} \times CO_2 \text{ emission cost}\right)$$

The objective function involves a combination of the following:

1. Minimizing the cost components that consist of the capital investment cost for equipment (CC_i), installation cost (IC_i), raw material cost (RMC_i), and operating cost (OC_i) associated with utility consumption (electricity, cooling water, and steam);

2. Maximizing revenues from the sales of the refined products (S_i); and

3. Minimizing the environmental risk cost. Thus, the objective function is expressed as:

$$\min z = \underbrace{\sum_{i \in I} \left(CC_i + IC_i + RMC_i + OC_i - S_i \right)}_{\text{economic-based costs}} + \underbrace{\sum_{i \in I} \sum_{p \in P} CO_2 EmissionRate \times CO_2 Cost}_{\text{environmental risk indices}}$$

3.4 CO_2 Emission Calculation

The calculation is done based on Allan and Shonnard Method of LCA analysis. One assumption is made that is the CWT factor is taken as emission factor because of CWT factors are used as weighing factors between individual units within the refinery [15]. The actual benchmarking (i.e. measuring difference in performance) is done when comparing the actual emissions to total CWT of the refinery. Since the CWT factors serve as weighting factors for different process units, changing a factor would only change the relative impact of that process unit.

Example of Calculation

CO_2 Emission Rate = Unit Capacity *Emission Factor

$$= \frac{1\ lbs}{1000 bbl} * \frac{130000\ bbl}{day} * \frac{365 day}{year}$$

= 47,450 lbs/year

= 21522.96 kg/year

CO_2 Emission Cost = CO_2 Emission Rate * CO2 Cost

= 21522.96 kg/year *RM10/kg

= RM215, 230/year.

3.5 Constraints

3.5.1 Material Balances

3.5.1.1 Overall Material Balances around Mixing and Splitting units

- Material Balance in Splitter 1 (SPLT-1)

  f ('CR') = f('NAP1')+f('LSRN1')+f('HSRN1')

- Material Balance on Splitter 2 (SPLT-2)

  f ('H2') = f('H2_1')+f('H2_2')

- Material Balance on Splitter 3 (SPLT-3)

  f ('LSRN4') = f('LSRN5')+f('LSRN6')

- Material Balance on Mixer 1 (MIX-1)

  f('HSRN1')+f('VIS_1')+f('COK_1')+f('FCC_1')+f('HCR_1')+f('PCHN1_1') = f('HSRN2')

- Material Balance on Mixer 2 (MIX-2)

  f('NAP1')+f('VIS_2')+f('COK_2')+f('FCC_2')+f('HCR_2')+f('PCHN1_2') = f('NAP2')

- Material Balance on Mixer 3 (MIX-3)

  f ('LSRN1')+f('LSRN2')+f('LSRN3')+f('PCHN2') = f('LSRN4')

- Material Balance on Mixer 4 (MIX-4)

  f ('HSRN3')+f('HSRN4')+f('PCHN3_1')+f('HCR_3') = f('HSRN5')

- Material Balance on Mixer 5 (MIX-5)

  f ('NAP3')+f('NAP4')+f('PCHN3_2')+f('HCR_4') = f('NAP5')

3.5.1.2 Overall Material Balances around Process Unit

- Material Balance around Atmospheric Distillation Unit (ADU)

  0.0555*f ('CR') = f ('LSRN1')

  0.1533*f ('CR') = f ('HSRN1')

  0.2088*f ('CR') = f ('NAP1')

  0.4176*f ('CR') = f ('NAP1') + f ('HSRN1') + f ('LSRN1')

- Material Balance around Isomerization Unit (ISO)

  0.01*f ('LSRN5') = f ('FG4')

  0.99*f ('LSRN5') = f ('ISO')

- Material Balance around Sulfur Recovery Unit (SRU)

  0.8478*(f ('H2S1') +f ('H2S2')) = f ('S')

  0.1522*(f ('H2S1') +f ('H2S2')) = f ('TG')

- Material Balance around Catalytic Reforming Unit (REF)

  0.0320*(f ('HSRN5') +f ('NAP5')) = f ('H2')

  0.0370*(f ('HSRN5') +f ('NAP5')) = f ('FG3')

  0.0780*(f ('HSRN5') +f ('NAP5')) = f ('LPG2')

  0.8530*(f ('HSRN5') +f ('NAP5')) = f ('REF')

3.5.1.3 Material Balance for HDT operating Mode

- Material Balance on HDT-1 mode

  0.0109*(f ('HSRN2') +f ('H2_1')) = f ('FG1')

  0.0012*(f ('HSRN2') +f ('H2_1')) = f ('H2S1')

  0.0058*(f ('HSRN2') +f ('H2_1')) = f ('LPG1')

  0.9821*(f ('HSRN2') +f ('H2_1')) = f ('LSRN2') +f ('HSRN3') +f ('NAP4')

  2.763*f ('LSRN2') =f ('HSRN3')

0.9821*(f ('HSRN2') +f ('H2_1')) = f ('NAP4')

- Material Balance on HDT-2 mode

0.0109*(f ('NAP2') +f ('H2_2')) = f ('FG2')

0.0012*(f ('NAP2') +f ('H2_2')) = f ('H2S2')

0.0058*(f ('NAP2') +f ('H2_2')) = f ('LPG3')

0.2610*(f ('NAP2') +f ('H2_2')) = f ('LSRN3')

0.7211*(f ('NAP2') +f ('H2_2')) = f ('HSRN4')

0.9821*(f ('NAP2') +f ('H2_2')) = f ('NAP3')

3.5.2 Market Demand for Products

Table 3.5.2: Market Demand for Products

Product	Production Requirement (kg/hr)
Crude, CRs	≥10000000
Crude, CRs	≤50000000
Gasoline, GSLNs	≥7000000
Liquefied Petroleum Gas, LPG5s	≥1000000
Fuel Gas, FG5s	≥1000000
Petro Chemical Naphtha, PCHN3_1s	≤1000
Petro Chemical Naphtha ,PCHN3_2s	≤1000
Fluid catalytic Cracking, FCC_1s	≤2000000
Fluid catalytic Cracking ,FCC_2s	≤2000000

3.5.3 Logical Constraint

3.5.3.1 Big-M Logical Constraint

The purpose of this constraint in the model is to make sure that when a process unit and operating modes is selected , the material streams is exist in the model solution. Sometimes, this constraint is called the 'switching constraint' representing the flow rates of material streams exist only if the corresponding binary variables, denoting the existence of a process unit that means take the value of one or vice versa. The general form of this constraint is given by this inequality [15]:

$$f_j \leq M_j y_j$$

In which M_j is derived upper bound (maximum or minimum value) on the value of f_j, the flow rate of component j in any feasible solution.

But, in our case, the value for M_j is the maximum capacity of the process unit of f_j, is an outlet stream. For instance, the Big-M logical constraint for our model is consist of 2 main constraints:

M1 (I) upper bound or maximum capacity of process units =1000000

$$f_{COK\_1} \leq M_{COK\_1} y_{COK\_1}$$

So that if,

$$y_{COK\_1} = 0, f_{COK\_1} = 0$$

$$y_{COK\_1} = 1, f_{COK\_1} = 1000000$$

M2 (J) upper bound or maximum capacity of stream piping =1000000

$$f_{PCHN\_1} \leq M_{PCHN\_1} y_{PCHN\_1}$$

so that if,

$$y_{PCHN\_1} = 0, f_{PCHN\_1} = 0$$

$$y_{PCHN\_1} = 1, f_{PCHN\_1} = 1000000$$

General Big-M Logical Constraints for Modeling Section:

$$f_j \leq M_j Z_j$$

$$y_j = 1 : f_j \leq M_j$$

But $f_j \geq 0$

So, $0_j \leq f_j \leq M_j$

3.5.3.2 Design specifications

This constraint is about the selection of process units and process streams based on engineering knowledge, heuristics, and experience. This logical constraint enforces the design specification for the process alternatives of the processing of naphtha. For instance:

Selection process stream from ADU:

Integer Linear inequality Constraint: $Z_{('LSRN1s')} + Z_{('NAP1s')} \leq 0$

Desired Binary Output:

$Z_{('LSRN1s')}$	$Z_{('NAP1s')}$
1	0
0	1
0	0

This constraint tell us that, **at most** only one of 2 opearting modes of the naphtha processing unit can be selected among the two options of: (i) LSRN or (ii) NAP.

3.5.3.3 Structural Specifications

This constraint is about Interconnectivity between states (process unit) and tasks (process stream). This logical constraint enforces interconnectivity relationships of the state and task compromising the process unit and process streams in the superstructure. For instance:

Selection process stream from ADU:

Integer Linear inequality Constraint:

$$Y_{('HDT1u')} \leq Z_{('HSRN2s')} + Z_{('H2\_1s')}$$

$$Z_{('HSRN2s')} + Z_{('H2\_1s')} \geq Y_{('HDT1u')}$$

Desired Binary Output:

$Y_{('HDT1u')}$	$Z_{('HSRN2s')}$	$Z_{('H2\_1s')}$
0	0	0
1	1	0
1	0	1
1	0	0
1	1	1

This constraint tells us that, **the selection of the stream H2-1s or HSRN2s is only allowed if and only if HDT1 is selected.**

3.6 GAMS Modeling

The General Algebraic Modeling System (GAMS) is specifically designed for modeling linear, nonlinear and mixed integer optimization problems. The system is especially useful with large, complex problems. GAMS are available for use on personal computers, workstations, mainframes and supercomputers [2].

