Planning of Petrochemical Industry under Environmental Risk and Safety Considerations

by

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A thesis
presented to the University of Waterloo
in fulfilment of the
thesis requirement for the degree of
Master of Applied Science
in
Chemical Engineering

Waterloo, Ontario, Canada, 2008

I hereby declare that I am the sole author of this thesis. This is a true copy of the thesis, including any required final revisions, as accepted by my examiners.

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ABSTRACT

The petrochemical Industry is based upon the production of chemicals from petroleum and also deals with chemicals manufactured from the by products of petroleum refinery. At the preliminary stages of chemical plant development and design, the choice of chemical process route is the key design decision. In the past, economics were the most important criterion in choosing the chemical process route. Modified studies imply that the two of the important planning objectives for a petrochemical industry, environmental risk and the industrial safety involved in the development. For the economic evaluation of the industry, and for the proposed final chemicals products in the development, simple and clear economic indicators are needed to be able to indicate an overall economic gain in the development. Safety, as the second objective, is considered in this study as the risk of chemical plant accidents. Risk, when used as an objective function, has to have a simple quantitative form to be easily evaluated for a large number of possible plants in the petrochemical network. The simple quantitative form adopted is a safety index that enables the number of people affected by accidents resulting in chemical releases to be estimated.

Environmental issues have now become important considerations due to the potential harmful impacts produced by chemical releases. In this study third objective of planning petrochemical industry was developed by involving environmental considerations and environmental risk index. Indiana Relative Chemical Hazard Score (IRCHS) was used to allow chemical industries routes to be ranked by environmental hazardous.

The focus of this work is to perform early planning and decision-making for a petrochemical plants network for maximum economical gain, minimum risk to people from possible chemical accidents and minimum environmental risk.

The three objectives, when combined with constraints describing the desired or the possible structure of the industry, will form an optimization model. For this study, the petrochemical planning model consists of a Mixed Integer Linear Programming (MILP) model to select the best routes from the basic feedstocks available in Kuwait -as a case study- to the desired final products with multiple objective functions.

The economic, safety and environmental risk objectives usually have conflicting needs. The presence of several conflicting objectives is typical when planning. In many cases, where optimization techniques are utilized, the multiple objectives are simply aggregated into one single objective function. Optimization is then conducted to get one optimal result.

This study, which is concerned with economic and risk objectives, leads to the identification of important factors that affecting the building-up of environmental management system for petrochemical industry. Moreover, the procedure of modelling and model solution can be used to simplify the decision-making for complex or large systems such as the petrochemical industry. It presents the use of simple multiple objective optimization tools within a petrochemical planning tool formulated as a mixed integer linear programming model. Such a tool is particularly

useful when the decision-making task must be discussed and approved by officials who often have little experience with optimization theories.

ACKNOWLEDGMENTS

I would like to thank several people who have, in one way or another, made this thesis possible. First, I would like to thank Professor Ali Elkamel for his great supervision and encouragement during this work. My gratitude is extended to my co-supervisor, Dr. Ghanimah Al-Sharrah who continued to provide me with support, very useful ideas and discussion.

Also I would like to thank the readers of the thesis Prof. Peter Douglas and Dr. Mazda Biglari for their valuable notes and comments.

Last but not least, I wish to express my gratitude to my family for their moral support and understanding throughout the period of my study. Without their encouragement, this thesis would never have come to fruition.

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ABBREVIATIONS

ABS	Acrylonitrile Butadiene Styrene
ACGIH	American Conference of Governmental Industrial Hygienists
AHI	Atmospheric Hazard Index
AP	Acidification Potential
AT	Aquatic Toxicity
CEI	Chemical Exposure Index
CERCLA	Comprehensive Environmental Response, Compensation, and Liability Act
CFC	Chlorofluorocarbon Compounds
CMTI	Clean Manufacturing Technology and Safe Material Institute
CP	Criteria Pollutant
CL	Short-term Critical Acid Deposition on Vegetation
DOT	Department of Transportation
EHI	Environmental Hazardous Index
EHS	Extremely Hazardous Substance
EP	Eutrophication Potential
EPA	Environmental Protection Agency
EPa	Kuwait Environmental Public Authority
ERI	Environmental Risk Index
F&EI	Fire and Explosion Hazard Index
GCC	Gulf Cooperation Council
GW	Global Warming
HAP	Hazardous Air Pollutant
HE	Human Toxicity Potential by Either Inhalation or Dermal Exposure
HI	Human Toxicity Potential by Ingestion
HPV	High Production Volume
HRP	High Risk Pollutant
HSE	Health, Safety and Environmental
HV	Hazardous Value
IPCC	Intergovernmental Panel on Climate Change

IPPI	Indiana Pollution Prevention and Safe Material Institute
IR	Infrared Radiation
IRCHS	Indiana Relative Chemical Hazard Score
KNPC	Kuwait National Petroleum Company
KPC	Kuwait Petroleum Corporation
LCA	Life Cycle Assessment
LC_{50}	Median Lethal Concentration 50
LD_{50}	Median Lethal Dose 50
LP	Linear Programming
MILP	Mixed Integer Linear Programming
MO	Multiple Objectives
NESHAP	National Emissions Standards for Hazardous Air Pollutants
NFPA	National Fire Protection Association
NSF	The Public Health and Safety Company
OD	Ozone Depletion
ODP	Ozone Depletion Potential
OPEC	Organization of the Petroleum Exporting Countries
PIC	Petrochemical Industries Company (Kuwait)
PO	Photochemical Oxidation Potential (or Smog)
PPIS	Pollution Prevention Incentives for States
PS	Polystyrene
PVA	Polyvinyl Acetate
PVC	Polyvinyl Chloride
SEGC	Sustainable Environmentally Preferable Cleaning Product Standard
SO	Single Objective
SOD	Stratospheric Ozone Depleter
SRI	Stanford Research Institute
STEL	Short Term Exposure Limit
TLV	Threshold Limit Value
TRI	Toxic Release Inventory
TT	Terrestrial Toxicity Potential
UNEP	United Nations Environment Program
UTN	University of Tennessee
VAM	Vinyl Acetate Monomer

NOMENCLATURE

Bg	Budget available for the development, $
B_j	Minimum economic production rate of plant *j*, kg/yr
cap_j	Capital investment cost for plant *j*, $
C_i	Price (or cost) of chemical *i*, $/kg
D_i	World demand of chemical *i*, kg/yr
ERI_j	Environmental risk index for plant j
F_i	Annual amount of chemical *i* used as a feedstock**,** kg/yr
f_m	Objective function number *m*
$Freq$	Frequency of accidents, number of accidents per process per year
H	Valid upper bound on production rates, kg/yr
Haz	Hazardous effect of a chemical, number of people affected per tonne of chemical released
I_i	imports of chemical i
Inv	Inventory of chemical released, tonne per accident
$IRCHS_i$	Indiana relative chemical hazardous score for chemical i
K	Risk index, people affected per year
M	Total number of plants
N	Total number of chemicals
o_{ij}	Output coefficient of chemical *i* from plant *j*
P	Number of the desired final product
Q_i	Annual amount produced of chemical *i*, kg/yr
S_i	Supply availability of feedstock chemical *i*, kg/yr
$Size$	Size of plant, number of major processes in plant
U	Upper limit of the country's share in petrochemical market, %
X_j	Annual level of production for plant *j*, kg/yr
Y_j	Binary variable for selecting plant *j*

CHAPTER 1

INTRODUCTION

Petroleum is the most valuable feedstock for both fuels and chemicals. It is clear that the value of the products from a barrel of oil is far more than the selling price of a barrel, even considering the cost of manufacturing. For example, 100 litres of naphtha, weighing 70 kg, will yield:

- 16 kg of ethylene, enough for 21 shirts and 18 plastic buckets, or 160 m of a garden hose;
- 11 kg of propylene, enough for 21 sweaters;
- 18 kg of cracked gasoline, enough for 200 nylon slips or 500 panty hoses;
- 7 kg of butylene, enough for one car tire or 13 bicycle tires;
- 14 kg of gas, enough for 17 days for a household;
- 4 kg of cracked heavy oil**.**

Very wide ranges of chemicals are manufactured from oil and gas. These consist of synthesis resins and plastics, textile fibres, rubber, industrial chemicals, agricultural chemicals, solvents, pesticides, and detergents. Chemicals can be standard chemicals such as ammonia, acetone, glycerol, etc., or specialty chemicals

such as plastics, detergents, sulfates, pesticides, etc. Due to the complex nature of the petrochemical industry, especially the multiple methods of producing chemicals, the petrochemical industry is cross-linked and can be visualized as a network of chemical processes connecting basic feedstock chemicals to the desired final products.

The selection of the chemical process route in the network is the key decision for preliminary stages of chemical plant design and development. In the past, economics were the most important criteria in choosing the chemical process routes. Safety and environmental risk have now become important considerations since the earlier the environmental friendliness of a proposed chemical process plant is considered the better. This is because the impact upon the final plant design depends on the decision made in the initial stages and the changes are easier and consequently the cost is less (Cave et al., 1997; Young, et al., 1999).

An environmental hazard is potential to cause harm to the environment. Chemical plants are usually environmentally hazardous because they typically contain large inventories of ecotoxic chemicals in addition to the emissions and releases from the chemical process. The hazard to the environment due to a chemical has been defined as a function of two elements (Cave et al., 1997):

1. The damage that the chemical could cause to the environment following a loss of contaminant that is the effect of chemical.
2. The quantity of chemical involved that is the exposure of the chemical.

The objective of our work is to build up an environmental management based system. The required outcome of this approach is continual improvement in environmental management and sustainability. The establishment of the environmental management systems has a long detailed program, but it always starts by setting the policy and planning. By setting the environmental policy, the aspects of the environmental concerns and problems will be of a clear firm. Previous definition of environmental hazard will help to develop a control strategy for the negative sides of the environmental aspects and will help to clearly define the required objectives and target of the planned environmental system. Next, planning can be accomplished, based on a clear understanding of the environmental problem and using the available solution strategies and tools (EPA, Your Organization ISO 14001 Guidance Manual, 1998). In our case, we will use modelling, optimization tools, economics, safety and environmental risk assessment concepts for planning. As illustrated by Al-Sharrah et al. (2001), the highly universal quest and pressurized demand for pollution prevention and accounting for environmental considerations makes sustainability an important objective function. Therefore, in this study sustainability is quantified by environmental risk and safety indices and increasing profit represented by process added value. In the model, it is assumed that the overall industry seeks to utilize its available resources in an optimal environmental way.

Consequently, the objective of this study is to develop a model that translates the network of the petrochemical industry into mathematical relations and plans for the projected development in Kuwait petrochemical industry as a case study.

Kuwaiti officials have expressed interest in accelerating development of the country's relatively small petrochemical industry. The petrochemical industry is considered to be the most suitable sector for development in Kuwait with the economic justification of (1) the availability of cheap natural gas, which is the feed stock for basic petrochemicals (2) petrochemical industries are labour-intensive industries, characteristics which coincide with Kuwait needs; and (3) the petrochemicals industry is an integrated industry consisting of basic intermediates, and final products.

Rudd (1975) and Stadther et al., (1976) did the first formulation of the model and it was a Linear Programming model used to model the petrochemical industry of the United States in 1975. Since that time, many researchers have expanded and improved the model. A major change to the model was done by Jimenez et al. (1982 and 1987) which was the transfer to a Mixed Integer Programming model. This study uses a modified Mixed Integer Programming model to select the routes from the basic feedstocks available in Kuwait to the desired final products with the objective function of some sustainability elements, namely, economics, safety and the environment.

This thesis is structured in seven chapters and two appendices. The next chapter, chapter 2 describes the structure of the petrochemical industry and the mathematical models that have been used to model the petrochemical industry under the classification of Linear Programming and Mixed Integer Programming. Chapter 3 outlines the Kuwait development needs and environmental concerns and shows the

importance and usage of the proposed final products for the development. Chapter 4 presents tools to evaluate environmental and safety impacts and presents different levels of environmental assessment with an overview of the impacts of the petrochemical industry. Chapter 5 gives a new two-step environmental risk assessment tool useful for planning a large industry. Chapter 6 deals with a Mixed Integer Linear Programming Model for petrochemical industry planning under economic, environmental risk and safety objectives; it gives the resulted optimal structure of the development in the petrochemical industry of Kuwait and some observations on the model's solution. Discussion, conclusions and some suggestions for further research are presented in the last chapter.

CHAPTER 2

PETROCHEMICAL INDUSTRY & MODELLING ASPECTS

2.1 The Structure of the Petrochemical Industry

The petrochemical industry, as the name implies, is based upon the production of chemicals from petroleum. However, there is more to the industry than just petroleum products. The petrochemical industry also deals with chemicals manufactured from the by-products of petroleum refining, such as natural gas, natural gas liquids, and tar.

The structure of the petrochemical industry is extremely complex, involving thousands of chemicals and processes. It is severely cross-linked, with products of one process being the feedstocks of many others. For most chemicals, the production route from feedstock to final products is not unique, but includes many possible alternatives. As complicated as it may seem, however, this structure is comprehensible, at least in general form.

At the beginning of the production chain are the raw feedstocks: petroleum, natural gas, and tar. From these are produced a relatively small number of important building blocks. These include primarily, but not exclusively, the lower olefins and aromatics, such as ethylene, propylene, butylenes, butadiene, benzene, toluene, and xylene. These building blocks are then converted into a complex array of thousands of intermediate chemicals. Some of these intermediates have commercial value in and of themselves, and others are purely intermediates. The final products of the petrochemical industry are generally not consumed directly by the public, but are used by other industries to manufacture consumer goods. To give some idea of the scale of complexity of the industry, a small portion is shown in Figure (2.1).

Figure (2.1) is a small extraction of much larger and more complete flow diagrams found in Stanford Research Institute (SRI) reports. Note in Figure (2.1), that certain chemicals, Acetaldehyde and Acetic acid for example, appear in more than one place in the flowchart. This reflects the multitude of production routes available for most chemicals. In the actual industry, many chemicals are products of more than one method, depending upon local conditions, corporate polices, and desired by-products (Bell, 1990). There are also additional methods available, which have either become obsolete and are no longer used, or which have never been used commercially but could become important as technology, supplies and other factors change. Such versatility, adaptability, and dynamic nature are three of the important features of the modern petrochemical industry.