The model is being working right now and for that MILP computational result cannot be placed here yet. Anyway below are screenshot of the model I been working of this following few weeks. Basically, the model that I been worked is focusing on one pool only which is the Naphtha Hydroprocessing (NHT) processing pool (pool 1).

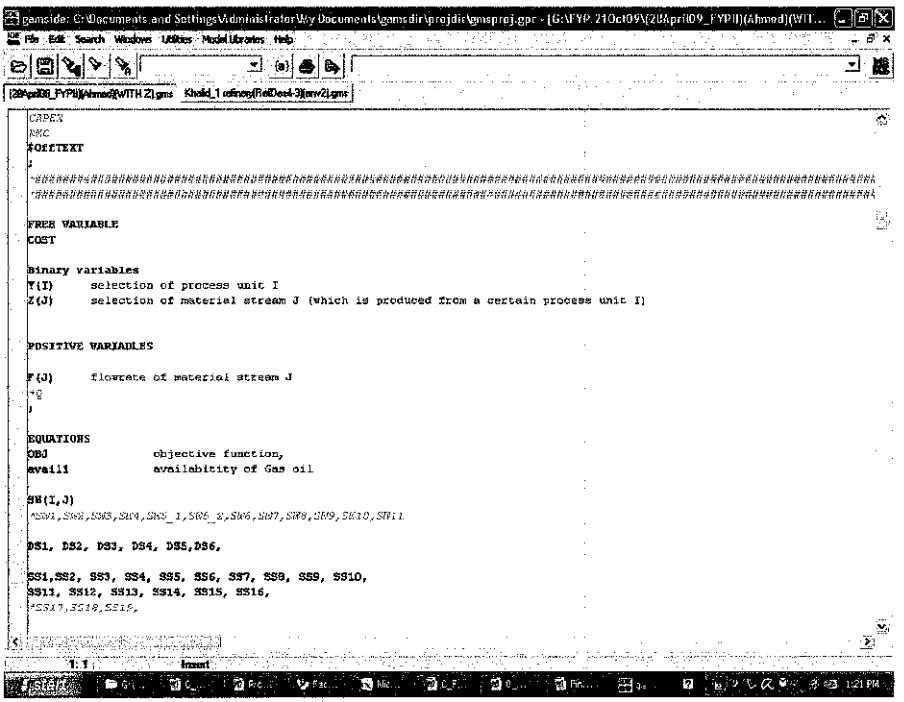


Figure 3.6: GAMS Modeling

CHAPTER 4

COMPUTATIONAL EXPERIENCE AND NUMERICAL RESULTS

4.1 INTRODUCTION

Computational experiments and numerical studies of the MILP model formulation for the flowsheet superstructure optimization problem developed in this work are coded and implemented using GAMS software. The numerical examples are then solved using branch-and-cut algorithms as executed in GAMS. The associated computational statistics are reported in the table below:

Table 4.1: Model and Computational Statistic in Model Formulation

Type Of Model	**Mixed-Integer Linear Program (MILP)**
Solver	GAMS/Cplex 10
Block of Equations	228
Blocks of Variables	5
Single Equation2	339
Single Variables	161
Discrete Variable	80
Generation Time	0.015 s
Execution Time	0.015 s
MILP Solution (Objective Value)	3553770.7628 (17 iterations, 0 nodes)

To determine whether the logical constraints for interconnectivity relationships could effectively account for the selection of the process units as well as for both the process units and the material streams, computational experiments using GAMS has been carried out to investigate both cases. The result then been analyzed in order to determine the most probable process route the process need to take for. The rule is based on Big-M Logical constraint which reflects that whenever there are flowrates in the stream, there stream should be taken into the process routes.

4.2 MODEL DATA

In this computational experiment, there are some data that we need to assumed for (since there are no exact data for them) for the cost minimization objective function:

Table 4.2.1: Assumption Data for Model Formulation

Data	Details
Upper bound or maximum capacity of process units (j)	1000000 unit
upper bound or maximum capacity of stream piping (i)	1000000 unit
Capital Cost for Mixer	100 unit
Capital Cost for Splitter	100 unit
Crude Oil Cost (RM per bbl)	120
Crude Oil Amount (kg per bbl)	127.7
Purchased Naphtha Cost (RM per kg)	0.524
API Gravity of Crude Charge	30
Cost of CO2 Emissions	10 unit

The process routes of the naphtha processing routes has been determined using the Big-M logical constraint which states that when a unit is selected, there must be associated inlet flows and also outlet flows by the way of material balances in order to obtain a consistent result.

The result for this is being reflected in the figure below:

Table 4.2.2: Computational Results model with Selection of Material Streams

Stream	Flowrate (kg/day)	Stream	Flowrate (kg/d)	Stream	Flowrate (kg/day)
BLNDs	0	HCR_3s	0.00E+00	NAP2s	0.00E+00
COK_1s	2.00E+06	HCR_4s	0.00E+00	NAP3s	0.00E+00
COK_2s	0	HSRN1s	0.00E+00	NAP4s	2.35E+07
CRs	0	HSRN2s	1.12E+07	NAP5s	2.35E+07
FCCs	0	HSRN3s	0.00E+00	PCHN1s	0.00E+00
FCC_1s	2.00E+06	HSRN4s	0.00E+00	PCHN1_1s	5.21E+06
FCC_2s	0	HSRN5s	0.00E+00	PCHN1_2s	0.00E+00
FG1s	1.30E+05	ISOs	0.00E+00	PCHN2s	0.00E+00
FG2s	0	LPG1s	69398.411	PCHN3s	0.00E+00
FG3s	8.70E+05	LPG2s	1.83E+06	PCHN3_1s	0.00E+00
FG4s	0	LPG3s	0.00E+00	PCHN3_2s	0.00E+00
FG5s	1.00E+06	LPG4s	1.90E+06	REFs	2.00E+07
GSLNs	2.00E+07	LPG5s	1.90E+06	Ss	12172.96
H2s	7.52E+05	LSRN1s	0.00E+00	SOLDs	2.20E+07
H2_1s	7.52E+05	LSRN2s	0.00E+00	TGs	2185.332
H2_2s	0.00E+00	LSRN3s	0.00E+00	VISs	0.00E+00
H2S1s	14358.292	LSRN4s	0.00E+00	VIS_1s	0
H2S2s	0.00E+00	LSRN5s	0.00E+00	VIS_2s	0.00E+00
HCR_1s	2.00E+06	LSRN6s	0.00E+00		
HCR_2s	0E+00	NAP1s	0.00E+00		

From the table above we can see that, through a careful modeling using logical constraint representing qualitative design knowledge on design and specification, and it is sufficient to model a process synthesis problem on refinery design by assigning binary variables for the selection of process unit. This means that we can find the best process route using this model by removing the entire process stream that does not have any flow rate in them. All the work done is reflected on the figure below:

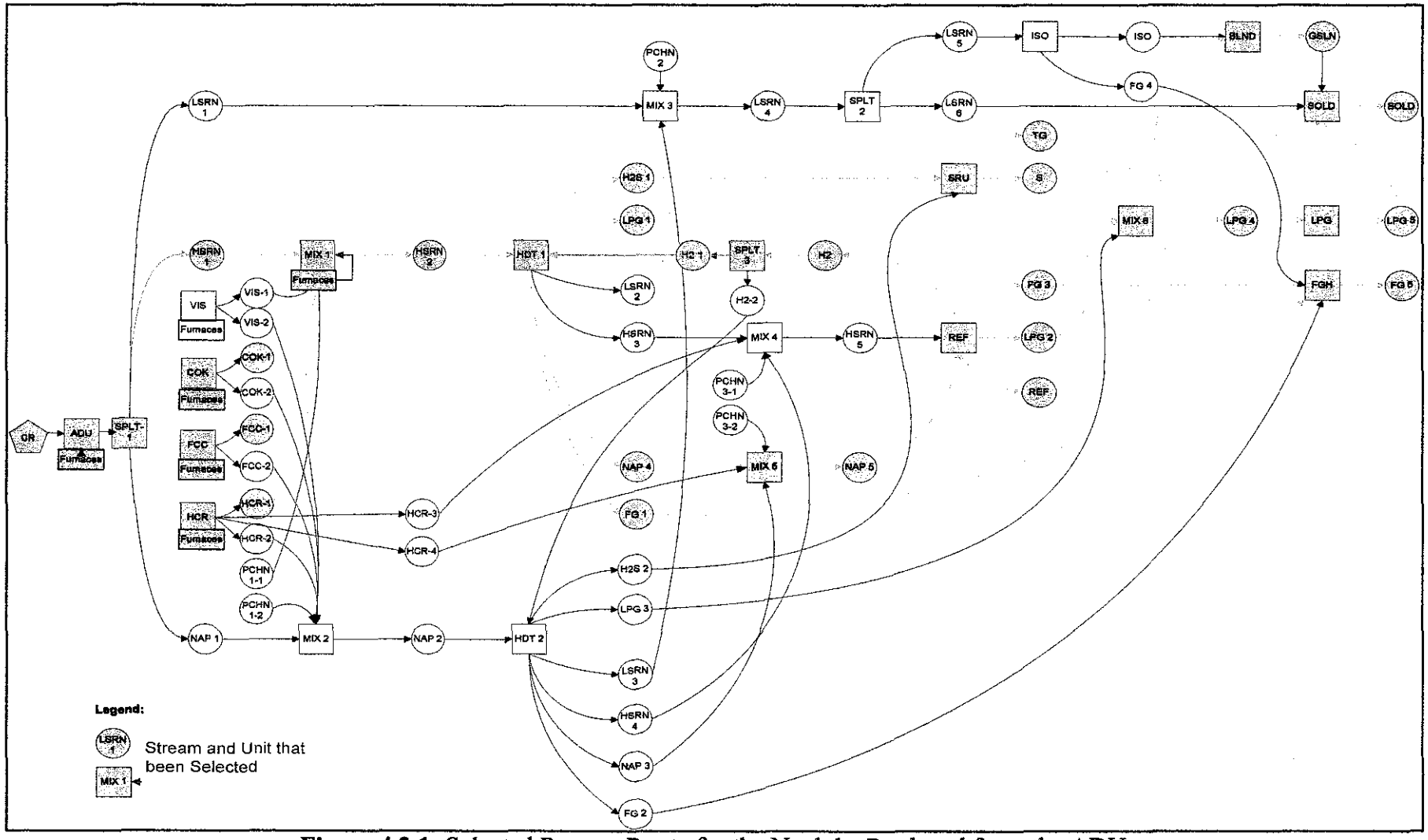


Figure 4.2.1: Selected Process Route for the Naphtha Produced from the ADU

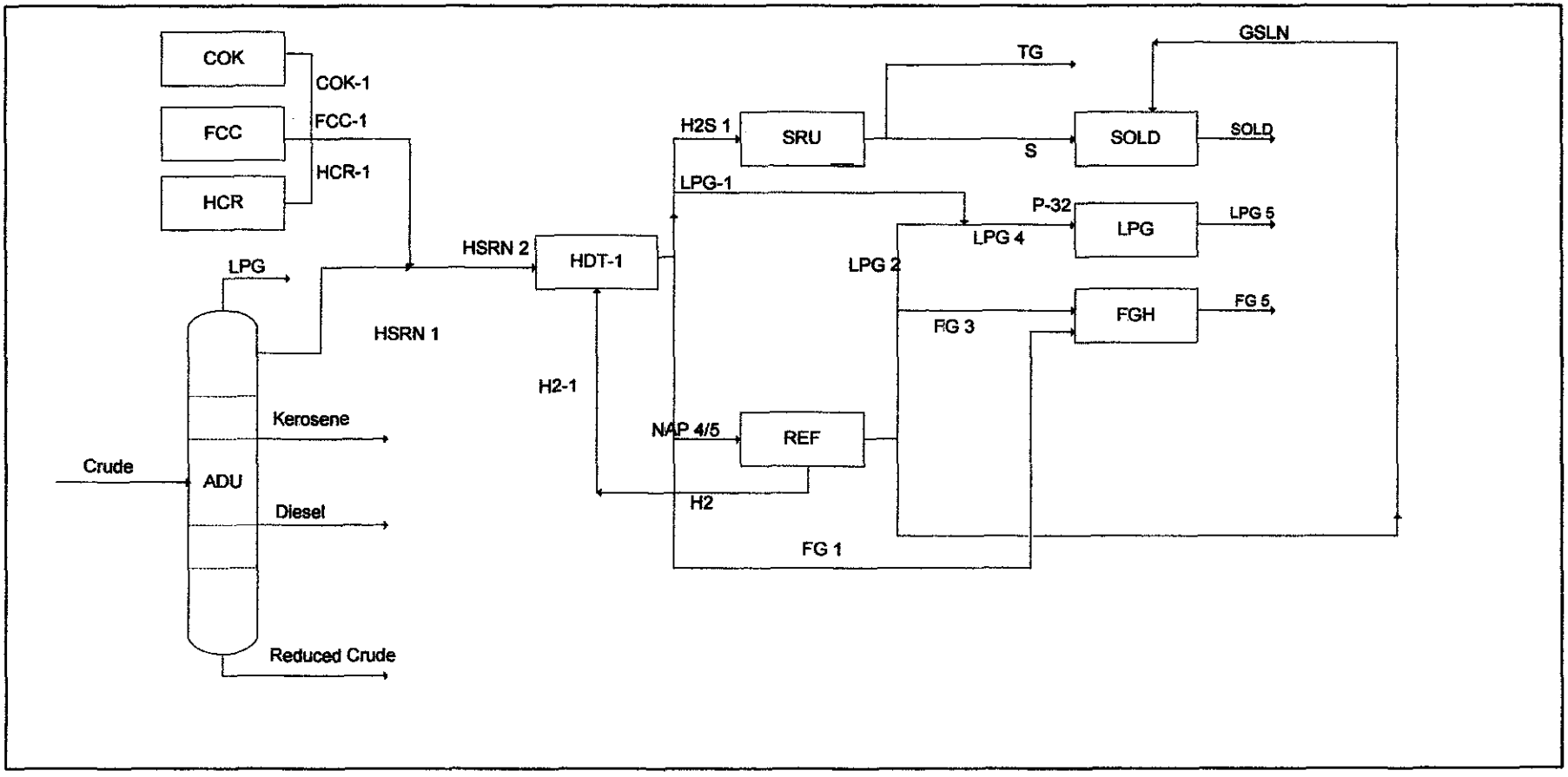


Figure 4.2.2: Optimal Flowsheet for the Processing Alternatives of Naphtha

4.3 REMARKS ON COMPUTATIONAL EXPERIENCE

It is been understood that when unit is selected, there must be associated inlets flow and also outlets flows by way of the material balances in order to obtain a consistent result. This can be accomplished by enforcing the big _M Logical Constraint. The process route that been was figures out to be the best process route for naphtha processing is been detailed in the paragraph below:

Based on the solved model and depending on the distillation column design as well as the refinery economics, the naphtha processing best configuration is to produce heavy straight run naphtha (HSRN–1). HSRN–1 is mixed with naphtha from the cracking of heavier fractions in MIX–1 that contains COK-1, FCC-1 and HCR-1 streams before being sent to HDT–1 to be desulfurized. HDT–1 produces hydrogen sulfide gas (H2S–1), liquefied petroleum gas (LPG–1), NAP–4), and fuel gas (FG–1). H2S–1 is sent to the sulfur recovery unit (SRU) where sulfur (S) is extracted and finally sold. All LPG (LPG–1, LPG–2) are sent to MIX–6 and subsequently to the LPG recovery unit (LPG), from which treated LPG (LPG–5) is sold. FG–1 goes to the fuel gas header (FGH) which supplies fuel gas (FG–5) to the entire refinery. In the case that NAP–4 is produced from HDT–1, whose output of NAP–5 is sent to the reformer. The products from the reformer are hydrogen gas (H2), fuel gas (FG–3), liquefied petroleum gas (LPG–2), and reformate (REFs). H2 is a feed to the HDTs while reformate is used as a gasoline blending component. FG–3 is sent to the FGH.

In the nutshell, the solved model has managed to provide the optimal solution (configuration) or process routes to the naphtha processing process and this model can be the basic model to find the best configuration for the refinery.

CHAPTER 5

CONCLUSION AND RECOMMENDATION

5.1 CONCLUSIONS

Process synthesis or conceptual process design is concerned with the identification of the best flowsheet structure to perform a given task. The complexity associated with synthesis problems in general and petroleum refinery design in particular, necessitates the development and implementation of a systematic and automated approach to efficiently and rigorously consider the elaborate interactions and trade-offs among the design variables. In this regard, powerful formal optimization strategies potentially offer promising tools to undertake the task. This work presents a superstructure optimization approach for synthesizing an oil refinery topology using an aggregated model to facilitate the preliminary screening stage of design alternatives.

As a result of this research projects, a mathematical model optimization has been developed to determine optimal topology for petroleum refinery, more specifically the subsystem of naphtha processing unit. The result that been produced also provide the optimal solution which means the result is succeed to provide the refinery with the optimal configuration and also parameters for the naphtha processing subsystem.

5.2 RECOMENDATIONS

Optimization Model for the Entire Refinery Subsystem

The needs to be consider to be done at the other three subsystems which are:

- Processing Pool 1: Alternatives for Atmospheric Reduced Crude (ARC)
- Processing Pool 3: Alternatives for Vacuum Gas Oil (VGO) Processing
- Processing Pool 4: Alternatives for Vacuum Residue or Vacuum Reduced Crude (VRC) Processing and Upgrading

This is really important before the model can be used fully as the optimization model for the refinery topology in order to minimize cost and also minimize the CO2 Emission.

Clarification of Data for the Modeling

Some of the data like unit cost and also maximum flow rates of the unit have been assumed in the project. So for the future work, it is recommended for us to find the most exact data for the model in order to develop an established and accurate model for the optimization model.

REFERENCES

[1] Allen, D. T. and D. R. Shonnard (2002). *Green Engineering: Environmentally Conscious Design of Chemical Processes*. Upper Saddle River, New Jersey: Prentice Hall.

[2] Brooke, A., D. Kendrick, A. Meeraus, and R. Raman (1998). *GAMS—A User's Guide* [Textfile]. Retrieved January 17, 2006 from: http://www.gams.com/docs/gams/GAMSUsersGuide.pdf. Washington DC: GAMS Development Corporation.