Mathematical models of the petrochemical industry have the objective of defining the technical structure within which the petrochemical industry must function. The structure is formed by the large but linked number of chemicals that are available on a commercial scale and by the rigid feedstock, by-products, and energy requirements of these chemicals. The products of one segment of the industry become the feedstock for another segment; thereby defining a network of material and energy flows that constrain business activities.

Petrochemical companies seeking to upgrade their hydrocarbon raw materials have integrated forward into the petrochemical industry towards fibres, elastomers, plastics, and other consumer products. Rubber, textile, and steel companies, seeing synthetic material as competition for their traditional market, have integrated backward towards the production of synthetic polymers.

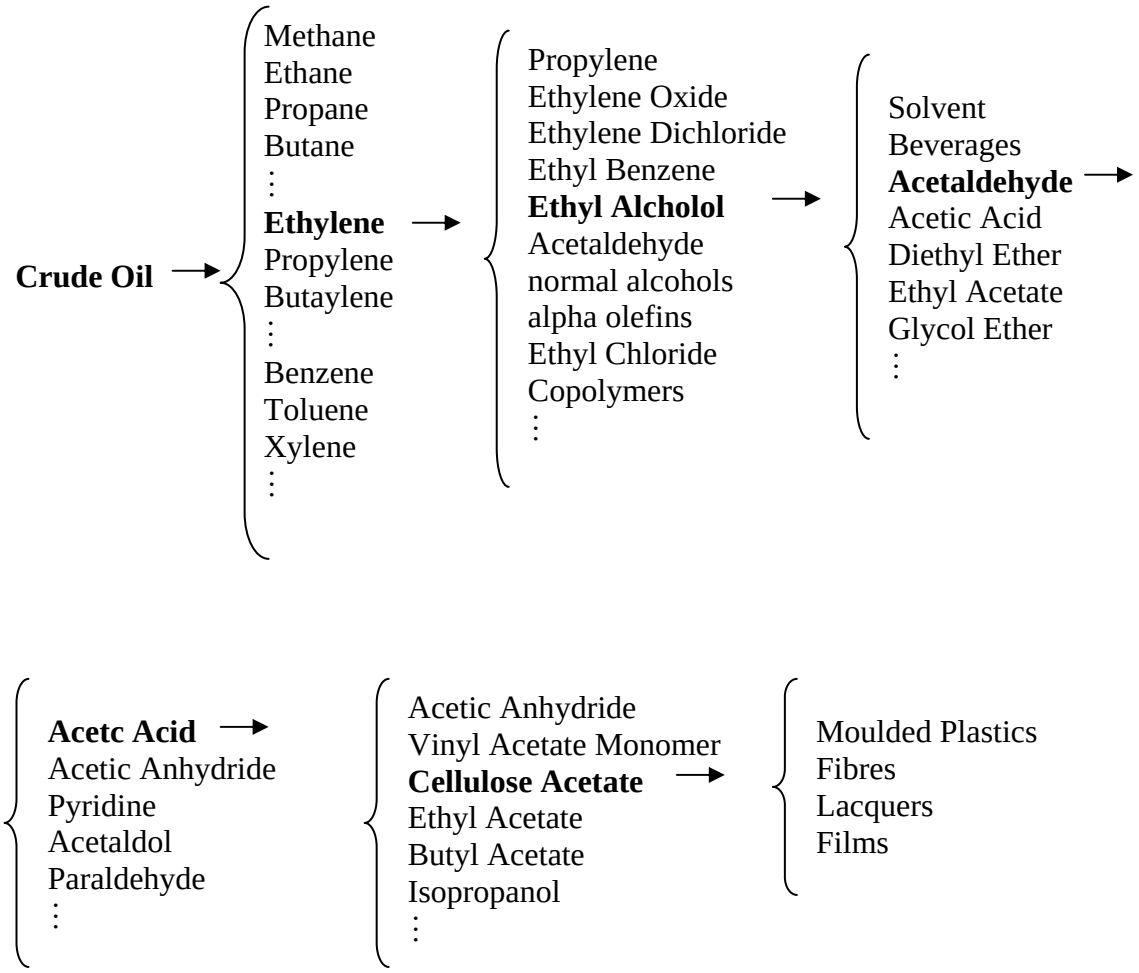

Figure (2.1): One Route from Crude Oil to Products

Chemical companies are increasingly concerned with the development of planning techniques for their process operation. The incentive for doing so derives from the interaction of several factors. Recognizing the potential benefit of new resources when these are used in conjunction with an existing process is the first factor. Another major factor is the dynamic nature of the economic environment. Companies must assess the potential impact of important changes in the external environment on their business. Included, are changes regarding demand, prices,

technology, markets, environmental and safety concerns. Hence, due to technology obsolescence, the increasing competition, and the fluctuating prices and demand for chemicals, there is an increasing need for quantitative techniques to plan the selection of a new process, the expansion and shutdown of an existing process, and the production of chemicals.

2.2 Petrochemical Industry Modelling

Many models have been proposed to plan the petrochemical industry in the form of optimization and non-optimization models. Optimization models include linear, integer or non-linear programming under deterministic or uncertainty probalistic approaches. The non-optimization models, that are not common, include relatively new methods, for example, a graphical representation called structural simulation (Chavez et al., 1991) and black and white Petri-nets (Harhalakis et al., 1993). Linear Programming and Mixed Integer Linear Programming models will be presented below; these models have importance and wide use in modeling the petrochemical industry.

2.2.1 Linear Programming Model

It is required to select the optimal technology paths for the production of a given amount of chemicals. For this, it is assumed that a set of feedstocks is locally available in a limited quantity. Also, several alternative processes technologically are accessible for transforming the feedstock into final products. These technologies

are characterized by technical coefficients of consumption of raw materials, chemicals, utilities, labour, by-products production, investment cost for different plant sizes and operation and maintenance costs. These technologies introduce intermediate chemicals, which are produced and consumed in the system.

The pioneering work of Stadtherr et al. (1976, 1978) defined the intermediate chemicals as a network and formulated the behaviour of the petrochemical industry as a system of linear equations. Figure (2.2) shows the overall perception of the Linear Programming (LP) model (Fathi-Afshar et al., 1981). The petrochemical industry is viewed as a system of M chemical transformations (processes) that produce or consume N chemicals. Let F_i be the amount of chemical i used as a primary feedstock; let Q_i be the amount of chemical i emerging as a final product; and let X_j be the total amount of the main chemical produced from process j. If the chemical i is produced by process j, let o_{ij} be the amount of i produced per unit X_j; if i is consumed by j, let $-o_{ij}$ be the amount of i consumed per unit of X_j; if neither an input or output of j, let o_{ij} =0. The industry is also constrained by the supply of feedstocks S_i, the demand of products D_i and a limit on the capacity of each chemical transformation L_j, where the production of each process X_j is usually lower than the current capacity of similar plants.

It is worth mentioning that the term *process* used in this section refer to a production plant using main feedstocks to produce final products while in section 4.4, the term *process* has a different implication; it is a section of a plant.

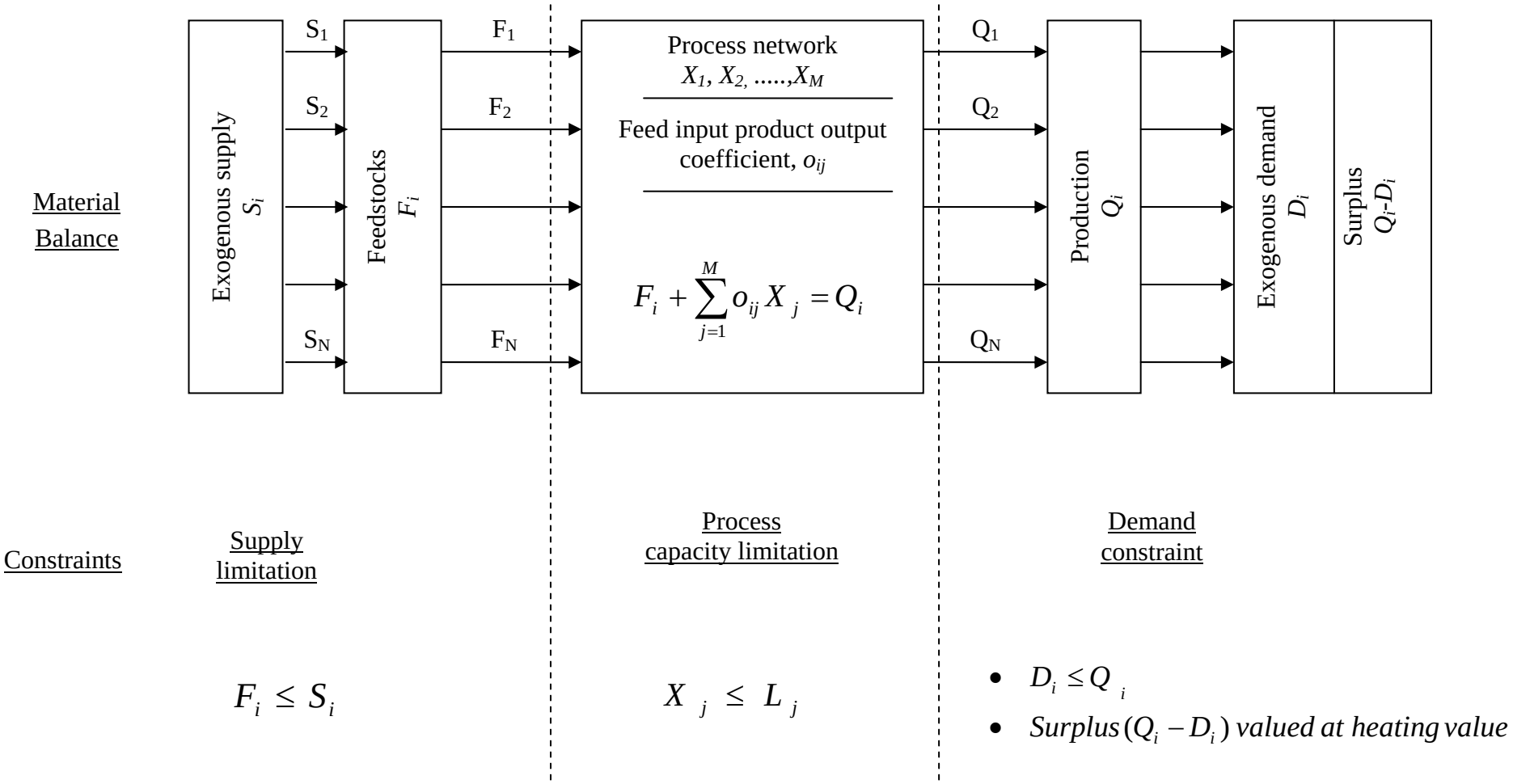

Figure (2.2): Linear Programming Model Structure (Fathi-Afshar et al. 1981)

The process capacity limitation constraint will impose the current industrial structure on the solution (Stadtherr et al., 1976); therefore, it can be neglected. Relaxing the capacity constraint was used in the models of Sophos et al. (1980), Sokic et al. (1983), Fathi-Afshar et al. (1985), De Santiago et al. (1986) and Al-Fadli et al. (1988). Different applications of the LP model were studied to identify the optimal structure of the petrochemical industry. Some of these applications were optimal resource allocation (Stadtherr et al., 1978); the economical impact of new chemical technology (Fathi-Afshar et al., 1981); the impact of converting a petrochemical complex to a trigenerate petrochemical complex on the total CO_2 emission (Dijkema et al. 2003). Trigeneration represents a novel, functional view of the large-scale petrochemical industry; it not only provides petrochemicals but also acts as a large heat sink that enables a net CO_2 emission reduction.

The LP model showed its ability to identify the technological structure of the petrochemical industry that meets the needs of the economy, natural resources or environment as well as to test different development scenarios. However, the LP model must be applied with care since its result may recommend small production rates or the production of a single chemical using more than one technology. Using different technologies for one chemical was against investor strategy in some small countries. The studies of Al-Fadli et al. (1988) and Fathi-Afshar et al. (1981) for example, did not consider that the results of a model recommending the production of a chemical using more than one technology as a problem, because they modelled the Kingdom of Saudi Arabia and the United States respectively (large countries with large petrochemical industries).

2.2.2 Mixed Integer Linear Programming Model

Mixed Integer Programming deals with the solution of mathematical programming problems in which some of the variables can assume non-negative integer values. If the objective and constraints are linear, the resulting model is called Mixed Integer Linear Programming (MILP) model.

A MILP model was proposed by Jimenez et al. (1982) and Jimenez et al. (1987) to study the Mexican petrochemical industry. The MILP model proposed selects a process to be installed if the production cost of its product reaches a favourable level with respect to the cost of importing the chemical. The MILP model permits the determination of the economic break-even point and it can be recursively used to study the impact of different development policies. Figure (2.3) shows a general structure of the MILP model (Jimenez et al. 1982). The model parameters are the same as the LP model described in the previous section with the addition of the imports $\boldsymbol{I_i}$ for chemicals and the binary variable $\boldsymbol{Y_j}$ that reflects the event of building ($\boldsymbol{Y_j}$=1) or not building ($\boldsymbol{Y_j}$=0) a plant.

The development of the petrochemical industry in the Kingdom of Saudi Arabia was also studied with a MILP model. Al-Amir et al. (1998), proposed a MILP model similar to Jimenez et al. (1982) model but with the modification that the constraint imposed on the process capacity:

$$0 \leq X_j \leq L_j Y_j \tag{2.1}$$

is replaced by:

$$B_j Y_j \leq X_j \leq K Y_j \tag{2.2}$$

where, K is a valid upper limit on production rates applicable to all processes.

The above constraint states that if only process ***j*** is selected, the production level must be at least equal to the process minimum economic capacity $\boldsymbol{B_j}$. Also, since the Kingdom of Saudi Arabia is a large petrochemical country, no imports of chemicals and no constraints on the supply of feedstocks were included in the model. The sensitivity analysis on the model indicated that it was quite insensitive with respect to the overwhelming majority of given parameters. Thus, the solution can tolerate a wide range of change in selling price, production costs, and supply deficit data. A newer MILP model for Saudi Arabia by AlFares et al. (2002) included feedstock constraints for some chemicals and expressed the production rate $\boldsymbol{X_j}$ as a linear combination of low, medium and high production rates as defined by the industry common standards.