[3] Chemical Engineering. Marshall & Swift Equipment Cost Index (2007). *Chemical Engineering* [Online textfile]. Retrieved February 10, 2008 from: http://www.che.com.

[4] Douglas, J. M. A hierarchical decision procedure for process synthesis. *AIChE Journal* 31 (1985), 3: 353–362.

[5] Gary, J. H. and G. E. Handwerk (1994). *Petroleum Refining: Technology and Economics*. 3rd Ed. New York: Marcel Dekker.

[6] Drake, F. (2000). "Global Warming," *The Science of Climate Change*, Oxford University Press.Inc New York.

[7] Petroleum Resource Development, PETRONAS (2006): Acid Gas Management Roadmap Presentation Package. *Exploitation of High CO_2 Field.*

[8] Weyant, J. and Yanisigawa, Y. (1998): Energy and industry. In Raynor, S. and Malone, E.L. (eds), *Human choice and climate change: volume 2 resources and technology*. Columbus: Batelle Press.

[9] Ramkumar Karuppiah, Ignacio E. Grossmann (2006). Global optimization for the synthesis of integrated water systems in chemical process. *Computers and Chemical Engineering*, 30: 650-673.

[10] Quesada and I.E. Grossman (1995). Global Optimization of Bilinear Process Networks with Multicomponent Flow. *Computer Chemical Engineering*, Volume 19 No.12, 1219-1242.

[11] Smith Robin (2005). *Chemical Process Design and Integration.*

[12] Manuscript LPET-2009-0075.R1, *Petroleum science and Technology* by James Speight 2009.

[13] C. E. Burklin, *et al., Revision Of Emission Factors For Petroleum Refining*, EPA-450/3-77-030, U. S. Environmental Protection Agency, Research Triangle Park, NC, October 1977.

[14] *Energy and Environmental Profile of US Petroleum Refinery*, Joan Pellegrino, Sabine Brueske, Tracy Carole, and Howard Andres of Energetics, 2007.

[15] *Methodology for the free allocation of emission allowances in the EU ETS post 2012*, Ecofys, Fraunhofer Institute for Systems and Innovation Research Öko-Institu

APPENDIX A1:

Objective Function (DESCRIPTION)

Minimize Cost, C =e=

*TCI(total capital investment)

+

*Electricity used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

*Fuel used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

+

*HP Steam used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

+

*CW used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

+

*Electricity used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

+

*Fuel used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

+

*HP Steam used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

+

*CW used for ADU, VIS, COK, FCC, HCR, HDT1, HDT2, REF, ISO, SRU

+

PCHN cost

+

*Capital cost for mixers and splitters

+

Piping cost for the selected stream

+

SUM (I, CO2_COST* CO2 (I) (environmental cost)

APPENDIX B

Emission Factors for Petroleum Refineries

Process	Particulate	Sulfur Oxides (as SO_2)	Carbon Monoxide	Total Hydro-carbons[b]	Nitrogen Oxides (as NO_2)	Aldehydes	Ammonia	EMISSION FACTOR RATING
Boilers and process heaters								
Fuel oil	See Section 1.3 - "Fuel Oil Combustion"							
Natural gas	See Section 1.4 - "Natural Gas Combustion"							
Fluid catalytic cracking units (FCC)[c]								
Uncontrolled								
kg/10^3 L fresh feed	0.695 (0.267 to 0.976)	1.413 (0.286 to 1.505)	39.2	0.630	0.204 (0.107 to 0.416)	0.054	0.155	B
lb/10^3 bbl fresh feed	242 (93 to 340)	493 (100 to 525)	13,700	220	71.0 (37.1 to 145.0)	19	54	B
Electrostatic precipitator and CO boiler								
kg/10^3 L fresh feed	0.128[d] (0.020 to 0.428)	1.413 (0.286 to 1.505)	Neg	Neg	0.204[e] (0.107 to 0.416)	Neg	Neg	B
lb/10^3 bbl fresh feed	45[d] (7 to 150)	493 (100 to 525)	Neg	Neg	71.0[e] (37.1 to 145.0)	Neg	Neg	B
Moving-bed catalytic cracking units[f]								
kg/10^3 L fresh feed	0.049	0.171	10.8	0.250	0.014	0.034	0.017	B
lb/10^3 bbl fresh feed	17	60	3,800	87	5	12	6	B
Fluid coking units[g]								
Uncontrolled								
kg/10^3 L fresh feed	1.50	ND	ND	ND	ND	ND	ND	C
lb/10^3 bbl fresh feed	525	ND	ND	ND	ND	ND	ND	C
Electrostatic precipitator and CO boiler								
kg/10^3 L fresh feed	0.0196	ND	Neg	Neg	ND	Neg	Neg	C
lb/10^3 bbl fresh feed	6.85	ND	Neg	Neg	ND	Neg	Neg	C

Process	Particulate	Sulfur Oxides (as SO_2)	Carbon Monoxide	Total Hydro-carbons[b]	Nitrogen Oxides (as NO_2)	Aldehydes	Ammonia	EMISSION FACTOR RATING
Delayed coking units	ND	ND	ND	ND	ND	ND	ND	NA
Compressor engines[h]								
Reciprocating engines								
kg/10^3 m^3 gas burned	Neg	2s	7.02	21.8	55.4	1.61	3.2	B
lb/10^3 ft^3 gas burned	Neg	2s	0.43	1.4	3.4	0.1	0.2	B
Gas turbines								
kg/10^3 m^3 gas burned	Neg	2s	1.94	0.28	4.7	ND	ND	B
lb/10^3 ft^3 gas burned	Neg	2s	0.12	0.02	0.3	ND	ND	B
Blowdown systems[k]								
Uncontrolled								
kg/10^3 L refinery feed	Neg	Neg	Neg	1.662	Neg	Neg	Neg	C
lb/10^3 bbl refinery feed	Neg	Neg	Neg	580	Neg	Neg	Neg	C
Vapor recovery system and flaring								
kg/10^3 L refinery feed	Neg	0.077	0.012	0.002	0.054	Neg	Neg	C
lb/10^3 bbl refinery feed	Neg	26.9	4.3	0.8	18.9	Neg	Neg	C
Vacuum distillation column condensers[m]								
Uncontrolled								
kg/10^3 L vacuum feed	Neg	Neg	Neg	0.14 (0 to 0.37)	Neg	Neg	Neg	C
lb/10^3 bbl vacuum feed	Neg	Neg	Neg	50 (0 to 130)	Neg	Neg	Neg	C
Controlled (vented to heater or incinerator)	Neg	Neg	Neg	Neg	Neg	Neg	Neg	C

APPENDIX C:

Downstream capital cost index

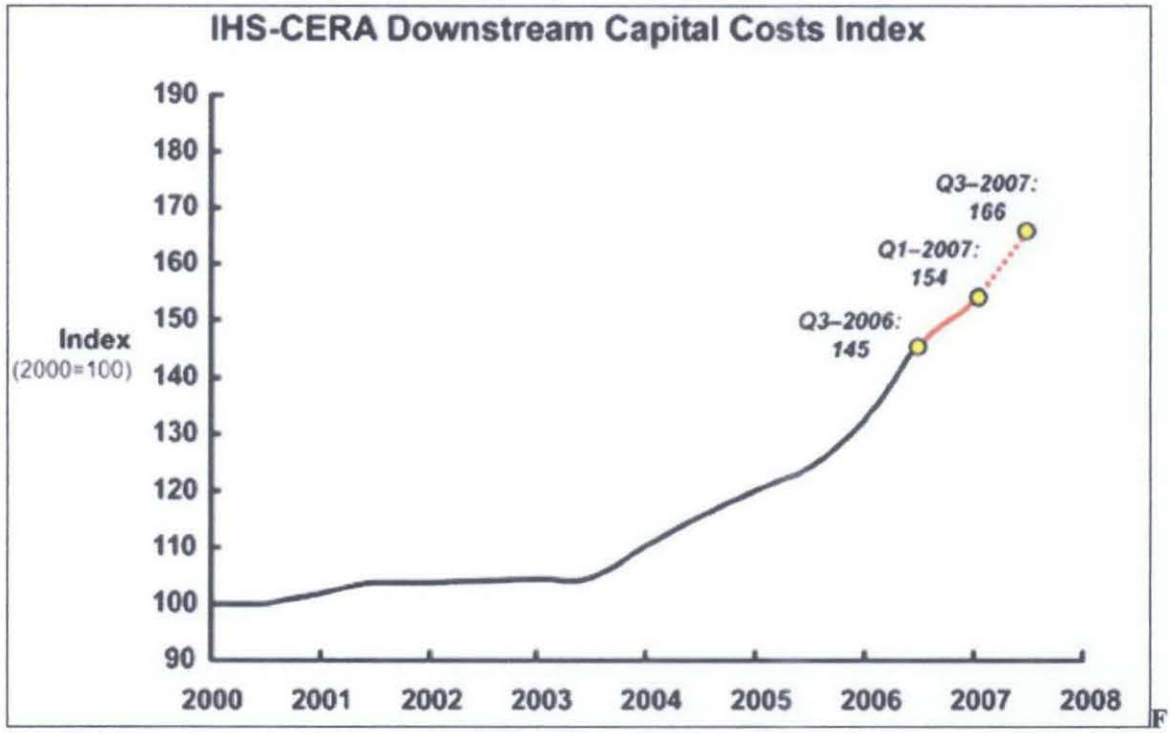


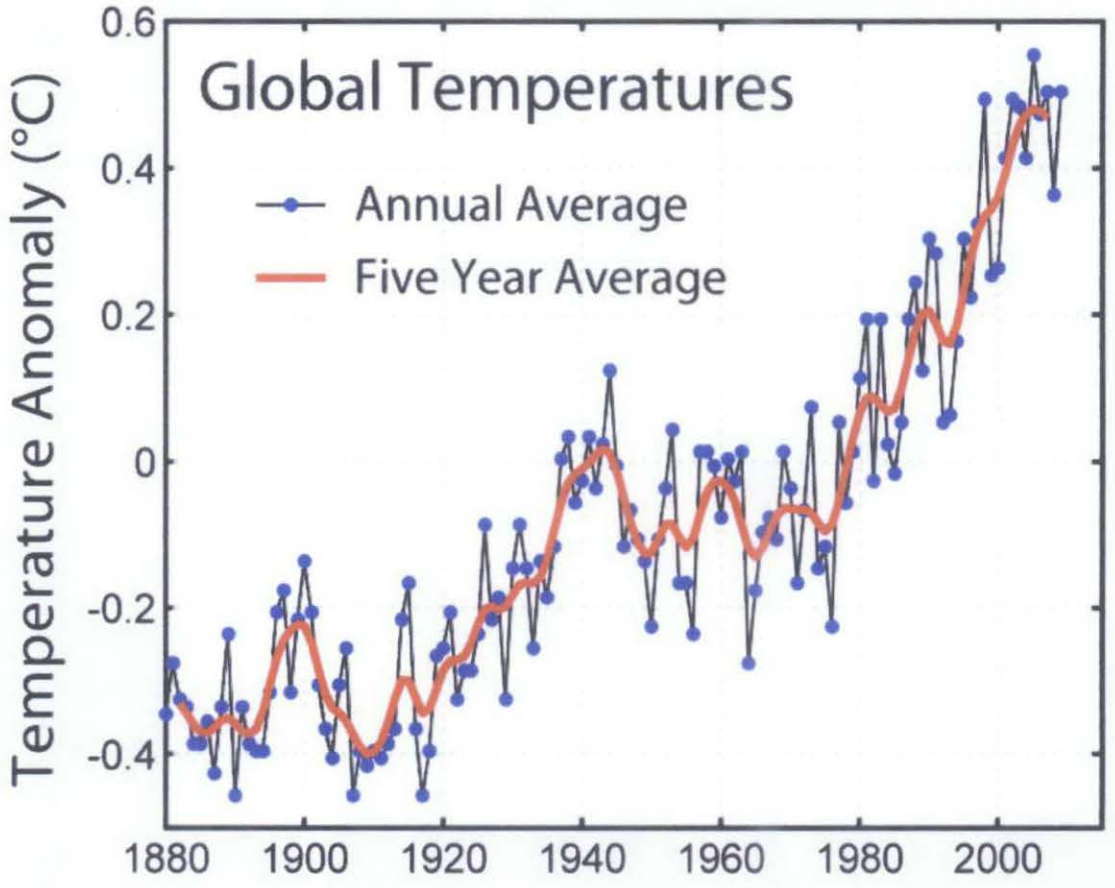
Figure AC: Downstream capital cost index

(Cambridge Energy Research Associates, 2007)

Figure 1.1 shows the rapid increasing downstream capital cost index from middle of year 2003 to year 2008. Automated approach that guarantees optimal refinery design is increasingly important due to increase in capital costs, higher energy costs, depleting energy sources. The rising consumption of fuel has led to a higher demand for petroleum products despite tight supplies, have witnessed the call for the construction of new grassroots petroleum refineries in countries notably the US (such as in the states of Arizona and Louisiana) and also in the Middle East countries. Consequently, consumer demand provided the incentive for the construction of new refineries.

APPENDIX D:

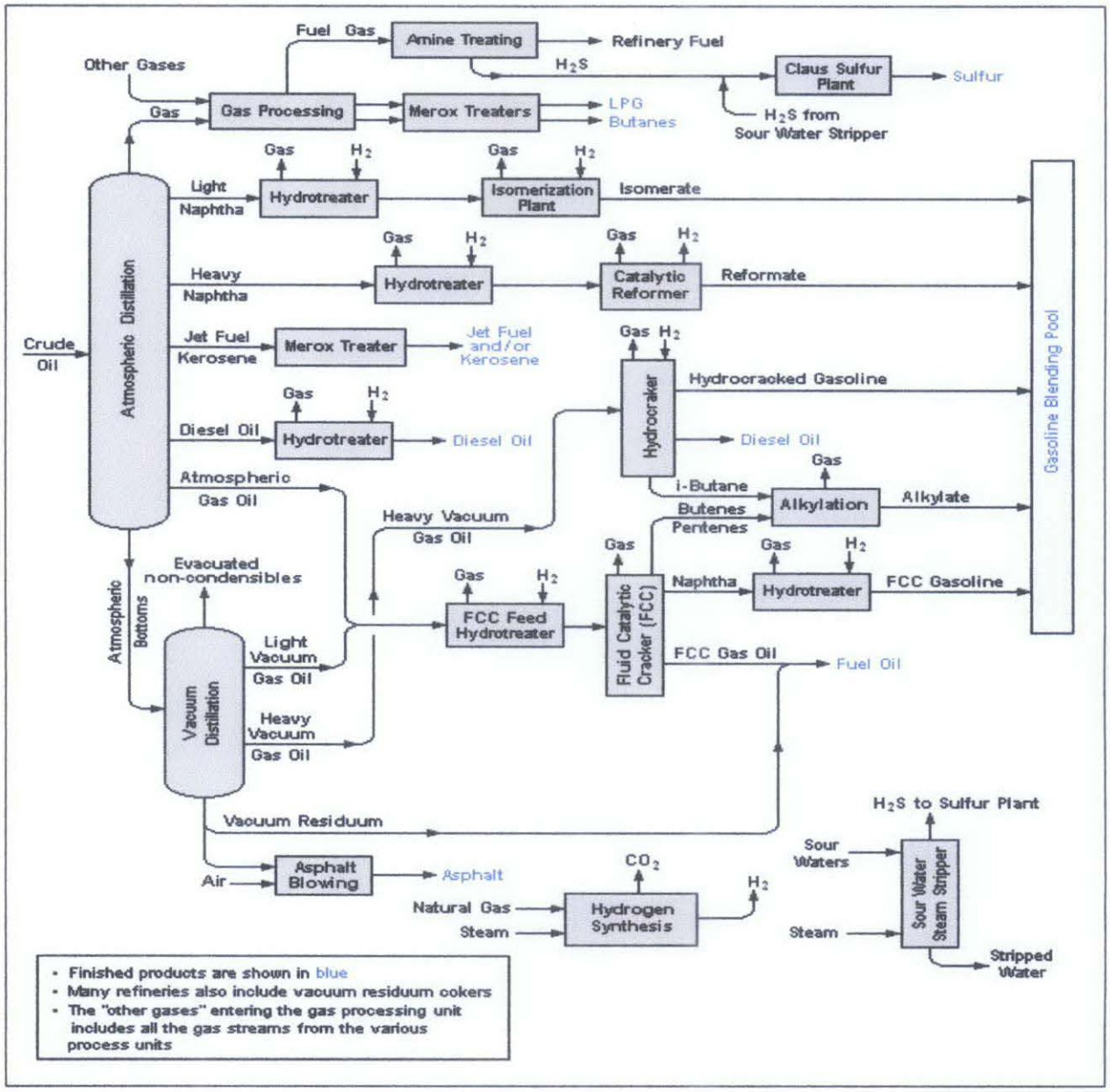
The instrumental record of global average temperatures



This image shows the instrumental record of global average temperatures as compiled by the NASA's Goddard Institute for Space Studies. The data set used follows the methodology outlined by Hansen, J. (2006) "Global temperature change".