Al-Sharrah et al. (2001, 2002, 2003 and 2006) used a MILP model similar to Al-Amir et al. (1998) with some modifications and applied it to plan the petrochemical industry of Kuwait. The main modifications were to include a constraint to limit the selection to one technology only to produce a chemical and to

modify the demand constraint in line with the country's share of the petrochemical market.

Examples of other application of MILP models, in the process industry, include multi-period planning and optimal plant layout. Sahinidis et al. (1989) presented a MILP model for long-range planning presented by periods up to the fifth year. They planned a network of processes and chemicals consisting of existing as well as potentially new processes. Georgiadis et al. (1997) used a MILP model to find the optimal layout design in multi-purpose batch plants. They also presented some simple heuristic rules to aid in the solution of large-scale models. Heuristic rules mean rules of thumb to aid in getting the best model solution.

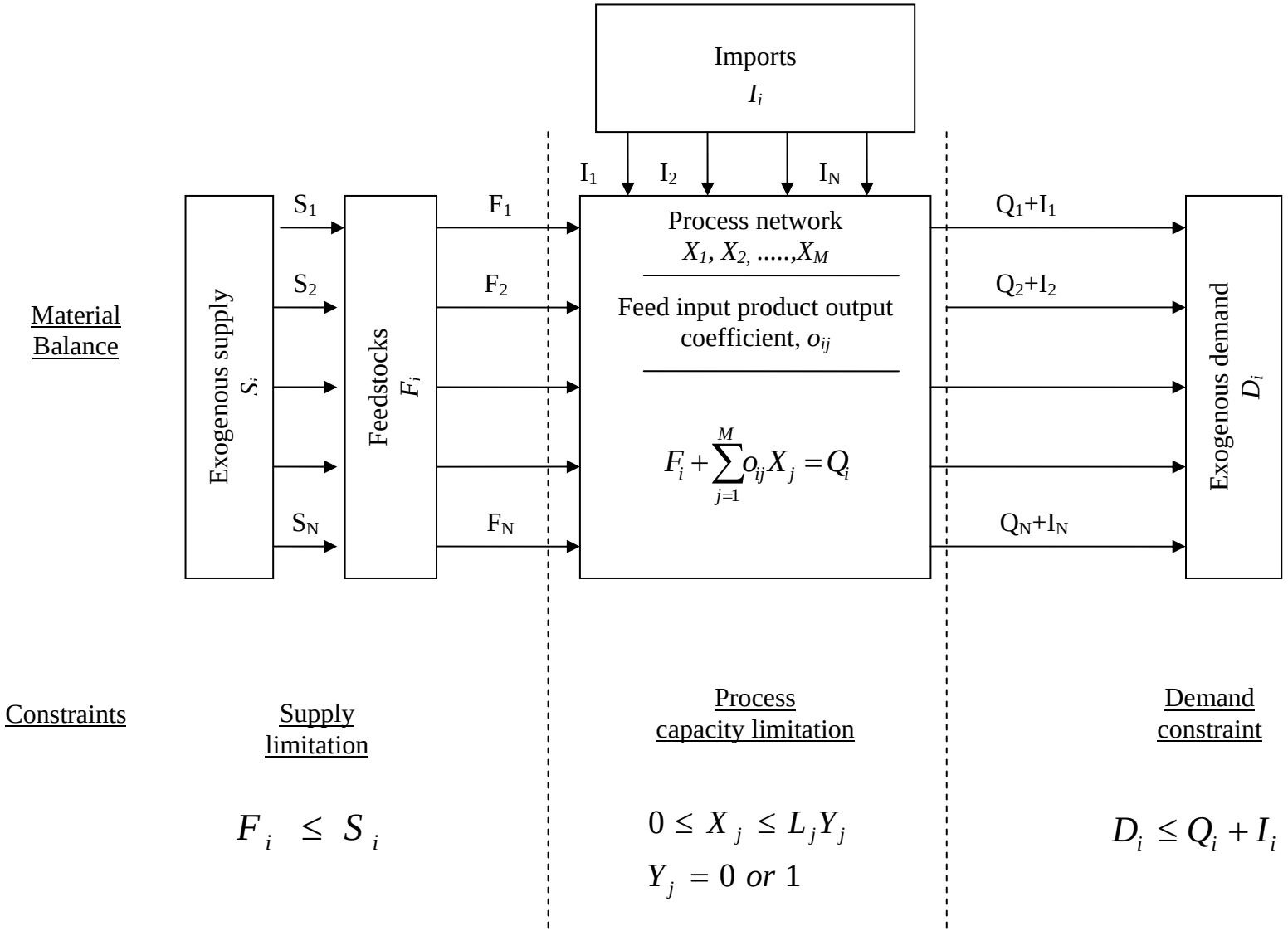

Figure (2.3): Mixed Integer Programming Model Structure (Jimenez et al. 1982)

2.3 Objective Functions

An objective function specifies the direction of improvement of a criterion, i.e., maximize or minimize the criterion. A criterion is a measure of effectiveness of performance, which forms a basis for decision-making. Examples of a criterion are cost, profit, return of investment, or any measure of effectiveness that guides the decision making process; note that cost and profit are examples of two conflicting criteria. The objective function(s) considered within a petrochemical model vary extensively in the literature. Researchers have selected a single objective function or multiple objective functions with different aspects

2.3.1 Single Objective Function

For the single objective function, Rudd (1975), Al-Fadli et al. (1988), and Fathi-Afshar et al. (1981) selected the minimization of the total production cost. Other studies, Stokic et al. (1983), and Stadtherr et al. (1976, 1978), selected minimizing feedstock consumption.

2.3.2 Multiple Objective Functions

The notion of Multiple Objectives (MO) in planning the petrochemical industry is used extensively due to the number of objectives decision-makers aim to achieve; most important of which are: profit, cost, environmental concerns and safety. MO analysis in modelling the petrochemical industry has been considered with objectives of maximization of the thermodynamic availability change (a

measure of ideal performance), minimization of entropy creation (lost work), and minimization of feedstock consumption in the studies of Sophos et al. (1980), and minimizing cost and gross toxicity in the studies of Fathi-Afshar et al. (1985). Song et al. (2002) considered maximization of total profit and minimization of environmental impact. Al-Sharrah et al. (2006) used maximum economic gain and minimum risk due to a plant accidents resulting in a chemical release.

CHAPTER 3

KUWAIT DEVELOPEMENT NEEDS ENVIRONMENTAL AND SAFETY CONCERNS

The reconstruction of Kuwait following the Iraqi invasion provided unique opportunities for foreign investors and contractors as the country rapidly rebuilt its infrastructure and its oil industry. The economy is dominated to an unusual extent by the oil sector, which provides well over 84% of national revenues (Country Report 2004). Kuwait's oilfields are a crucial feature as are its oil port and shipping facilities. It also has large oil refineries and processing facilities and has invested in a range of light industries, including glass, textiles, paper, furniture, mineral and construction materials.

3.1 Development Needs

Petrochemical Industries Company (PIC), a subsidiary of Kuwait Petrochemical Company (KPC), was established by an Amiri Decree issued on July 23, 1963, to develop the ammonia and nitrogen fertilizers industry in Kuwait. Petrochemical derivatives constitute one of the main building blocks of the modern

industrial economy. The market's exponential growth in recent years has led PIC to embark upon several ambitious projects for petrochemical production in Kuwait. Over the years, PIC's plants have undergone expansion and new plants have been installed for the production of liquid ammonia with a total capacity of 858,000 tonnes/year and three urea plants with a total capacity of 792,000 tonnes/year. In 1997, the Company started a polypropylene plant with an annual capacity of 100,000 tonnes.

PIC has also approved building two new petrochemical complexes, one for the production of aromatics and methanol and one for the production of olefins that could enter production in 2008. The first stage of the $1.4 billion aromatic complex has been granted by the Kuwait Petroleum Company (KPC). The complex, which was first suggested in 1995, will be established and run by PIC. The complex will produce 1,000,000 tonnes/year of aromatic compounds such as para-xylene, benzene and toluene for the manufacture of synthetic fibres, using naphtha from the country's refineries. The olefin complex is planned to have a production of 850,000 tonne/year ethylene and 600,000 tonnes/year ethylene oxide/ethylene glycol.

Kuwaiti officials have expressed interest in accelerating development of the country's relatively small petrochemical industry. This would accomplish several goals; boosting the value of Kuwait's crude oil reserves; helping to protect Kuwait's revenues during periods of low crude prices; and boosting Kuwait revenues while adhering to Organization of Petroleum Exporting Countries (OPEC) crude oil quota

limitation. The proposed final products (Al-Sharrah et. al, 2003) for the development in the petrochemical industry are:

- Vinyl acetate monomer
- Polystyrene
- Polyvinyl chloride
- Acrylonitrile Butadiene Styrene
- Cumene

The desired final products were defined by the criteria of their importance to the global petrochemical industry and the relevance of each final product to Kuwait. The economic importance for the proposed chemicals is discussed below.

1. Vinyl Acetate Monomer (VAM):

Vinyl acetate monomer (VAM) is a chemical building block in the manufacturing of a wide variety of industrial consumer products. Including polyvinyl acetate (PVA), emulsion polymers used in paints, adhesives, textile sizing and finishes, non-woven textile binders, paper coating and special coating for flexible substrates. Nearly half of the VAM produced in the US is used in PVA production, polyvinyl alcohol, ethylene-vinyl acetate copolymers, and ethylene-vinyl alcohol. VAM can be produced by the reaction of ethylene, acetylene or ethane with acetic acid.

2. Polystyrene (PS):

Polystyrene was first produced in 1831 but has only become commercially significant over the last 50 years. Present consumption is measured in millions of tonnes per year. Polystyrene is made industrially in large quantities because the equipment is expensive and the process requires several days between intake and discharge. Benzene under pressure is added to ethylene in the presence of aluminium trichloride to produce ethyl benzene. The product is reduced to styrene monomer by passing it over an oxide catalyst at high temperatures. Free styrene is then mixed with peroxide and the resulting polymer is passed through a cylindrical tower where the reaction is controlled by heaters. It is extruded and granulated. The characteristics of styrene-based polymers include:

- Wide range of properties
- Low cost of basic material.
- Low cost of processing because of relatively low processing temperature.
- Low mould shrinkage.
- Low water absorption.
- Clear and transparent.
- Easily produced as foam.
- Excellent dielectric properties.

3. Polyvinyl Chloride (PVC):

Polyvinyl chloride is manufactured from the polymerization of vinyl chloride monomer, which in turn is produced from ethylene, either directly, or with an ethylene dichloride intermediate. By itself, PVC is brittle and susceptible to heat decomposition. The use of a plasticizer, however, produces PVC having much more desirable properties, and indeed a wide range of properties depending on the amount and type of plasticizer used.

PVC can be manufactured to be either rigid or flexible. Some uses for rigid PVC include pipe and tubing, ductwork and credit cards. Other uses are film and sheet, electrical insulation, floor coverings, hoses, footwear (soles and heels), packaging, coating, adhesives, toys, and household goods.

4. Acrylonitrile Butadiene Styrene (ABS):

ABS plastics are a family of thermoplastics offering a balance of properties, the most outstanding being impact resistance, tensile strength and scratch resistance. Three methods of manufacturing are employed for ABS plastics: emulsion, suspension and bulk polymerization. In emulsion and suspension polymerization, the monomer and the many chemicals used to control the reaction are finely dispersed or dissolved in water. In bulk polymerization, the monomer itself serves as a solvent for the polymer particles. Some typical applications of ABS plastics are

domestic appliances like vacuum cleaners, luggage cases, safety helmets, toys, and furniture.

5. Cumene:

Almost all the world's supply of Cumene is now produced as an intermediate for phenol and acetone manufacture. Cumene is oxidized to Cumene hydroperoxide, which is then cleaved catalytically to phenol and acetone. The Cumene projects are being driven by a shift to zeolite catalyst-based technology, which promises higher yields, reduced production cost and possibilities for debottlenecking leading to an increase of one-third or more in the existing capacity. Some refinery units still produce Cumene for use as an antiknock constituent of gasoline but it is doubtful whether new plants would be constructed for this purpose. Cumene may be prepared commercially by alkylating benzene with propylene.

3.2 Environmental and Safety Concerns

Minimizing the risks arising from industrial and economic development and the resultant degradation of the environment has been a matter of great concern to Kuwait for a number of years. Various institutions have come together for the preservation of the environment. These integrated efforts resulted in the passing of a decree in 1980, which enforced basic rules for the protection of the environment in Kuwait.

The Environmental Public authority (EPa) was established in 1995; in 1996 a High Council of the EPa was created to define the EPa's aims, objectives and policy. The High Council is headed by the First Deputy Prime Minister and the Foreign Minister and has the following members:

- The Minister for Health.
- The Minister for Planning.
- The Minister for Oil.
- The Minister for Commerce and Industry.
- The Minister for Communications.
- The Municipality Chief.
- The Chairman - the Director General of the Public Authority for the Agriculture Affairs and Fish Resources.
- The Director General of Kuwait Institute for Scientific Research.

The High Council of the EPa also includes, for four renewable years, three qualified and experienced individuals in the field of environment protection. The EPa has recently promulgated a 10-year strategy aimed at protecting Kuwait's environment, and addressing specific concerns about the atmosphere, water resources, environment preservation, education and awareness as well as industry and power. It also provides an environmental framework to protect and preserve components of the infrastructure and the urban environment.

In spite of the unfavourable global business environment and the unusual events witnessed in the Arabian Gulf during the past few years, KPC proceeded with efforts to constantly promote the level of occupational safety at its various facilities to ensure optimal safety of both employees and the installations and to protect the environment outside, as well as within, its production areas. The achievements of KPC in the field of occupational safety and industrial security are outlined below (KPC annual report 2002/2003):

- Opening a dedicated training centre for industrial safety and occupational environmental health at Mina Al-Ahmadi Refinery.
- Executing over 23% of the "Health Safety and Environmental Management System" scheme at KNPC's Refinery
- Achieving four million accident-free work hours in the new Southern Pier Project and Mina Al-Ahmadi Refinery Rehabilitation Project.
- Conducting several evacuation and emergency drills at manufacturing facilities and headquarters of KPC and its subsidiaries.
- Conducting a sweeping inspection of buried pipes at all production facilities.
- Organizing several awareness campaigns and contests on safety issues, which included dissemination of bulletins, media flyers and posters.