APPENDIX E

Schematic of an example integrated petroleum refinery



APPENDIX F

GAMS Modeling Result

MODEL STATISTICS

BLOCKS OF EQUATIONS	228	SINGLE EQUATIONS	339
BLOCKS OF VARIABLES	5	SINGLE VARIABLES	161
NON ZERO ELEMENTS	947	DISCRETE VARIABLES	80

GENERATION TIME = 0.016 SECONDS 4 Mb WIN230-230 Feb 12, 2009

EXECUTION TIME = 0.016 SECONDS 4 Mb WIN230-230 Feb 12, 2009

SOLVE SUMMARY

MODEL naphtha_opt_hvy OBJECTIVE c
TYPE MIP DIRECTION MINIMIZE
SOLVER CPLEX FROM LINE 1856

**** SOLVER STATUS 1 NORMAL COMPLETION
**** MODEL STATUS 8 INTEGER SOLUTION
**** OBJECTIVE VALUE 3553770.7628

RESOURCE USAGE, LIMIT 0.093 1000.000
ITERATION COUNT, LIMIT 17 10000

MIP Solution: 3553770.762757 (17 iterations, 0 nodes)
Final Solve: 3553770.762757 (0 iterations)

Best possible: 3553636.560460
Absolute gap: 134.202297
Relative gap: 0.000038

	LOWER	LEVEL	UPPER	MARGINAL
---- EQU objfn	.	.	.	1.000
---- EQU mat_bal1	.	.	.	.
---- EQU mat_bal2	.	.	.	0.304
---- EQU mat_bal3	.	.	.	.
---- EQU mat_bal4	.	.	.	.
---- EQU mat_bal5	.	.	.	.
---- EQU mat_bal6	.	.	.	.
---- EQU mat_bal7	.	.	.	EPS
---- EQU mat_bal8	.	.	.	EPS
---- EQU mat_bal9	.	.	.	EPS
---- EQU mat_bal10	.	.	.	-7.639
---- EQU mat_bal11	.	.	.	0.076
---- EQU mat_bal12	.	.	.	0.681
---- EQU mat_bal13	.	.	.	0.681
---- EQU mat_bal14	.	.	.	.
---- EQU mat_bal15	.	.	.	.
---- EQU mat_bal16	.	.	.	.
---- EQU mat_bal17	.	.	.	0.304
---- EQU mat_bal18	.	.	.	.

objfn min total cost in (mil RM)

---- EQU MAT_BAL_MIXER

	LOWER	LEVEL	UPPER	MARGINAL
MIX1u.HSRN2s	.	.	.	.
MIX2u.NAP2s	.	.	.	.
MIX3u.LSRN4s	.	.	.	.
MIX4u.HSRN5s	.	.	.	.
MIX5u.NAP5s	.	.	.	.
MIX6u.LPG4s	.	.	.	EPS

	LOWER	LEVEL	UPPER	MARGINAL
---- EQU mat_bal20	-INF	2.0000E+6	2.0000E+6	-0.681
---- EQU mat_bal21	-INF	.	2.0000E+6	.
---- EQU mat_bal22	-INF	2.0000E+6	2.0000E+6	-0.681
---- EQU mat_bal23	-INF	.	2.0000E+6	.
---- EQU mat_bal24	-INF	.	2.0000E+6	.
---- EQU mat_bal25	-INF	.	2.0000E+6	.
---- EQU mat_bal26	.	.	.	-0.681
---- EQU mat_bal27	.	.	.	.
---- EQU prodreq3	7.0000E+6	2.0047E+7	+INF	.
---- EQU prodreq4	1.0000E+6	1.9026E+6	+INF	.
---- EQU prodreq5	1.0000E+6	1.0000E+6	+INF	7.639
---- EQU prodreq6	-INF	.	1000.000	.
---- EQU prodreq7	-INF	.	1000.000	.
---- EQU prodreq8	-INF	2.0000E+6	2.0000E+6	-0.681
---- EQU prodreq9	-INF	.	2.0000E+6	.
---- EQU yield1	.	.	.	.
---- EQU yield2	.	.	.	.
---- EQU yield4	.	.	.	7.334
---- EQU yield5	.	.	.	-0.305
---- EQU yield6	.	.	.	-0.304
---- EQU yield8	.	.	.	.
---- EQU yield10	.	.	.	.
---- EQU yield11	.	.	.	.
---- EQU yield12	.	.	.	.
---- EQU yield13	.	.	.	.
---- EQU yield14	.	.	.	.
---- EQU yield15	.	.	.	.
---- EQU yield16	.	.	.	7.639
---- EQU yield17	.	.	.	.
---- EQU yield18	.	.	.	EPS
---- EQU yield19	.	.	.	EPS
---- EQU yield20	.	.	.	0.681
---- EQU yield21	.	.	.	7.639
---- EQU yield22	.	.	.	EPS
---- EQU yield23	.	.	.	EPS
---- EQU yield24	.	.	.	.
---- EQU yield25	.	.	.	-0.764

---- EQU BIG_M_LOGICON1

	LOWER	LEVEL	UPPER	MARGINAL
ADUu .CRs	-INF	-1.000E+8	.	.
BLNDu .ISOs	-INF	-1.000E+8	.	.
BLNDu .REFs	-INF	-7.995E+7	.	.
FGHu .FG1s	-INF	-9.987E+7	.	.
FGHu .FG2s	-INF	-1.000E+8	.	.
FGHu .FG3s	-INF	-9.913E+7	.	.

FGHu .FG4s	-INF	-1.000E+8	.	.
HDT1u .H2_1s	-INF	-9.925E+7	.	.
HDT1u .HSRN2s	-INF	-8.879E+7	.	.
HDT2u .H2_2s	-INF	.	.	.
HDT2u .NAP2s	-INF	.	.	.
ISOu .LSRN5s	-INF	-1.000E+8	.	.
LPGu .LPG4s	-INF	-9.810E+7	.	.
MIX1u .COK_1s	-INF	-9.800E+7	.	.
MIX1u .FCC_1s	-INF	-9.800E+7	.	.
MIX1u .HCR_1s	-INF	-9.800E+7	.	.
MIX1u .HSRN1s	-INF	-1.000E+8	.	.
MIX1u .PCHN1_1s	-INF	-9.479E+7	.	.
MIX1u .VIS_1s	-INF	-1.000E+8	.	.
MIX2u .COK_2s	-INF	.	.	.
MIX2u .FCC_2s	-INF	.	.	.
MIX2u .HCR_2s	-INF	.	.	.
MIX2u .NAP1s	-INF	.	.	.
MIX2u .PCHN1_2s	-INF	.	.	.
MIX2u .VIS_2s	-INF	.	.	.
MIX3u .LSRN1s	-INF	-1.000E+8	.	.
MIX3u .LSRN2s	-INF	-1.000E+8	.	.
MIX3u .LSRN3s	-INF	-1.000E+8	.	.
MIX3u .PCHN2s	-INF	-1.000E+8	.	.
MIX4u .HCR_3s	-INF	.	.	.
MIX4u .HSRN3s	-INF	.	.	.
MIX4u .HSRN4s	-INF	.	.	.
MIX4u .PCHN3_1s	-INF	.	.	.
MIX5u .HCR_4s	-INF	-1.000E+8	.	.
MIX5u .NAP3s	-INF	-1.000E+8	.	.
MIX5u .NAP4s	-INF	-7.650E+7	.	.
MIX5u .PCHN3_2s	-INF	-1.000E+8	.	.
MIX6u .LPG1s	-INF	-0.999E+8	.	.
MIX6u .LPG2s	-INF	-9.817E+7	.	.
MIX6u .LPG3s	-INF	-1.000E+8	.	.
REFu .HSRN5s	-INF	-1.000E+8	.	.
REFu .NAP5s	-INF	-7.650E+7	.	.
SPLT1u.LSRN4s	-INF	-1.000E+8	.	.
SPLT2u.H2s	-INF	-9.925E+7	.	.
SRUu .H2S1s	-INF	-1.000E+8	.	.
SRUu .H2S2s	-INF	-1.000E+8	.	.
SOLDu .GSLNs	-INF	-7.995E+7	.	.
SOLDu .LPG5s	-INF	-9.810E+7	.	.
SOLDu .LSRN6s	-INF	-1.000E+8	.	.
SOLDu .Ss	-INF	-1.000E+8	.	.

---- EQU BIG_M_LOGICON2

	LOWER	LEVEL	UPPER	MARGINAL
BLNDs	-INF	.	.	.
COK_1s	-INF	-9.800E+7	.	.
COK_2s	-INF	.	.	.
CRs	-INF	-1.000E+8	.	.
FCCs	-INF	.	.	.
FCC_1s	-INF	-9.800E+7	.	.
FCC_2s	-INF	.	.	.
FG1s	-INF	-9.987E+7	.	.
FG2s	-INF	.	-7.639	
FG3s	-INF	-9.913E+7	.	.
FG4s	-INF	-1.000E+8	.	.
FG5s	-INF	-9.900E+7	.	.
GSLNs	-INF	-7.995E+7	.	.

H2s	-INF	-9.925E+7	.	.
H2_1s	-INF	-9.925E+7	.	.
H2_2s	-INF	.	.	.
H2S1s	-INF	-1.000E+8	.	.
H2S2s	-INF	.	.	.
HCR_1s	-INF	-9.800E+7	.	.
HCR_2s	-INF	.	.	.
HCR_3s	-INF	.	.	.
HCR_4s	-INF	.	.	-0.304
HSRN1s	-INF	.	.	-0.681
HSRN2s	-INF	-8.879E+7	.	.
HSRN3s	-INF	.	.	.
HSRN4s	-INF	.	.	.
HSRN5s	-INF	.	.	-0.304
ISOs	-INF	-1.000E+8	.	.
LPG1s	-INF	-0.999E+8	.	.
LPG2s	-INF	-9.817E+7	.	.
LPG3s	-INF	.	.	.
LPG4s	-INF	-9.810E+7	.	.
LPG5s	-INF	-9.810E+7	.	.
LSRN1s	-INF	-1.000E+8	.	.
LSRN2s	-INF	.	.	.
LSRN3s	-INF	.	.	.
LSRN4s	-INF	-1.000E+8	.	.
LSRN5s	-INF	-1.000E+8	.	.
LSRN6s	-INF	.	.	-0.687
NAP1s	-INF	.	.	.
NAP2s	-INF	.	.	.
NAP3s	-INF	.	.	-0.304
NAP4s	-INF	-7.650E+7	.	.
NAP5s	-INF	-7.650E+7	.	.
PCHN1s	-INF	.	.	.
PCHN1_1s	-INF	-9.479E+7	.	.
PCHN1_2s	-INF	.	.	.
PCHN2s	-INF	.	.	.
PCHN3s	-INF	.	.	.
PCHN3_1s	-INF	.	.	.
PCHN3_2s	-INF	.	.	.
REFs	-INF	-7.995E+7	.	.
Ss	-INF	-1.000E+8	.	.
SOLDs	-INF	-7.804E+7	.	.
TGs	-INF	-1.000E+8	.	.
VISs	-INF	.	.	.
VIS_1s	-INF	.	.	.
VIS_2s	-INF	.	.	.