CHAPTER 4

EVALUATING POTENTIAL ENVIRONMENTAL AND SAFETY IMPACTS IN THE INDUSTRY

Health, Safety and Environmental (HSE) issues are high up the agenda for all industries, but particularly for the petrochemical industry. The consumers, employees, shareholders, legislators and the communities for which the industry operates are all becoming increasingly aware of HSE issues and demand ever-higher standards. Over the last few decades, the petrochemical industry has reduced its harmful emissions significantly, by using environmental and technological developments together with an increased awareness of the safety aspects of plant operation. HSE legislation is being proposed and/or refined continuously aiming for a better living and working environment in the whole world. HSE issues are not easily resolved because of the enormity of the task and its components. However, identifying the nature of the safety problem and to which stages of planning it can be applied is an essential task.

The selection of appropriate measures of environmental or safety performance for a process will depend on the nature of the environmental concerns, the type and quantity of information available and the degree of accuracy required in

the representation. Several environmental analysis indices have been developed, some of them are internationally known and proven, and some have been used in limited case studies. Data required for each index is different and the results produced may vary. The different environmental indices are suitable for different stages of process development, design and operation. Some can be applied at a very early stage of planning and require an overall knowledge of the system under consideration, and some must be applied to existing units with full knowledge of all aspects of the unit. The indices are aimed to evaluate a potential harm to the environment which has many forms as presented in below.

4.1 Environmental impacts

Over the last 20 years, there has been a very rapid growth in environmentally related legislation affecting the petrochemical industry. Regulations now cover products, air and water quality, waste disposal, soil reclamation, noise abatement, and related matters. Looking ahead a further 20 years, it seems likely that the global petrochemical industry will face a major challenge in responding to the political and social imperative of continuous improvement in environmental performance whilst, at the same time, ensuring its economic and financial viability.

The development of environmentalism in the industry has proceeded along two waves (Ulhoi, 1998). The first wave was building during the 1960s and peaked in 1972 when the Rome Club published its ‘Limit to Growth’ report. Industry responded in a protesting and reactive way. Protection of the environment was seen

by industry as an extra and unnecessary cost in production. However, regulation regimes were slowly introduced by public authorities in most part of the Western industrialized world based on ‘identify-and-repair’ followed by a sanctioning approach towards the polluter. In the mid-1970s the ‘Polluter-Pays-Principle’ was introduced and broadly accepted by most countries. The regulation was characterized by expensive ‘end-of-pipe’ pollution abatement arrangement.

The second wave was building during the 1970s and began to take shape in the 1980s when the Executive Director of the United Nations Environment Program published a collection of his former speeches. During the late 1970s, he had persistently argued for a production philosophy that did not destroy the ecological basis to sustain economic development.

With the first environmental wave primarily based on the nature declining capacity to provide essential raw materials such as fossil energy, metals, etc., the second wave was primarily concerned with nature’s capacity to absorb the waste from economic development. The effects of global warming and the destruction of the ozone layer dominated the debate during the 1980s.

However, this second wave crested in 1987 when the World’s Commission on Environmental and Development published its report and introduced the new well-known concept of sustainable development. At this point in historical development, environmental strategies increasingly left the former ‘identify-and-repair-approach’ and adopted an ‘anticipated-and-prevent-approach’. The issue is no

longer a growth or no growth, but what type of growth. The quest for pollution prevention and increased pressure and demand for environmentally being and sustainable processes and products have been creating a new ethos in the process industry. Within the petrochemical industry, support for the concept of Sustainable Development is based on (Kohlhase, 1994):

- Protecting and improving the quality of the environment
- Prudent management of available resources including development of new, clean, and energy efficient technology
- The transition towards a cleaner and more sustainable mix of energy sources and consumption patterns (including a switch from high carbon to low carbon fuels).

According to the literature (Young et al., 1999; Das 2005; Jia et al., 2004,) potential impacts produced by chemical releases are classified into nine categories, including global warming (GW) , photochemical oxidation potential (or smog) (PO), ozone depletion (OD), acidification potential (AP), eutrophication potential (EP), human toxicity potential by ingestion (HI), human toxicity potential by either inhalation or dermal exposure (HE), aquatic toxicity potential (AT), and terrestrial toxicity potential (TT). Under the guide lines of US EPA Science Advisory Board, (United Sate Environmental protection Agency, US EPA, 1990) they classified global warming, ecological toxicity, human toxicity, ozone depletion, and smog as relatively high risk problems, acidification and eutrophication as relatively medium-risk problems. Impact associated with solid wastes is neglected. Jia et al. (2004)

gave weights for important criterion as three times higher than the medium-risk criterion. These environmental impacts are explained below:

4.1.1 Global warming (GW)

Global warming is a global environmental impact, which is revealed by climate changes. The sun radiation to Earth is absorbed by the surface and re-emitted as infrared (IR) radiation. Some gases, known as greenhouse gases, in the atmosphere trap the heat that would otherwise be radiated back to the space and influence the atmospheric temperature. In order to determine the global warming impact, due to chemical substances releases into the atmosphere, the warming caused by the total quantity of the chemical released is determined.

The principal greenhouse gas is carbon dioxide. In 2002 about 40% of U.S carbon dioxide emissions stem from the burning of the fossil fuels (US Emissions Inventory 2004). Coal emits around 1.7 times as much carbon per unit of energy when burned as does natural gas and 1.25 times as much as oil. Natural gas gives off 50% of the carbon dioxide that is released by coal and 25% less carbon dioxide than oil, for the same amount of energy produced. It is known that burning fuel is essential factor in the whole industries where the type of the used fuel is different depending on the fuel source. So that whenever there is an industry, that means there is carbon dioxide emissions.

While carbon dioxide is the principal greenhouse gas, methane is the second most important. According to the Intergovernmental Panel on Climate Change (IPCC), methane is more than 20 times as effective as carbon dioxide at trapping heat in the atmosphere. There are many sources for methane emissions but the most common one is fossil fuel production (US Emissions Inventory 2004).

Another greenhouse gas is nitrous oxide, a colourless, non-flammable gas with a sweetish odour. Man-made sources of nitrous oxide include nylon and nitric acid production and the burning of organic matters. It is obvious that the three previous nitrous oxide sources are highly related to the petrochemical industry. In general, we can observe that petrochemical industry is an important source for the most three principal greenhouse gases.

4.1.2 Photochemical oxidation potential (PO)

Ground level production of photo oxidants such as ozone and peroxiacetylnitrate has caused the build–up of photochemical smog, which causes damage to the environment such as plant growth reduction and damage to leaf tissue. Theses photo oxidants are formed from the reaction of reactive hydrocarbons and oxides of nitrogen in the presence of sunlight.

The impact due to photochemical smog is measured in parts per billion (ppb) ozone (by volume) produced by the substances released into the atmosphere. Research studies have shown that a concentration of 2 ppm propene can produce

about 0.75 ppm ozone in the atmospheric environment (Hatakeyama et al., 1991). Many substances lack the data needed to determine the amount of ozone that can be produced in the troposphere to create smog. Therefore the propene equivalent concentration of the chemical is determined in order to estimate the amount of ozone that can be produced. The Propene-Equiv concentration is the concentration in parts per billion carbon (ppbC) of propene required to yield a carbon oxidation rate equal to that of the volatile organic compound released into the atmosphere.

4.1.3 Ozone depletion (OD)

Stratospheric ozone depletion is a global environmental impact that also affects the Earth's climate. If the pollutant contains Cl or Br atoms and its atmospheric lifetime is long enough to allow for transport to the stratosphere, it may have an effect on stratospheric ozone. Therefore, the hazard due to ozone depletion is estimated using the atmospheric lifetime of the substance and the number of Cl and Br atoms per molecule.

The Montreal Protocol is the first worldwide agreement designed to protect human health and the environment against the adverse effects of the depletion of the stratospheric ozone layer. The protocol is administrated by the United Nations Environment Program (UNEP), which maintains the list of ozone depletion substances that are targeted for control practices, reductions, or total phase-outs. Chemicals Ozone Depletion Potential (ODP) formed the primary basis for inclusion on that list. ODP is defined as the ratio of calculated ozone column change for each

mass unit of gas emitted into the atmosphere relative to the calculated depletion for the reference gas CFC-11 (ODP=1.0). EPA utilizes a different classification system for identifying chemicals for regulatory controls, dividing the universe of substances covered by the Montreal Protocol into class I and class II depletion substances.

4.1.4 Acidification potential (AP)

The impact on vegetation is used to estimate the impact due to acid deposition. The exposure of vegetation to substances in the atmosphere is mainly due to dry deposition. Dry deposition includes the gravitational settling of particulate material and adsorption of gases by vegetation, soil and surface water. In vegetation, the main part of the plant that is exposed to dry deposition is its leaves. Therefore, the transfer of substances into the vegetation through leaves by dry deposition is considered for determining the impact due to acid deposition. The short-term Critical Loads (CL) values are used in estimating the impact due to acid deposition on vegetation.

4.1.5 Eutrophication (EP)

Eutrophication is a process whereby water bodies, such as lakes, estuaries, or slow-moving streams receive excess nutrients that stimulate excessive plant growth (algae, periphyton attached algae, and nuisance plants weeds). This enhanced plant growth, often called an algal bloom, reduces dissolved oxygen in the water when dead plant material decomposes and can cause other organisms to die. Nutrients can come

from many sources, such as fertilizers applied to agricultural fields, golf courses, and suburban lawns; deposition of nitrogen from the atmosphere; erosion of soil containing nutrients; and sewage treatment plant discharges. Water with a low concentration of dissolved oxygen is called hypoxic.

4.1.6 Human toxicity (HI and HE)

The effect of toxic substances may be acute, chronic, systemic, or local. Acute toxicity is manifested from a single dose or one-time exposure within a short period of time, usually from a few minutes to several days. Chronic toxicity results from several exposures of small concentrations for long periods of times, usually greater than an 8-hour work shift; certain substances cause illness after several years. A systemic effect is the toxic effect of a chemical at one area in the body, the chemical having entered the body at another point. When a substance affects the tissues at the point of contact or where it enters, it is termed a local effect.

Toxicology data are available for most chemicals. The most commonly used in the industry are LC_{50}, LD_{50}, TLV and STEL. Their definitions are:

- LC_{50} Median Lethal Concentration 50: Calculated concentration of a chemical in air exposure, which can cause the death of 50% of experimental animals in a specified period of time.

- LD_{50} Median Lethal Dose 50: Calculated dose of a chemical that is expected to cause the death of 50% of experimental animals when administered by any route other than inhalation.

- TLV Threshold Limit Value: Concentration of a substance in the air to which workers can be exposed without adverse effect.

- STEL Short Term Exposure Limit: is the maximum permissible concentration of a material, generally expressed in ppm in air, for a defined short period of time (typically 5 or 15 minutes, depending upon the country). This "concentration" is generally a time-weighted average over the period of exposure.

4.1.7 Aquatic toxicity (AT)

Aquatic toxicity means potential or actual properties of a substance to cause adverse effects to aquatic organisms, which live predominantly or entirely in the water**.** This effect is observed during exposures which are determined in relation to the life-cycle of the organism.

4.1.8 Terrestrial toxicity (TT)

Terrestrial toxicity means potential or actual properties of a substance to cause adverse effects to aquatic organisms, which live predominantly or entirely on land**.** This effect is observed during exposures which are determined in relation to the life-cycle of the organism.

4.2 Environmental Indices

World wide one can recognize a trend in environmental reporting away from purely qualitative description. Environmental practices go towards a more comprehensive, quantitative depiction of environmental performance by the use of input-output material flow-analysis and environmental indicators. Environmental indicator systems are an important tool in planning, steering and control of environmental strain, performance and costs. Indicators are used to depict the vast quantity of environmental data of a firm in a comprehensive and concise manner. They are mostly applied to set absolute material and energy data in relation to other variables in order to increase the informational value of quantitative data (Jasch, 2000). Environmental indicators have the following purposes as described by (Jasch, 2000)**:**

- Comparison of environmental performance over time
- Highlighting of optimization potentials
- Derivation and pursuit of environmental target
- Identification of market chances and cost reduction potentials
- Evaluation of environmental performance between firms
- Communicational tool for environmental reports
- Feedback instrument for information and motivation of the workforce

Data used for environmental performance indicators can be expressed as absolute or relative measurements, and, depending on their use and application, can be aggregated or weighted. Indicators can be classified as follows:

- Absolute indicators; e.g. tons of raw materials, emissions, taken from input-output analysis;
- Relative indicators, where input figures are referenced to other variables such as production in tons, revenue, number of employees, office space in m^2; e.g. detergent per m^2;
- Indexed indicators, where figures are expressed as percentage with respect to a total, or as a percentage change to values of previous years etc.;
- Aggregated depictions, where figures of the same units are summed over more than one production step or product life cycle;
- Weighted evaluations, which try to depict figures of varying importance by means of conversion factors.

Chemical process and plant design must start with choosing a route, which is defined here as the raw materials and the consequence of reaction steps that converts them to the desired products, quantifying environmental risk and safety must be performed for all alternatives. The selection of appropriate measures of environmental or safety performance for a process will depend on the nature of the environmental concerns, the type and quantity of information available and the degree of accuracy required in the representation. Indexed indicators are widely used currently to evaluate the chemical process routes. Several hazard analysis indices

have been developed, some of them are internationally known and proven, and some have been used and developed inside companies. Data required for each index is different and the results produced may vary. The different hazard indices are suitable for different stages of process development, design and operation. Some can be applied at a very early stage of planning and require an overall knowledge of the system under consideration, and some must be applied to existing units with full knowledge of all aspects of the unit. Some hazard indices are presented below.

4.2.1 Simple Environmental Indices in Planning

Simple indices have been used in the earliest stage of planning and when the most detailed process information is still lacking. Developing a simple hazard index for systems is not an easy task; it requires knowledge of what is important for the viability of the system involved and how that contributes to the environment. The number of representative indicators in the index should be as small as possible, but as large as essential. Such simple indices are, by their nature, applicable only for specific functions and should not be employed for more general safety comparison.

In the petrochemical industry, the first forms of simple toxicity indices for planning started in the 1980s after the development of optimization models for that industry. The indices at that time were very simple; they were the first introduction of toxicity into planning. Fathi-Afshar et al. (1985) selected the chemical TLV as an indicator for a health objective function. Chemical 1 is considered more harmful

than chemical 2 if TLV_1 is less than TLV_2; so the index is represented as the reciprocal of TLV.

A number of index type methods have been implemented to evaluate the environmental impact of the emissions of a chemical process, Grossman et al. (1982) proposed a toxicity index by multiplying the effluent flow rate of a chemical by the inverse of its LD_{50} value and Heinzle et al. (1998) and Koller et al. (1998) proposed ecological indices based on classification approach to assess the environmental impact of a process.

Also, very simple hazard indices were used when planning involved hazard identification for a large number of plants. The National Fire Protection Association (NFPA), (1994); has developed a system for indicating the health, flammability and reactivity hazards of chemicals. The system is based on giving a number (from 0 to 4) to a chemical indicating its effect. Al-Sharrah et al. (2001) used these NFPA health ratings as an index for an environmental objective in planning. This model was composed of 83 plants with 65 chemicals.

4.2.2 Comprehensive and Detailed Environmental Indices in Planning

Detailed indices usually consider many different environmental effects or study, in details, certain effects throughout the plant life. Cave et al. (1997) proposed the Environmental Hazard Index (EHI) that ranks routes (raw materials and reactions to produce the final product) in chemical plant development by the

estimated environmental impact of a total release of chemical inventory. The index considers the hazard to the aquatic and the terrestrial ecosystems. Also, an index by Gunasekera et al. (2001, 2003), called the Atmospheric Hazard Index (AHI), can be used to assess the potential impact of airborne releases from a chemical production plant. A catastrophic failure of the plant is assumed and the impact on the atmospheric environment is estimated. The method is designed to assess possible alternative process routes to make a chemical, in order to determine the route that has the least adverse atmospheric environmental impact. Thus, the routes that are inherently environmentally hazardous can be identified and avoided when the selection is made in the early stage of production plant design. The atmospheric impact categories considered were the toxicity, photochemical smog, acid deposition, global warming and ozone depletion of a chemical when it is released catastrophically into the environment.

Ideally, environmental index approach should be to look at the full life-cycle of a manufactured product (Canadian Standards Association, Feb 1994a, and Feb 1994b), from design, through manufacture, use and final disposal, to assess the environmental impacts for each of these product life stages (Purdue Research Foundations, 1997). Koller et al. (2000), has the same conclusion, they described the Life Cycle assessment (LCA) as a good analyzing method to all impacts to humans and the environment caused by a product or process during its whole cycle from being raw material extraction to the stage of being disposal or decommissioning.

Some serious attempts have been made to do this such as, the US EPA Use Cluster Scoring System (Office of Pollution Prevention and Toxics), the US EPA Mark I system (Stephan et al., 1994). Also the University of Tennessee, Knoxville study for the US EPA, which also developed some examples of chemical-use trees to follow chemicals of concern through the economy to their various uses (Davis et al, 1994b). In addition, different simple attempts to account for environmental impacts of input streams have been presented by Heinzle et al. (1998). However, LCA approach requires massive amounts of data and the main limitations for this approach is that the data are readily available for a small number of bulk chemicals and collecting new data is far time intensive for process development. These limitations emphasise that methods, which are simple to understand and apply will be more readily accepted for use in pollution management and prevention.

Many index methods developed for environmental risk assessment, rely on a specific data, they are neither flexible enough to incorporate additional information which might not be available, nor can they be applied if substance data are missing (Koller et al., 2000). The highly complex nature of environmental effects makes it difficult to link environmental and design calculations with either sufficient scope or detail. For environmental assessment of chemical substances and process, different concepts have been developed and were implemented into a large variety of methods. For chemical process, environmental assessment usually concentrates on the direct emissions and neglects the input streams (Koller et al., 2000).

4.3 Safety Impacts

Safety engineering has to protect the people and the environment, as far as possible, from the dangers that can arise from an industrial plant. On the other hand, the application of safety engineering must avoid restricting production or increasing costs of these plants more than is necessary.

In this work, an additional objective is to incorporate safe production of petrochemicals into planning by identifying an industry structure that has minimum risk following the accidental release of chemicals.

During the last 30 years, individual chemical plants have grown larger, often increasing 10 times in size, to take advantage of the economics of scale. A chemical plant today will typically produce 300,000 to 600,000 tonnes of products per year. Storage tanks at plants may hold as much as 50,000 m^3 of product or raw material. The primary hazard in the chemical industry resides in the material, because materials are a hazard even if only in storage, with no processing or other activity being performed. The raw material, the intermediate, and the finished products present the primary independent hazard element (Ward, 2002). A major factor, which has a decisive influence on the safety performance of the chemical industry, and production safety in particular, is the toxicity of the chemicals. Overlooking this increasingly important factor would be to ignore one of the major forces that shape the development of the industry. The issue of safely producing hazardous chemicals

is as important as the economics of producing and selling them. Examples of hazardous substances prevailing within the petrochemical industry are:

- Gases (flammable, toxic, compressed).
- Liquids (flammable, toxic, acidic, alkaline, cryogenic).
- Solids (flammable, volatile).
- Viscous materials.
- Oxidizing, reactive and corrosive substances.

The hazardous effect of chemicals comes through three ways: fire, explosion and toxicity. The first essential step towards greater plant safety is being aware of the potentially dangerous properties of the substances, i.e. whether they are flammable, explosive or toxic.

4.3.1 Fire

Fire, or combustion, is a chemical reaction in which a substance combine with oxygen and heat is released (Lees, 2001). To produce combustion, three conditions must coexist: flammable substance, oxygen, and a source of ignition. Determining the fire potential of a chemical substance is accomplished through its flammability characteristics; no single factor, however, defines a substance's flammability. When a flammability comparison is to be made between different substances, the following factors should be considered:

- Flammability limits (or explosion limits)
- Flash point
- Autoignition temperature
- Vapour pressure
- Burning velocity
- Ignition energy

The most important and widely used factors are the first three, i.e. flammability limits, flash point and autoignition temperature. Flammability limits of a gas define the concentration range of a gas-air mixture within which an ignition source can start a self-propagating reaction. The flash point of a liquid is the lowest temperature at which the liquid releases vapour in a sufficient amount to form an ignitable mixture with air near its surface. The autoignition temperature is the minimum temperature required to cause or initiate self-sustained combustion independent of the source of heat. In other words, a substance will ignite spontaneously when it reaches its autoignition temperature. Most fire hazards involve flammable liquids (Patnaik, 1999). The flammable liquid does not burn itself, the vapours from the liquid burn. Thus, the flammability of a liquid depends also on the degree to which the liquid forms flammable vapours; in other words, its vapour pressure.

4.3.2 Explosion

Explosion is a sudden and violent release of energy (Lees, 1980). This energy could be physical energy, chemical energy and nuclear energy. The physical and chemical energies will be considered due to their relevance to the process industries. Most chemical explosions involve a limited set of simple reactions, all of which involve oxidation. An explosion can be spontaneous or initiated by light, heat, friction, impact, or a catalyst. Explosions are not confined to closed systems; explosions may occur in an open area such as a process plant in which case the pressure wave will expand itself until the pressure gradient becomes insignificant.

4.3.3 Toxicity

Toxicity is defined as the ability of toxic (poisonous) substances, when absorbed by living tissues (either ingested or via the skin), to cause injury or destroy life. Injuries, caused by the toxic effects of chemicals, vary and occur both close to and distant from the point of release of these chemicals, especially when the correct precautions to chemical releases are ignored. The injuries include eye, skin, poisoning, asphyxia and respiratory system injuries.

The effect of toxic substances may be acute, chronic, systemic, or , same as section 4.1.6 on human toxicity in the environmental impact section. This makes toxicity as a common issue between safety and environmental impacts, the difference comes from the source and size of the chemical release. Day-to-day and

small releases are considered as an environmental problem and accidental and large release are considered as safety problems.

4.4 Safety Indices

Simple safety indices can be taken similar to the human toxicity effect indices presented in section 4.1.6, i.e. LC_{50}, LD_{50} , TLV and STEL. Or any simple measure of flammability or explosiveness of the chemical. Koller et al. (2000) used, among others, National Fire Protection Agency (NFPA) flammability index, the different between the autoignition temperature and the process temperature, and combustion enthalpy in the evaluation of the fire/explosion index. However, a simple yet comprehensive safety index developed by Al-Sharrah et al. (2007) was very useful for planning and it is explained in the following paragraphs.

Starting from the basic definition of risk, which was the product of the incident probability and the magnitude of the harmful effects, a simple risk index ***K*** is proposed. It is an index that can be applied to chemical plants using the properties of the major chemicals associated with production. It is an index to quantify risk to human life and falls into the group of simple early stage planning and route selection hazard indices. The index is:

$$\boldsymbol{K} = Freq \times Haz \times Inv \times Size \qquad (4.1)$$

where,

Freq = Frequency of accidents, number of accidents per process per year

Haz = Hazardous effect of a chemical, number of people affected per tonne of chemical released

Inv = Inventory of chemical released, tonne per accident

Size = Size of plant, number of major processes in plant

This gives an overall unit of the index ***K*** as number of people affected per year, and it represents the potential maximum number of people affected if an accident caused the release of all the plant inventory of a chemical. Affected people include fatalities, people injured and hospitalized. The plant is assumed to have major processes in which a major chemical is being treated and an accident in any part of the plant may cause, in an extreme case, the release of the plant inventory.

Details for calculating this index are available in Al-Sharrah et al. (2007); In general, the frequency of accidents (*Freq)* are taken from Belke (2000). The hazard of a chemical (*Haz*) is calculated from any avialable accidents database by looking at all the available accidents associated with the chemical and dividing the number of people affected by the amount released.

The inventory (*Inv*) is taken as the maximum production inventory in a petrochemical plant; usually it is one month of production. The minimum economic production rate can be used for evaluating the inventory if the actual production rate

has not been determined or planned. Minimum economic production rates are usually known for most plant from plant economics references such as Stanford Research Institute (SRI) reports. Finally, *Size* of a plant, in term of major processes, can vary from one plant to another but usually a chemical goes through production stage, purification stage and a final product storage stage. Therefore, a general number for *Size* is taken as three. Values of the index for some chemicals are listed in Table (A.3).

The values used for the index parameters are best estimates if other information is unavailable. Certainly, detailed information about a production plant and the chemical involved will result a more realistic evaluation of the risk index. The index can also be used in other cases as follows:

1. The index can be applied to a chemical plant including major and non-major chemicals. The index in this case is calculated as the summation of the individual chemicals indices.
2. The inventory of one month of production is used for calculating a theoretical maximum for the risk. Consequently, a high value for inventory is used. The index can give a more realistic (non maximum) value of the risk if it is applied to existing plants with accurate inventories.
3. The number used for the size is a representative number (an average). The actual number of major processes can be used.
4. The index can be applied for chemicals in the plant which are not stored. In this case, an estimate for their inventory in the process equipment can be used.

5. The index can be used to estimate risk from a single process in a plant; in this case the *Size* will be taken as one and *Inv* will be taken as the inventory of chemicals within the process equipment.

Al-Sharrah et al. (2007) indicate that the index includes experience from previous accidents databases, which are considered as valuable sources of information. This index can be considered as an inherent safety index; it has the characteristics of an inherent hazard index indicated by Tyler (1985) as:

1. It should be applied at an early stage in the process development, and require only the flowsheet and other information normally available at that stage.
2. It should cover both continuous and batch processes over a wide range of scale, and apply to single units as well as to complete processes.
3. Ranking of separate hazards and overall hazards should be produced, and the fundamental causes of the rankings should be apparent.
4. The results should tend to promote simplified processes, safer methods of handling and should not unreasonably penalize novel technology.
5. The method must be easily learned, convenient, and quick to use.
6. The ranking must be in the correct relative order and there should be an absolute level which is normally acceptable for routine operation.

The accuracy with which the index is determined depends on the accuracy of its four factors, namely accidents frequency (*Freq*), the hazardous effect of the chemical (*Haz*), the inventory (*Inv*) and the size of the plant (*Size*). In any stage of

planning, even in the first stages, an estimate of the plant size and inventory can be found with good accuracy. This makes estimating the frequency of accidents and the hazardous effect of the chemical the main two factors that affect the accuracy of the index or estimating the effect of the plant accidents on people. Good values of *Haz* come from good accidents databases, the number of historical incidents has to be as high as possible and the number of affected people has to be accurately counted together with the amount of chemical released.

Identifying and addressing the factors contributing to industrial chemical accidents is a first step in reducing and hopefully eliminating such accidents. One way of doing that is to translate the large number of system components and features in the HSE fields to a representative number as an index. The new index that was developed by Al-Sharrah et al. (2007) was formulated to represent a potential maximum number of people affected if an accident caused the release of the whole of the plants chemical inventory. This index was used as a safety objective for route selection in planning petrochemical networks by Al-Sharrah et al. (2006). The merits of this index can be expressed as follows:

- Can be simply used for risk comparison.
- Can be applied in initial process assessment, even as early as the conceptual design stage of a plant.
- Incorporates past experience and data on chemical accidents into risk evaluation and comparison.
- Can be used for the planning of new plants.

In the following chapter, we will present the environmental risk index that will be used in the multiobjective function of modelling petrochemical industry.

CHAPTER 5

PROPOSED ENVIRONMENTAL ANALYSIS: INDIANA RELATIVE CHEMICAL HAZARD SCORE (IRCHS) INDEX

5.1 Introduction

Production planning in petrochemical industry requires a model that can account for different interactions, needs, and features and provide at the same time suitable mathematical representation. The quest for pollution prevention and increased pressure and demand for environmental considerations makes sustainability an important objective function (Al-Sharrah et al., 2001). In this study, sustainability is quantified by an environmental index, safety index and increasing profit represented by process added value. The environmental hazard index allows the environmental impact of a chemical process route to be evaluated and it will be discussed in this chapter since it is used for the first time in planning a petrochemical industry.