	LOWER	LEVEL	UPPER	MARGINAL
---- EQU LOGICON1	1.000	1.000	1.000	.
---- EQU LOGICON2	.	.	.	.
---- EQU LOGICON3	.	.	.	.
---- EQU LOGICON4	.	.	.	.
---- EQU LOGICON5	.	.	.	.
---- EQU LOGICON6_1	.	.	+INF	.
---- EQU LOGICON6_2	.	1.000	+INF	.
---- EQU LOGICON6_3	.	.	+INF	.
---- EQU LOGICON7	.	.	.	.
---- EQU LOGICON8	.	.	.	.
---- EQU LOGICON9	.	2.000	+INF	.
---- EQU LOGICON10	.	1.000	+INF	.
---- EQU LOGICON11	.	2.000	+INF	.
---- EQU LOGICON12	.	1.000	+INF	.

---- EQU LOGICON13 . 3.000 +INF .
---- EQU LOGICON14 . 2.000 +INF .
---- EQU LOGICON15 . 3.000 +INF .
---- EQU LOGICON16 . 2.000 +INF .
---- EQU LOGICON17 . . . .
---- EQU LOGICON18 . . . .
---- EQU LOGICON19 . . . .
---- EQU LOGICON20 . . . .
---- EQU LOGICON21 . . +INF .
---- EQU LOGICON22 . 1.000 +INF .
---- EQU LOGICON23 . . +INF .
---- EQU LOGICON24 . . +INF .
---- EQU LOGICON25 . 2.000 +INF .
---- EQU LOGICON26 . . . .
---- EQU LOGICON27 . . . .
---- EQU LOGICON28 . . +INF .
---- EQU LOGICON29 . 1.000 +INF .
---- EQU LOGICON30 . . . .
---- EQU SS1 -INF . . .
---- EQU SS2 -INF . . .
---- EQU SS3 -INF . . .
---- EQU SS4 -INF . . .
---- EQU SS5 -INF -1.000 . .
---- EQU SS6 -INF -1.000 . .
---- EQU SS7 -INF -1.000 . .
---- EQU SS8 -INF . . .
---- EQU SS9 -INF . . .
---- EQU SS10 -INF -3.000 . .
---- EQU SS11 -INF . . .
---- EQU SS12 -INF . . .
---- EQU SS13 -INF -1.000 . .
---- EQU SS14 -INF -1.000 . .
---- EQU SS15 -INF . . .
---- EQU SS16 -INF . . .
---- EQU SS17 -INF . . .
---- EQU SS18 -INF . . .
---- EQU SS19 -INF . . .
---- EQU SS20 -INF . . .
---- EQU SS21 -INF . . .
---- EQU SS22 -INF . . .
---- EQU SS23 -INF . . .
---- EQU SS24 -INF . . .
---- EQU SS25 -INF . . .
---- EQU SS26 -INF . . .
---- EQU SS27 -INF . . .
---- EQU SS28 -INF . . .
---- EQU SS29 -INF -1.000 . .
---- EQU SS30 -INF . . .
---- EQU SS31 . . . .
---- EQU SS32 -INF . . .
---- EQU SS33 -INF . . .
---- EQU SS34 -INF -1.000 . .
---- EQU SS35 -INF -1.000 . .
---- EQU SS36 -INF . . .
---- EQU SS37 -INF . . .
---- EQU SS38 -INF . . .
---- EQU SS39 -INF -1.000 . .
---- EQU SS40 -INF . . .
---- EQU SS41 -INF -3.000 . .
---- EQU SS42 -INF . . .
---- EQU SS43 -INF . . .
---- EQU SS44 -INF . . .

---- EQU SS45 -INF . . .
---- EQU SS46 -INF -2.000 . .
---- EQU SS47 -INF -1.000 . .
---- EQU SS48 -INF . . .
---- EQU SS49 -INF . . .
---- EQU SS50 -INF . . .
---- EQU SS51 -INF . . .
---- EQU SS52 -INF . . .
---- EQU SS53 -INF -1.000 . .
---- EQU SS54 -INF . . .
---- EQU SS55 -INF . . .
---- EQU SS56 -INF . . .
---- EQU SS57 -INF . . .
---- EQU SS58 -INF . . .
---- EQU SS59 -INF . . .
---- EQU SS60 -INF . . .
---- EQU SS61 -INF . . .
---- EQU SS62 -INF -2.000 . .
---- EQU SS63 -INF . . .
---- EQU SS64 -INF -1.000 . .
---- EQU SS65 -INF . . .
---- EQU SS66 -INF . . .
---- EQU SS67 -INF . . .
---- EQU SS68 -INF . . .
---- EQU SS69 -INF . . .
---- EQU SS70 -INF . . .
---- EQU SS71 -INF . . .
---- EQU SS72 -INF . . .
---- EQU SS73 -INF -1.000 . .
---- EQU SS74 -INF . . .
---- EQU SS75 -INF . . .
---- EQU SS76 -INF . . .
---- EQU SS77 -INF . . .
---- EQU SS78 -INF -1.000 . .
---- EQU SS79 -INF -3.000 . .
---- EQU SS80 -INF -1.000 . .
---- EQU SS81 -INF -1.000 . .
---- EQU SS82 -INF . . .
---- EQU SS83 -INF . . .
---- EQU SS84 -INF . . .
---- EQU SS85 -INF . . .
---- EQU SS86 -INF . . .
---- EQU SS87 -INF . . .
---- EQU SS88 -INF . . .
---- EQU SS89 -INF . . .
---- EQU SS90 -INF . . .
---- EQU SS91 -INF . . .
---- EQU SS92 -INF . . .
---- EQU SS93 -INF . . .
---- EQU SS94 -INF . . .
---- EQU SS95 -INF . . .
---- EQU SS96 -INF . . .
---- EQU SS97 -INF . . .
---- EQU SS98 -INF . . .
---- EQU SS99 -INF -1.000 . .
---- EQU SS100 -INF -1.000 . .
---- EQU SS101 -INF -1.000 . .
---- EQU SS102 -INF . . .
---- EQU SS103 -INF . . .
---- EQU SS104 -INF . . .
---- EQU SS105 -INF . . .
---- EQU SS106 -INF . . .

---- EQU SS107 -INF . . .
---- EQU SS108 -INF . . .
---- EQU SS109 -INF . . .
---- EQU SS110 -INF . . .
---- EQU SS111 -INF . . .
---- EQU SS112 -INF -1.000 . .
---- EQU SS113 -INF . . .
---- EQU SS114 -INF -1.000 . .
---- EQU SS115 -INF -1.000 . .
---- EQU SS116 -INF . . .
---- EQU SS117 -INF . . .
---- EQU SS118 -INF -1.000 . .
---- EQU SS119 -INF . . .
---- EQU SS120 -INF . . .
---- EQU SS121 -INF -1.000 . .
---- EQU SS122 -INF . . .
---- EQU SS123 -INF . . .
---- EQU SS124 -INF . . .
---- EQU SS125 -INF . . .
---- EQU SS126 -INF . . .
---- EQU SS127 -INF . . .
---- EQU SS128 -INF . . .
---- EQU SS129 -INF -1.000 . .
---- EQU SS130 -INF . . .
---- EQU SS131 -INF . . .
---- EQU SS132 -INF -1.000 . .
---- EQU SS133 -INF . . .
---- EQU SS134 -INF . . .
---- EQU SS135 -INF -1.000 . .
---- EQU SS136 -INF -1.000 . .
---- EQU SS137 -INF -1.000 . .