The environmental hazard posed by a chemical process plant can be of two types. One set of hazards is due to the environmental impact of the pollutants released by daily operations in the plant. These include pollutants such as emissions from chimney stacks to the atmosphere and wastewater discharges. The second type of hazard is the potential impacts due to major environmental incident such as the total loss of chemical contaminant (Gunasekera et al., 2006). Based on the previous categories of the environmental hazardous, we were looking for recent modified indices that include the most effective parameters on the environment, health and safety.

The environmental risk and safety indices are always performed to express the environmental performance of chemicals in a specific environmental media. They are ranged between simple and comprehensive indices. The simple indices mainly include large number of chemicals since they are concentrated on a specific field, but they can not express the negative environmental effects of chemicals in other field. The comprehensive indices mostly include very small number of chemicals, since they include the environmental performance of these chemicals in many environmental compartments. These types of indices can be very accurate, but in the same time they can not be a basis for large data base of chemicals like those in the petrochemical industries especially if experimental work is needed. For the planning of petrochemical industry, the needed environmental index should combine between the different affected media in the industrial environment and the huge number of chemicals that are involved in the chemical processes routes.

The needs for environmental risk evaluation system that can be readily applied for the chemicals and the chemical process, in order to advice the decision-makers in a useful way, encourage the scientific environmental institutes to develop chemical ranking systems. Chemical ranking and scoring systems involve developing both chemicals ranking and relative quantitative score, based on chemical specific attributes. These systems create only a relative score, not a quantitative measure of risk (Purdue Research Foundation, 1997). The index that is resulted from these scoring systems should have specific facilities that enable this index to be used as a decision tool in the environmental management systems. Such facilities are:

- Flexibility: easily incorporate new data, new design and new products
- Easily understood
- Dynamic, providing feedback to identify needed changes
- Applicability for different uses
- Can be implemented for most of chemicals, unless all of them

Many attempts have been made to estimate chemical scoring and ranking systems. Attempts have been made to use Toxic Release Inventory (TRI) emission estimates to arrive at chemical scoring and ranking systems. The limitations of TRI data, that they give only masses emitted without distinguishing between the relative toxicities of the materials released. A group of Carnegie-Mellon have attempted to add weighting factor for toxicity to TRI release amounts to create a more meaningful product of mass times a toxicity weighting factor (Horvath et al, 1995). The group of

Carnegie-Mellon has emphasized that the major obstacle of developing and using chemical scoring and ranking systems is the serious gaps of data. Further problems arising for chemical scoring and ranking systems is that the available data always is acute data, while the most important data for the studying of the health and environmental impacts are the data related to chronic releases or exposures. Moreover, whenever chronic data is available, it focuses on environmental impacts of certain system (air, aquatic, soil….etc) not for full multimedia system.

Ideally, a chemical scoring and ranking system for the practical evaluation and expression of the environmental risk assessment from chemicals should involve pollution potential in all significant environmental media, particularly ambient air, indoor air, surface and groundwater, soil and sediment. The University of Tennessee (UTN), Knoxville, Centre for Clean Products and Clean Technologies developed environmental scoring system from releases of specific chemicals that related to specific environmental media of concern (Davis, 1994). It is especially strong in evaluating potential from aquatic environmental impact. However, it does not address other relevant media; nor anthropogenic global habitat degradation, such as global warming or stratospheric ozone depletion; nor hazard to workers. Indiana Pollution Prevention and Safe Material Institute (IPPI) have decided to improve the scope of environmental hazard score beyond the good start made by (UTN). They were thinking of scoring system that can be accepted, as being for practical use to manufacturers, to get them acclimated to the paradigm of shift reducing emissions and wastes, in a cost effective way and a way which takes into account environmental risk reduction in addition to the health and safety of the workers.

Based on the previous aspirations the Indiana Relative Chemical Hazard Score (IRCHS) was generated by the Clean Manufacturing Technology and Safe Material Institute (CMTI, Purdue University, Indiana).

In the following section the IRCHS is described, starting with the historical back ground toward the principles of chemicals ranking and scoring algorithms. IRCHS environmental hazard value scores indicate how a chemical compares with others in terms of its capacity to impact human health, ecosystems, or environmental health generally. The unique facilities of IRCHS lead us to use its chemicals scores to evaluate the environmental risk of chemical process routes that are involved in the petrochemical industry. IRCHS index in addition to the safety index and the chemical process routes added-value will be used in the multiobjective treatment of modelling and planning of the petrochemical industry.

5.2 IRCHS Historical background

Two U.S. EPA Pollution Prevention Incentives for States (PPIS) grants were awarded in 1994 and 1996 to the Indiana Clean Manufacturing Technology and Safe Materials Institute (CMTI) to develop a method for ranking chemicals by their environmental and workplace hazards. The original name of and acronym for the method, 3P2M, was changed to IRCHS by the Indiana Department of Environmental Management in 1997.

The major goal of the initial PPIS project was to develop a reliable measurement method applicable to Indiana manufacturers. This was accomplished with the assistance of the IRCHS Work Group, which consisted of industry representatives and academia researchers. The IRCHS team reviewed existing measurement methods and decided to expand upon the chemical ranking system developed by the University of Tennessee (UTN), pursuant to an earlier U.S. EPA grant. The UTN method evaluates each chemical separately and assigns the chemical a hazard value based upon hazard impact on environment, with emphasis upon the aquatic ecosystem. The team expanded the UTN algorithm to also include hazard impacts on air quality, potential soil and groundwater contamination, and stratospheric ozone depletion. This expanded algorithm assigns chemicals an environmental hazard value. The IRCHS team also developed an algorithm to assign a hazard value based upon a chemical's impact on workplace employees. The two hazard values are combined and the average of the two becomes the combined hazard value for the chemical.

Hazard values have been assigned to over one thousand chemicals. The hazard values are on Clean Manufacturing Technology Institute CMTI's website, www.ecn.purdue.edu/CMTI. All Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA) hazardous substances, plus any additional chemicals commonly used by manufacturers, have been ranked. Chemicals on the Extremely Hazardous Substance (EHS) list that were not previously assigned a hazard value have also been ranked, and High Production Volume (HPV) chemicals were being ranked in spring 2002.

The IRCHS system has been reviewed and used by several universities, government agencies and defense installations throughout the nation. Environmental Defence lists the IRCHS as the second of five "hazard ranking" systems that it uses to develop hazard scores for its Environmental Score Card (Scorecard, 2007). It is also considered in the work of Toffel et al. (2004) for environmental assessment, they indicated that IRCHS are well designed to provide an indicator for regulatory scrutiny; this may be useful for prioritizing compliance management. It has been used to evaluate the environmental and hazard of cleaning products in the work of (SEGC, 2005), where it was selected because it balances equally the human health and the environmental health effects of a product.

5.3 IRCHS Algorithms and Formulation Basis

According to IRCHS, the UTN method evaluates each chemical separately and assigns a hazard value based upon the chemical's hazard toward the environment, with emphasis upon the aquatic system. The IRCHS algorithm includes hazard towards the environment in the fields: air quality, potential for soil and groundwater contamination, and stratospheric ozone depletion. This expanded algorithm assigns for the chemicals an environmental hazard value. The IRCHS teams also developed an algorithm to assign for the chemicals hazard values based upon its hazard towards the factory workers. The two hazard values are combined and the average of the two becomes the combined hazard value for the chemical. Therefore, these hazard values permit ranking chemicals by hazard to the environment and workers.

5.3.1 Environmental Hazard Value

The environmental hazard component consists of four components. The IRCHS system assigns hazard scores between 0 and 100 based on the following algorithm:

Environmental Hazard = HVWater+ HVAir+ HVLand+ HVGlobal (5.1)

1. Water hazard value (HVWater):

The water hazard value (HVWater) is the normalized UTN total hazard value score. UTN total hazard value scores are based on toxicity and persistence considerations. Since persistence can be a useful surrogate for exposure potential, UTN total scores provide an improved indicator of the potential environmental health impacts of environmental releases.

The NTU system assigns hazard scores between 0 and 200 based on the following algorithms:

Total Hazard Value = (Human Health Effects + Environmental Effects) x Exposure Potential.

where:

Human Health Effects = HVoral LD50 + HVinhalationLC50 + HVcarcinogenicity + HVother

Environmental Effects = HVoral LD50 + HVfishLC50 + HVfish NOEL

Exposure Factor = HVBOD + HVhydrolysis + HVBCF

Four endpoints are used as indicators of human health effects: two measures of acute toxicity to mammals (LD50 is the dose that kills 50% of organisms via ingestion; LC50 is the concentration that kills 50% of organisms via inhalation) and two measures of chronic toxicity (a carcinogenicity score based on EPA/IARC weight of evidence schemes and a multiple endpoint score based on whether a chemical possesses evidence of mutagenicity, developmental effects, reproductive effects, neurotoxicity, and/or other chronic effects.)

Three endpoints are used as indicators of environmental effects: one measure of acute toxicity to mammals (LD50 is the dose that kills 50% of organisms in a test) and two measures of toxicity to aquatic organisms (LC50 is the concentration that kills 50% of organisms in an acute test; NOEL is the no observed effect level in a chronic test).

Exposure Factors in the UTN system are based on indicators of environmental persistence and bioaccumulation in an aquatic environment. There are two indicators of environmental persistence: BOD half-life is the number of days required to reduce the biological oxygen demand from a chemical in water by half due to biodegradation by microbes. Hydrolysis half-life is the time required to reduce the amount of a chemical in water by half through reaction with water. To characterize a chemical's propensity to bioaccumulate in the environment, the UTN system uses its bioconcentration factor. BCF is the ratio of the concentration of a chemical in an organism to its concentration in the test medium or environment, typically water.

2. Air hazard value (HVAir):

The air hazard value (HVAir) is the sum of hazard values assigned if the chemical is:

a. *A criteria pollutant (CP),(HV=20):*

Criteria pollutants must meet the following criteria (EPA, Office of Air Quality Planning and Standards. National ambient Air Quality Standards):

- Emissions cause or contribute to air pollution that may reasonably be anticipated to endanger public health or welfare.
- Presence in the ambient air results from numerous or diverse mobile or stationary source.

b. A hazardous air pollutant (HAP),(HV=40):

National emissions standards for hazardous air pollutants (NESHAPs) are issued to limit the release of specified HAPs from specific industrial sectors. These standards are meaning that they represent the best available control technology an industrial sector could afford (EPA, office of air quality, planning and standards. Section 112, hazardous air pollutants list).

c. A high risk pollutant (HRP), (HV=20)

d. An extremely hazardous substance (EHS), (HV=20):

The presence of EHSs in amounts in excess of a threshold planning quality requires that the certain emergency planning activities should be conducted. These substances are listed based on concerns about acute toxicity, reactivity, volatility, dispersability, combustability or flammability (EPA, office of solid waste and emergency response, Extremely hazardous substances (EHS) chemical profiles and emergency first aid guides).

3. Land hazard value (HVLand):

EPA regulations establish two ways of identifying solid wastes as hazardous. A waste may be considered hazardous if it exhibits certain hazardous properties (characteristics). EPA's regulations define four hazardous waste characteristic properties: ignitability, corrosivity, reactivity and toxicity. Also, waste is considered as hazardous because it found to pose sustainable present or potential hazards to human health or to the environment. Accordingly, EPA has determined four different lists of hazardous wastes. These four lists are:

a. The F list (non-specific source waste): the list F is designated as hazardous particular solid wastes from certain industrial or manufacturing processes. The chemicals in list F are known as wastes from non-specific sources, because the processes producing these wastes can occur in different sectors of industry.

b. The K list (source-specific wastes): the K list designated particular solid wastes from certain industries as hazardous.

c. The P list and the U list (discarded commercial chemical products): these two lists are similar in that both list as hazardous certain commercial chemical products when they are discarded or intended to be discarded. The difference is that the chemicals on the P list are identified as acute hazardous wastes and those on the U list are identified as toxic wastes.

The land hazard value (HVLand) that is included in the environmental hazard value component of the IRCHS, is the hazard value assigned if the chemical is:

i. On the hazardous waste P list (HV=70):

ii. On the hazardous waste F,K,U lists (HV=35):

iii. Exhibits the following hazardous waste characteristics of:

- Ignitability (HV=15).
- Reactivity (HV=15).
- Corrosivity (HV=15).
- Toxicity (HV=15).

4. Global hazard value (HVGlobal):

The global hazard value (HVGlobal) is the hazard value assigned if the chemical is considered as a stratospheric ozone depleter (SOD). ODP, as described in section 4.1.3, is a number that refers to the amount of ozone depletion caused by a substance. The ODP is the ratio of the impact on ozone of a chemical compared to

the impact of a similar mass of CFC-11. EPA used ODP values to utilize a different classification system for identifying chemicals for regulatory controls, dividing the universe of substances covered by the Montreal Protocol into class I and class II. Thus, the values of the HVglobal are based on these two classifications as follows:

a. 50 if the chemical is a class I SOD:

   Class I SOD is one of several groups of substances with an (ODP) of 0.2 and higher.

b. 25 if the chemical is a class II SOD.

   Class II SOD is a chemical with an (ODP) of less than 0.2.

Accordingly, the components of the Environmental Hazard Value of the IRCHS:

1. HVWater = normalized UTN HV
2. HVAir = HV (CP)+HV (HAP)+HV (HRP)+ HV (EHS)
3. HVLand = HV(P list) +HV(F,K,U list) + HV(Ignitability) + HV(Toxicity) + HV(Reactivity) + HV(Corrosivity)
4. HVGlobal = HV (SOD)

The values for the water, air and land hazardous portions of the algorithm are to be normalized to the highest probable score of 100. The value for the global hazard portion is normalized to a highest probable score of 50. These four parts are

added together and divided by 3.5 - since the global hazard value is considered 1/2 of the value of the other three - to determine the environmental hazard value. Therefore, the final environmental hazard value algorithm was:

HV(Environmental Hazard) = (HVWater+ HVAir+ HVLand+ HVGlobal)/3.5 (5.2)

5.3.2 Worker Hazard Value

The definition of pollution prevention in Indiana law considers the work place as one of the environmental media into which the release of pollution is to be reduced. IPPI has therefore interpreted this law to mean that a method is needed to quantify hazard to workers, when implementing pollution prevention in manufacturing. The worker exposure hazard value (HV Worker Exposure) components are consisting of three parts:

1. Health effects hazard value, HV(Health)
2. Routes of exposure hazard value, HV(Exposure)
3. Safety hazard value, HV(Safety)

Each part of the HV(Worker Exposure), has special classifications depend on the different affecting factors. The following points are explaining the most effective factors on the HV(Worker Exposure) (Purdue Research Foundation,1997).

1. The health effects hazard value, HVhealth:

The health effects hazard value is the sum of two parts, the "Chronic" hazard value and the "Acute" hazard value.

a. The Chronic Hazard Value, HV(Chronic):

HV(Chronic) is the more stringent of the toxic, as it is listed in Table (5.1), or the carcinogenic hazard values, as it is listed in Table (5.2).

- The toxic hazard value HV(Toxic) is based upon the chemical's Threshold Limit Value (TLV). The hazard values assigned are:

Table (5.1): The Assigned Toxic Hazard Values Based upon the TLV

No.	(TLV) (mg/m^3)	HVtox
1	>2500	0
2	≤2500 but >250	1
3	≤250 but >25	2
4	≤25 but >2.5	3
5	≤2.5 but >0.25	4
6	≤0.25	5

- The carcinogenic hazard value HV(Carcinogenic) is based upon classifications from EPA ratings and the American Conference of Governmental Industrial Hygienists (ACGIH) ratings. The hazard values assigned are presented in Table (5.2):

Table (5.2): The Assigned Carcinogenic Hazard Values Based upon the ACGIH Ratings

No.	EPA Rating	ACGIH Rating	HVCarcinoginic
1	E	A5	0
2	D	A4	1
3	C	N/A	2
4	B2	A3	3
5	B1	A2	4
6	A	A1	5

b. The Acute Hazard Value, HV(Acute):

HV(Acute) value is the hazard value assigned based upon the Short Term Exposure Limit (STEL) of the chemical. If a STEL exists, the "STEL" hazard value (HVstel) is 0.5. If a STEL does not exist, the (HVstel) is 0.0 (Purdue Research Foundation, 1997).

2. The exposure hazard value:

The routes of exposure hazard value are the sum of the vapour pressure hazard value, oral hazard value, skin hazard value and the dust/mist hazard value. These routes are described in the following four sections:

a. The Vapor Pressure Hazard Value HV(Vapor Pressure):

HV(Vapor Pressure) is based upon the vapor pressure of the chemical at 25° Celsius. The hazard values assigned are presented in Table (5.3):

Table (5.3): The Assigned Carcinogenic Hazard Values Based upon the ACGIH Ratings

No.	Vapor Pressure (torr)	HVvp
1	<0.076	0
2	≥0.076 but <0.76	1
3	≥0.76 but <7.6	2
4	≥7.6 but <76	3
5	≥76 but <760	4
6	≥760	5

b. The Oral Hazard Value, HV(Oral):

HV(Oral) is based upon whether or not the chemical can be absorbed through the mouth. Currently, only lead is scored as an oral hazard. If lead is in the chemical compound, the HVoral is 1.0. If lead is not in the chemical compound, the HVoral is 0.0.

c. The Skin Hazard Value, HV(Skin):

HV(Skin) is based upon whether or not the chemical can be absorbed through the skin. If it can be absorbed as defined by ACGIH, the HVskin is 0.5. If it cannot, the HVskin is 0.0.

d. The "Dust / Mist" Hazard Value,HV(D/M):

HV(D/M) is based upon the ability of the chemical to produce dusts or mists. For the gas conditions and boiling point less than 25^{o}C, HV(D/M) =0. HV(D/M) assigned values for solid and liquid conditions are presented in Table (5.4).

Table (5.4): Provisional Rules for Assigning Dust-Smoke-Mist Hazard Values*

	Conditions	
	SOLIDS	**HV(D/M)**
a.	Melting Point (MP) > 25°C, presumed solid at Standard Temperature & Pressure (STP), no note on TLV entry for dust	1.5
b.	TLV entry notes a value for "dust"	3.5
c.	If a chemical may be handled or used both as a solid dust and a sprayed solution of that solid (and neither "dust" or "mist" is present at its TLV entry), or is used in plating solutions and is capable of creating mist when heated or agitated, then it is given a combined score of (see Liquid category 3.)	3.0
d.	If the chemical's MP is close to 25°C; can exist either as liquid or solid at room temperature	2.0
e.	If a solid is entered in UTN list of compounds (using specific surrogates) only as a solution of soluble solid or characteristically used only as liquid solution	1.5
f.	If a solid tends to be present in airborne smoke particulates resulting from combustion, especially polycyclic aromatic hydrocarbons and chlorinated dibenzo-dioxins and furans	1.5
g.	Friable asbestos, all types	5.0
	LIQUIDS	**HV(D/M)**
a.	MP < 25°C, BP > 25°C, presumably liquid at STP, especially liquid inorganic acids and short-chain fatty acids, especially acetic acid, or alkalis or alkali solutions, presumed capable of creating mist, either when mechanically agitated or splashed or when heated, but no mention in TLV entry of "mist". Includes the gases hydrogen chloride,hydrogen bromide, hydrogen fluoride, hydrogen iodide, ammonia and hydrogen cyanide, which, when dissolved in water, are known respectively as hydrochloric acid, hydrobromic acid, hydrofluoric acid, hydroiodic acid, ammonium hydroxide.	1.5
b.	TLV entry notes a value for "mist"	3.5
c.	MP > 25°C, presumed solid at STP. No note on TLV entry for dust, but may be handled, sprayed or used as solution, in characteristic use usually a pesticide, herbicide or surface spray operation (see Solid, category 3.)	1.5

*© Purdue Research Foundation, 1997

3. The safety hazard value, HV(safety):

The safety hazard value will be the sum of the flammability hazard value, the reactivity hazard value and the corrosivity hazard value. These routes of safety hazard are described by the National Fire Protection Association (NFPA) except corrosivity hazard which is defined by the U. S. Department of Transportation (DOT).

a. <u>The flammability hazard value, HV(Flammability) and the reactivity hazard value, HV(Reactivity):</u>

HV(Flammability)is based upon the flammability of a chemical and HV(Reactivity) is based upon the reactivity of the chemical and both are defined by NFPA as the shown in Table (5.5).

Table (5.5): The Values HV(Flammability) and HV(Reactivity) the Same as that Given by NFPA

No.	NFPA	HVFlammability	HVReactivity
1	0	0.0	0.0
2	1	1.0	1.0
3	2	2.0	2.0
4	3	3.0	3.0
5	4	4.0	4.0

b. The corrosivity hazard value, HV(Corrosivity):

HV(Corrosivity) is based upon the corrosivity of the chemical as defined by DOT. The hazard values are presented in Table (5.6):

Table (5.6): The values of HV(Corrosivity) of Chemical as Defined by DOT

No.	U.S.DOT Classification	HVCorrosivity
1	None	0.0
2	III	2.0
3	II	3.0
4	I	4.0

Accordingly**,** the components of the worker exposure hazard value, HV(Worker Exposure) are:

1. HV(Health) = HV(Chronic)+HV(Acute)

2. HV(Exposure) = HV(Vapor Pressure)+HV(Oral)+HV(Skin)+HV(D/M)

3. HV(Safety) = HV(Flammability) + HV(Reactivity) + HV(Corrosivity)

Therefore, the final Worker Exposure algorithm is:

HV(Worker Exposure) = HV(Health)*HV(Exposure)+2*HV(Safety) (5.3)

The safety hazard value, HV(Safety) is multiplied by 2 as a weighting factor. IRCHS team multiplied the score for the sum of safety terms by coefficient of 2.0 to give adequate weight to workers safety, relative to worker health as presented by the score of the health product. As we can see in Equation (5.3), that the score of health is the sum of HV(Health) times HV(Exposure).

5.3.3 The Combined Index

The two hazard values are combined and the average of the two becomes the combined hazard value of the chemical. The final combined algorithm is:

Total hazard value = (normalized HV(Environmnetal Hazard) + normalized HV(Worker exposure))/2 (5.4)

or:

Total hazard value =[(HVWater+HVAir+HVLand+HVGlobal)/3.5 + (1.15) x (HVHealthxHVExposure+HVSafety)]/2 (5.5)

Illustrating the IRCHS algorithms does not mean that the assigned values have to be calculated, because IRCHS prepare data for many chemicals and the hazard values are on Clean Manufacturing Technology Institute CMTI's website, www.ecn.purdue.edu/CMTI. IRCHS total score are the only score that integrate concerns about ecological and occupational human health impacts into a combined score. This insures that chemicals that pose low human health hazard, for example, remain priorities if they pose high ecological hazards. The component of the total hazard value include a wide variety of measures relating to a chemical's toxicity and physical-chemical properties such as vapour pressure, tendency to bioaccumulate, corrosivity and so on. Moreover, simplicity, which is a perfect IRCHS facility, that when there is a mixture of chemicals, the algorithm does not take into account any benefits or detriments gained by the mixture. It simply multiplies the hazard value of

each component by percentage of that component, and then adds the scores for the final hazard value of the mixture. Previous advantages and facilities to the IRCHS, in addition to the huge number of the chemicals included in this data base, lead us to consider IRCHS the one of the best index that can be used for the evaluation of negative effects chemical's hazard toward environment.

Because of the illustrated simplicity and facilities, we will use the IRCHS to form the Environmental Risk Index (ERI) for the chemical process routes. As illustrated before, petrochemical industry can be expressed as a network that consists of many chemical process routes, in which each route is a specific chemical process with certain chemicals. In our work we will use the IRCHS to evaluate the environmental risk of the chemicals in the chemical process separately. These values will be used to calculate the Environmental Risk Index (ERI) for each chemical process route in the network of the petrochemical industry. ERI index and the safety index, that is related to the environmental incidents which was formulated by (Al-Sharrah, 2007), in addition to the chemical process routes added-value will be used in the multiobjective treatment of the modelling and planning of the petrochemical industry under environmental constrains.

CHAPTER 6

A PETROCHEMICAL INDUSTRY MODEL WITH THE PROPOSED ENVIRONMENTAL ASSESSMENT

The petrochemical industry is a large complex of processes and chemicals which are defined as a sector of the global chemical industry. Petrochemicals are chemicals that are made from feedstocks, which are derived from petroleum, coal, and natural gas. Examples of such feedstocks are ethane, propane, naphtha, and toluene. The end products of this industry are mainly plastics, resins fibres, and rubbers. Many of these end products are further processed by other sectors of the chemical industry and end up as daily consumable products. Besides the feedstocks and the end products, there are also intermediate products; these might also be end products in themselves, because there is a demand for them in other sectors of the chemical industry. Chemicals such as these are phenol, styrene, propylene and acrylonitrile. Modelling a petrochemical industry has to take into account the relationship between the chemicals and their sources and destinations. The petrochemical model in this work is an optimization model composed of constraints and objective function(s) under some assumptions. It is an extension and a

modification to the model proposed by Al-Sharrah et al. (2006) with the main model assumptions as follows:

1. The petrochemical network is constructed from plants each containing a number of processes achieving a main chemical transformation between the feedstock and the product.
2. The plant inventory of chemicals is mainly in the storage section. Equipment inventory is assumed much smaller than storage inventory and hence can be neglected in the calculation of risk of chemical release.
3. A number of intermediate chemicals are produced and then totally consumed in the petrochemical network; their net production rate is zero.

6.1 Model Constraints

Let:

N be the number of chemicals involved in the operation of M plants,

X_j be the annual level of production of plant j,

Q_i be the annual amount produced of chemical i,

F_i be the annual amount of chemical i used as a feedstock, and

o_{ij} be the output coefficient of chemical i from plant j.

The main constraints that govern the operation of the petrochemical network are the material balance constraints:

$$F_i + \sum_{j=1}^{M} o_{ij} X_j = Q_i \qquad i = 1,2,\cdots,N \qquad (6.1)$$

These constraints ensure that the total quantity produced of each material ***i*** is equal to the sum of all the amounts produced by all the plants plus its quantity as a feedstock. For all the intermediate chemicals, $\boldsymbol{Q_i}$ will be set to zero because no output of these chemicals is required from the desired petrochemical network. This constraint applies only to the main chemicals in the plant, not secondary feedstocks or by-products.

The final products in the planned petrochemical industry will be governed by their demands in the petrochemical market, according to the country's share in that market. Constraints on $\boldsymbol{Q_i}$ for all final products are needed and they are formulated as:

$$Q_i \leq D_i\ U \qquad i \in I_1 \qquad (6.2)$$

Where $\boldsymbol{D_i}$ is the world demand for chemical ***i*** and it is multiplied by the upper limit of country's share in the petrochemical market, ***U***. The above constraint is only applied for final products group $\boldsymbol{I_1}$.

Introducing the binary variables $\boldsymbol{Y_j}$ for each plant ***j*** will help in the selection requirement of the planning procedure. $\boldsymbol{Y_j}$ will be equal to 1 only if plant ***j*** is selected and zero if plant ***j*** is not selected. If plant ***j*** is selected, the production level must be

at least equal to the minimum economic capacity B_j, therefore, for each plant j the following constraint is used:

$$B_j Y_j \leq X_j \leq H Y_j \qquad j = 1,2,\cdots,M \qquad (6.3)$$

where, H is a valid upper bound on production rates applicable to all plants.

The proposed improvement of Kuwait's petrochemical industry is directed towards building new plants to produce petrochemicals, so it is logical that only one plant should be selected to produce a single chemical. Then the following constraint is included for each chemical:

$$\sum Y_j \leq 1 \qquad j \in J_1 \qquad (6.4)$$

where, J_1 is the group of plants that produces a single chemical. This constraint ensures that a maximum of one plant is selected from each group. For final products:

$$\sum Y_j = P \qquad j \in J_2 \qquad (6.5)$$

where, P is the number of final products selected from the proposed list of products, and J_2 is the group of all plants that produce a final product.