---- VAR F stream flowrates

	LOWER	LEVEL	UPPER	MARGINAL
BLNDs	.	.	+INF	EPS
COK_1s	.	2.0000E+6	+INF	.
COK_2s	.	.	+INF	7.2959E-6
CRs	.	.	+INF	5.5739E-6
FCCs	.	.	+INF	EPS
FCC_1s	.	2.0000E+6	+INF	.
FCC_2s	.	.	+INF	8.1639E-6
FG1s	.	1.3042E+5	+INF	.
FG2s	.	.	+INF	.
FG3s	.	8.6958E+5	+INF	.
FG4s	.	.	+INF	.
FG5s	.	1.0000E+6	+INF	.
GSLNs	.	2.0047E+7	+INF	.
H2s	.	7.5207E+5	+INF	.
H2_1s	.	7.5207E+5	+INF	.
H2_2s	.	.	+INF	0.681
H2S1s	.	14358.292	+INF	.
H2S2s	.	.	+INF	8.5723E-5
HCR_1s	.	2.0000E+6	+INF	.
HCR_2s	.	.	+INF	2.4736E-5
HCR_3s	.	.	+INF	2.4736E-5
HCR_4s	.	.	+INF	.
HSRN1s	.	.	+INF	.
HSRN2s	.	1.1213E+7	+INF	.
HSRN3s	.	.	+INF	0.304
HSRN4s	.	.	+INF	EPS

```
HSRN5s      .      .     +INF      .
ISOs        .      .     +INF      EPS
LPG1s       .  69398.411  +INF      .
LPG2s       .  1.8332E+6  +INF      .
LPG3s       .      .     +INF      EPS
LPG4s       .  1.9026E+6  +INF      .
LPG5s       .  1.9026E+6  +INF      .
LSRN1s      .      .     +INF      EPS
LSRN2s      .      .     +INF      0.304
LSRN3s      .      .     +INF      EPS
LSRN4s      .      .     +INF      .
LSRN5s      .      .     +INF      .
LSRN6s      .      .     +INF      .
NAP1s       .      .     +INF      EPS
NAP2s       .      .     +INF  1.3173E-5
NAP3s       .      .     +INF      .
NAP4s       .  2.3502E+7  +INF      .
NAP5s       .  2.3502E+7  +INF      .
PCHN1s      .      .     +INF      EPS
PCHN1_1s    .  5.2132E+6  +INF      .
PCHN1_2s    .      .     +INF      0.681
PCHN2s      .      .     +INF      0.681
PCHN3s      .      .     +INF      EPS
PCHN3_1s    .      .     +INF      0.681
PCHN3_2s    .      .     +INF      0.377
REFs        .  2.0047E+7  +INF      .
Ss          .  12172.960  +INF      .
SOLDs       .  2.1962E+7  +INF      .
TGs         .  2185.332   +INF      .
VISs        .      .     +INF      EPS
VIS_1s      .      .     +INF      .
VIS_2s      .      .     +INF  3.7730E-6
```

---- VAR CO2

```
            LOWER    LEVEL    UPPER   MARGINAL

ADUu            .        .     +INF     10.000
BLNDu           .        .     +INF     10.000
COKu            .        .     +INF     10.000
FCCu            .        .     +INF     10.000
FGHu            .        .     +INF     10.000
HCRu            .        .     +INF     10.000
HDT1u           .        .     +INF     10.000
HDT2u           .        .     +INF     10.000
ISOu            .        .     +INF     10.000
LPGu            .        .     +INF     10.000
MIX1u           .        .     +INF     10.000
MIX2u           .        .     +INF     10.000
MIX3u           .        .     +INF     10.000
MIX4u           .        .     +INF     10.000
MIX5u           .        .     +INF     10.000
MIX6u           .        .     +INF     10.000
REFu            .        .     +INF     10.000
SPLT1u          .        .     +INF     10.000
SPLT2u          .        .     +INF     10.000
SRUu            .        .     +INF     10.000
SOLDu           .        .     +INF     10.000
VISu            .        .     +INF     10.000
```

---- VAR Y existence or selection of process units

	LOWER	LEVEL	UPPER	MARGINAL
ADUu	.	1.000	1.000	382.903
BLNDu	.	1.000	1.000	EPS
COKu	.	1.000	1.000	EPS
FCCu	.	1.000	1.000	EPS
FGHu	.	1.000	1.000	EPS
HCRu	.	1.000	1.000	EPS
HDT1u	.	1.000	1.000	161.222
HDT2u	.	.	1.000	161.222
ISOu	.	1.000	1.000	70.535
LPGu	.	1.000	1.000	EPS
MIX1u	.	1.000	1.000	100.000
MIX2u	.	.	1.000	100.000
MIX3u	.	1.000	1.000	100.000
MIX4u	.	.	1.000	100.000
MIX5u	.	1.000	1.000	100.000
MIX6u	.	1.000	1.000	100.000
REFu	.	1.000	1.000	453.438
SPLT1u	.	1.000	1.000	100.000
SPLT2u	.	1.000	1.000	100.000
SRUu	.	1.000	1.000	50.382
SOLDu	.	1.000	1.000	EPS
VISu	.	.	1.000	EPS

---- VAR Z existence or selection of process streams

	LOWER	LEVEL	UPPER	MARGINAL
BLNDs	.	.	1.000	10.000
COK_1s	.	1.000	1.000	10.000
COK_2s	.	.	1.000	10.000
CRs	.	1.000	1.000	10.000
FCCs	.	.	1.000	10.000
FCC_1s	.	1.000	1.000	10.000
FCC_2s	.	.	1.000	10.000
FG1s	.	1.000	1.000	10.000
FG2s	.	.	1.000	-7.639E+8
FG3s	.	1.000	1.000	10.000
FG4s	.	1.000	1.000	10.000
FG5s	.	1.000	1.000	10.000
GSLNs	.	1.000	1.000	10.000
H2s	.	1.000	1.000	10.000
H2_1s	.	1.000	1.000	10.000
H2_2s	.	.	1.000	10.000
H2S1s	.	1.000	1.000	10.000
H2S2s	.	.	1.000	10.000
HCR_1s	.	1.000	1.000	10.000
HCR_2s	.	.	1.000	10.000
HCR_3s	.	.	1.000	10.000
HCR_4s	.	.	1.000	-3.044E+7
HSRN1s	.	.	1.000	-6.812E+7
HSRN2s	.	1.000	1.000	10.000
HSRN3s	.	.	1.000	10.000
HSRN4s	.	.	1.000	10.000
HSRN5s	.	.	1.000	-3.044E+7
ISOs	.	1.000	1.000	10.000
LPG1s	.	1.000	1.000	10.000

```
LPG2s      .     1.000    1.000   10.000
LPG3s      .       .      1.000   10.000
LPG4s      .     1.000    1.000   10.000
LPG5s      .     1.000    1.000   10.000
LSRN1s     .     1.000    1.000   10.000
LSRN2s     .       .      1.000   10.000
LSRN3s     .       .      1.000   10.000
LSRN4s     .     1.000    1.000   10.000
LSRN5s     .     1.000    1.000   10.000
LSRN6s     .       .      1.000 -6.875E+7
NAP1s      .       .      1.000   10.000
NAP2s      .       .      1.000   10.000
NAP3s      .       .      1.000 -3.044E+7
NAP4s      .     1.000    1.000   10.000
NAP5s      .     1.000    1.000   10.000
PCHN1s     .       .      1.000   10.000
PCHN1_1s   .     1.000    1.000   10.000
PCHN1_2s   .       .      1.000   10.000
PCHN2s     .       .      1.000   10.000
PCHN3s     .       .      1.000   10.000
PCHN3_1s   .       .      1.000   10.000
PCHN3_2s   .       .      1.000   10.000
REFs       .     1.000    1.000   10.000
Ss         .     1.000    1.000   10.000
SOLDs      .     1.000    1.000   10.000
TGs        .     1.000    1.000   10.000
VISs       .       .      1.000   10.000
VIS_1s     .       .      1.000   10.000
VIS_2s     .       .      1.000   10.000

                LOWER    LEVEL    UPPER   MARGINAL

---- VAR c        -INF  3.5538E+6   +INF      .

 c  total cost of refinery


**** REPORT SUMMARY :        0     NONOPT
                             0     INFEASIBLE
                             0     UNBOUNDED
E x e c u t i o n


---- 1859 VARIABLE c.L                  = 3553770.763  total cost of refiner
                                        y

---- 1859 VARIABLE F.L  stream flowrates

COK_1s 2000000.000,  FCC_1s 2000000.000,  FG1s   130421.153
FG3s   869578.847,   FG5s   1000000.000,  GSLNs  2.004732E+7
H2s    752068.192,   H2_1s  752068.192,   H2S1s  14358.292
HCR_1s 2000000.000,  HSRN2s 1.121318E+7,  LPG1s  69398.411
LPG2s  1833166.219,  LPG4s  1902564.630,  LPG5s  1902564.630
NAP4s  2.350213E+7,  NAP5s  2.350213E+7,  PCHN1_1s 5213175.169
REFs   2.004732E+7,  Ss     12172.960,    SOLDs  2.196206E+7
TGs    2185.332


---- 1859 VARIABLE Y.L  existence or selection of process units

ADUu 1.000,  BLNDu 1.000,  COKu 1.000,  FCCu 1.000,  FGHu 1.000
HCRu 1.000,  HDT1u 1.000,  ISOu 1.000,  LPGu 1.000,  MIX1u 1.000
```

MIX3u 1.000, MIX5u 1.000, MIX6u 1.000, REFu 1.000, SPLT1u 1.000
SPLT2u 1.000, SRUu 1.000, SOLDu 1.000

---- 1859 VARIABLE Z.L existence or selection of process streams

COK_1s 1.000, CRs 1.000, FCC_1s 1.000, FG1s 1.000
FG3s 1.000, FG4s 1.000, FG5s 1.000, GSLNs 1.000
H2s 1.000, H2_1s 1.000, H2S1s 1.000, HCR_1s 1.000
HSRN2s 1.000, ISOs 1.000, LPG1s 1.000, LPG2s 1.000
LPG4s 1.000, LPG5s 1.000, LSRN1s 1.000, LSRN4s 1.000
LSRN5s 1.000, NAP4s 1.000, NAP5s 1.000, PCHN1_1s 1.000
REFs 1.000, Ss 1.000, SOLDs 1.000, TGs 1.000