The supply of feedstock limitations will impose additional constraints on the selection and planning, i.e.:

$$F_i \leq S_i \qquad i \in I_2 \tag{6.6}$$

where, S_i is the supply availability of feed chemical i. The feedstock F_i is a function of the optimization variable X_i while the supply S_i is a deterministic input parameter to the model. The above constraint only applies for some feedstock chemicals represented by the group I_2. Not all the feedstock chemicals are included in I_2 because some are additives and some are needed in small quantities. Also, some petroleum-rich countries have few (if any) limitations on petroleum feedstocks.

An additional economic constraint is required for the limit on the investment budget. If cap_j is the capital investment cost for constructing plant j and Bg is the available budget, then the constraint is formulated as:

$$\sum_{j=1}^{M} cap_j \times Y_j \leq Bg \tag{6.7}$$

6.2 Model Objective Functions

Three objective functions are formulated in this study: an economic objective environmental risk objective and safety objective. For simplicity, the economic objective function is a maximum economical gain in the selected plants. The economical gain is represented by the overall added-value; it is the price of final products minus the cost of feedstocks for the petrochemical network. If C_i is the price (or cost) of chemical i, the added-value objective function will be represented by Equation (6.8):

$$\max \quad f_1 = \sum_{j}^{M} \sum_{i}^{N} o_{ij} C_i X_j \qquad (6.8)$$

Note that the output coefficient o_{ij} of chemical i from plant j will be positive for chemicals produced and negative for chemicals consumed.

There is no one standard calculation form for the added-value, but the usual basis is the difference between sales income and cost of goods and bought in services. What should be and what should not be included in the calculation can be argued at length and largely depends on the purpose for which the data are to be used and by whom. Considering the nature and the size of the petrochemical network, the simplest measure possible for the added-value should be used, provided there is a clear indication, in that form, to the success of the industry.

The second objective function is formulated starting from the safety index ***K*** developed by Al-Sharrah et al. (2007) and discussed previously in chapter 4, the index was:

$$\boldsymbol{K} = Freq \times Haz \times Inv \times Size$$

where,

Freq = Frequency of accidents, number of accidents per process per year

Haz = Hazardous effect of a chemical, number of people affected per tonne of chemical released

Inv = Inventory of chemical released, tonne per accident

Size = Size of plant, number of major processes in plant

This gives an overall unit of the index ***K*** as number of people affected per year, and it represents the maximum number of people affected if an accident caused the release of all the plant inventory of a chemical. People affected include fatalities, people injured and hospitalized. The plant is assumed to have major processes in which a major chemical is being treated and an accident in any part of the plant may cause, in an extreme case, the release of the plant inventory.

Each plant in the petrochemical network was investigated to identify the chemicals associated with production. The three terms (*Freq*, *Haz*, and *Size*) of the index ***K***, were calculated for each chemical in the plant, leaving the inventory (*Inv*) as a function of production (one month of production, or $\boldsymbol{X_j}$ divided by 12). This

represents a maximum inventory in a plant to calculate a representative maximum risk. The overall plant index was the summation of all plant chemicals indices, and the safety objective is formulated as:

$$\min\ f_2 = \sum_{j}^{M}\sum_{i}^{N} o_{ij}\left(Freq_i \times Haz_i \times Size_{ij} \times \frac{X_j}{12} \right) \tag{6.9}$$

This safety objective is minimized since it represents the risk to the people from chemical accidents.

The third objective function is formulated starting from the IRCHS environmental objective discussed previously in chapter 5, the index was:

Total hazard value = (normalized HV(Environmnetal Hazard) + normalized HV(Worker exposure))/2 (6.10)

Each plant in the petrochemical network was investigated to identify the chemicals associated with production. The environmental index was calculated for each chemical in the plant. The overall plant index was the summation of all plant chemicals indices multiplied by the production rate. Therefore, plant environmental risk index (ERI_j) is:

$$ERI_j = \sum_{i}^{N} o_{ij}\ IRCHS_i \tag{6.11}$$

And the environmental risk objective is formulated as:

$$\min \quad f_3 = \sum_{j}^{M} \sum_{i}^{N} o_{ij} \left(IRCHS_{\ i} \times X_{\ j} \right) \tag{6.12}$$

The three objectives, minimize environmental risk and safety, and maximize economic gain, are usually in conflict with one another; some valuable final products of resins and plastics need very hazardous chemicals for production. For example, Acrylonitrile Butadiene Styrene (ABS) resins needs acrylonitrile, which is very hazardous. Therefore, it is not possible, in many situations, to reduce the industrial risk without any decrease in economic gain. Therefore, one has to use multiple objectives techniques to reach a certain trade-off between them. Overall, the model described above is in the form of a Deterministic, Mixed Integer Linear Programming (MILP) model with Multiple Objectives (MO). This form of model will provide a strong planning and process selection tool. Deterministic means that all variables should be assigned a known value with no probability in their evaluation; Mixed Integer means that some variables are integer and some are continuous, Linear means that the model has linear constraints and linear objectives and finally, Multiple Objectives means having more than one objective function. The model will stay linear if all objectives are combined in a linear form.

6.3 Model Data: Planning for Kuwait Industry (Case study)

Data collection is, as always, a major difficulty with large industrial projects. Much of it simply does not exist, or is not known. The time spent dealing with parameter data was a considerable part of this work's effort. In situations where data was scarce, best estimates were used indiscriminately. This proved to be an acceptable practice for two reasons. First, it is almost impossible to begin to structure the model without any data whatsoever, thus these numbers aided the early formulations of the model. Second, they could easily be changed after the model was up and running.

To construct the petrochemical network, first, the desired final products were defined and they are listed in Table (6.1) with the classification of Primary Final product (PF). These products were discussed in detail in chapter 3 as the proposed final products for the development of Kuwait's petrochemical industry. The routes from the available basic feedstocks to the final product chemicals were determined by selecting a number of manufacturing plants and considering all the possible alternatives for producing these desired products. At the end, a network of 62 plants, linking the production and consumption of 51 chemicals, was formed; plants included in the model are listed in Appendix (A.1).

The chemicals that constitute the model are listed, numbered and classified according to their potential function in Table (6.1). The potential function of a chemical is determined assuming Primary Raw material (PR), Secondary Raw

material (SR), Intermediate (products and feedstocks) (I), Primary Final product (PF), and Secondary Final product (SF). Primary raw materials are chemicals derived from petroleum and natural gas and form the basic feedstocks of the plant, whereas the secondary raw materials represent chemicals that are needed as additives or needed in small quantities. The intermediate chemicals are the chemicals that are produced and then consumed in the petrochemical network. Finally, the final products are also classified as primary and secondary. The primary products are the selected final products produced for the country's development and the secondary are by-products associated with the plants in the network. There are 51 chemicals included in the petrochemical model; of these, 13 are only secondary raw materials and secondary final products, which will not take part in the model constraints due to their small quantities. There are 18 intermediates, being both produced and consumed by the model, and 5 end products (primary final products). Primary raw materials constitute 15 chemicals, of which 3 have limited supplies from Kuwait's petroleum sources and they are ammonia, chlorine and naphtha.

Plants included in the model form a network shown in a simple form in Figure (6.1) with each plant assigned an index ***j***. Not all the chemicals needed in the development are assigned a production plant, only chemicals that are needed in a considerable amount and which represent major intermediates, not additives or catalysts. The chemicals that are needed in small quantities would be purchased to satisfy their demand in the network.

Some plants included in the model may be old or not used in the current industry, but they were included to give a general model of the industry. Aresta et al. (1999) studied two alternatives for environmental assessment of synthetic processes with one of these not being applied at the industrial level. Their justification was that, although the process is not implemented on an industrial scale, it is fascinating from the environmental point of view and can be extended to other feedstocks. Therefore, in the model proposed, all plant alternatives were taken into consideration.

Table (6.1): A List of Chemicals Included in the Model

PR= primary raw material, SR= secondary raw material, I= intermediate, PF= primary final product, SF= secondary final product.

Chemical	Function	Chemical	Function
1. Acetaldehyde	SF+I	27. Hydrogen cyanide	I
2. Acetic acid	I	28. Methane	PR+SF
3. Acetylene	I	29. Methanol	I
4. Acrylonitrile	I	30. Naphtha	PR
5. Acrylonitrile butadiene styrene	PF	31. N-Butane	PR
		32. N-Butylenes(1-and2-)	PR
6. Ammonia	PR	33. Polybutadiene rubber	SR
7. Benzene	SF+I	34. Polystyrene (crystal grade)	PF
8. Butadiene	I		
9. Butenes –Mixed n-, iso, dienes, ...	SF	35. Polyvinyl alcohol	SR
		36. Polyvinyl chloride	PF
10. C-4 fraction (mixed butanes, -enes, …)	SF+PR	37. Propane	SF+PR
		38. Propylene (chemical grade)	SF+I
11. Carbon dioxide	SR		
12. Carbon monoxide	I	39. Propylene (refinery grade)	PR
13. Chlorine	PR		
14. Coke	PR	40. Propylene oxide	SF
15. Cumene	PF	41. Sodium hydroxide	SR
16. Ethane	PR	42. Styrene	I
17. Ethanol	I	43. Sulfuric acid	I
18. Ethyl benzene	I	44. Sulfur	PR
19. Ethylene	SF+I	45. Synthesis gas 3:1	I
20. Ethylene dichloride	I	46. Synthesis gas 2:1	SF
21. Formic acid	SF	47. Toluene	PR+SF
22. Fuel gas	SF	48. Vinyl acetate monomer	PF
23. Fuel oil	SF+PR	49. Vinyl chloride	I
24. Gas oil	PR	50. Xylene (mixed)	SF
25. Gasoline	SF		
26. Hydrogen	SR+SF		

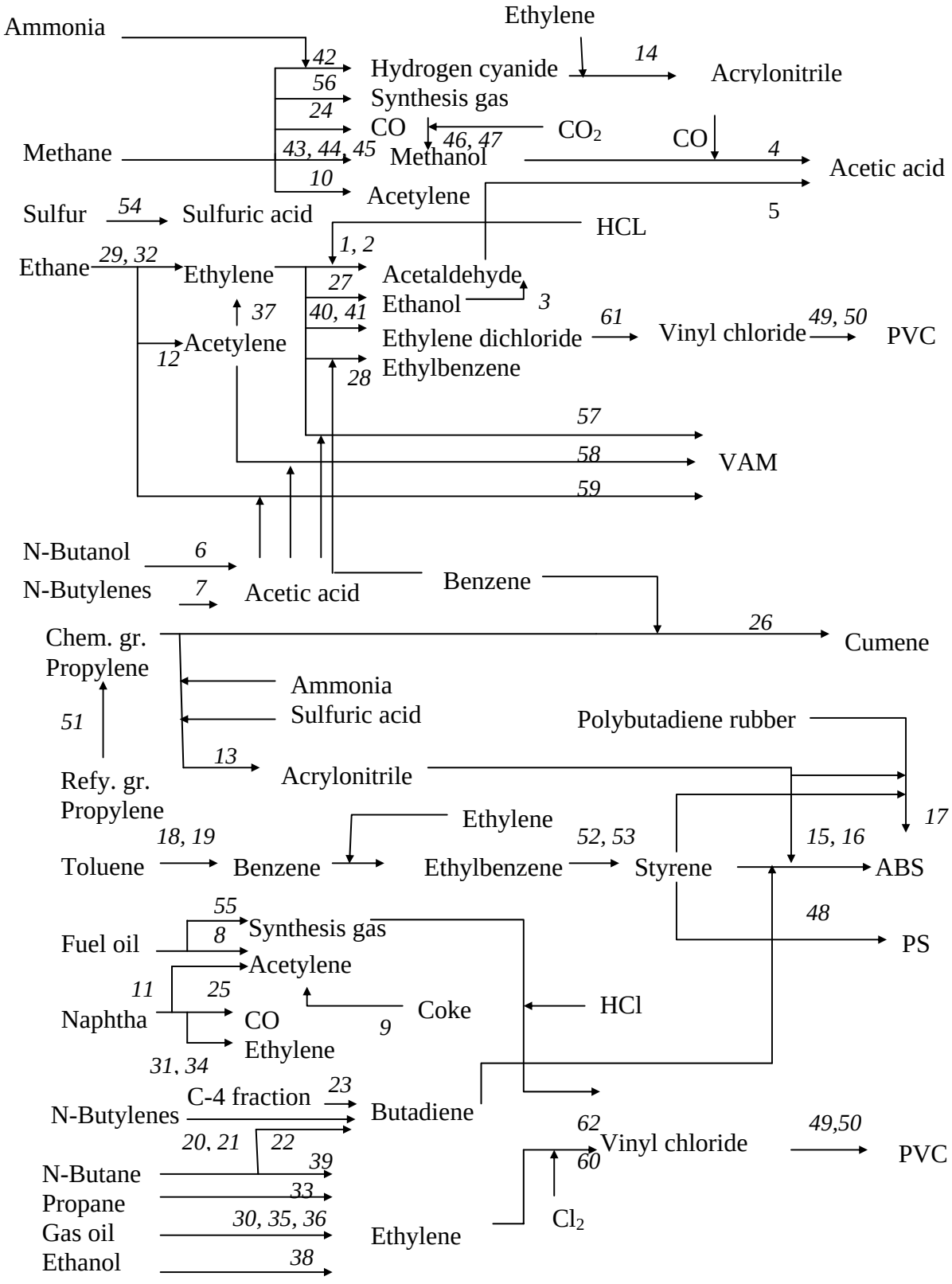

Figure (6.1): A Simplified Network of the Plants and Chemicals in the Model (numbers on the figure correspond to plants listed in Appendix A)

The heart of the model is the material balance constraints. Hence, estimation of the output coefficients, o_{ij}, is a key step in constructing the model. For this purpose, yield data for each chemical transformation is required. In many cases, plant yields are variable and depend on what product mix is desired or on what capital expenditure can be afforded. The model uses average yields reported at commercial installations and were taken from Stanford Research Institute (SRI) reports (1992).

The supply of feedstock and demand for final products are needed to complete the construction of the model constraint set. Supply and demand data were taken from different sources mainly from recent SRI reports and Kuwait's Petrochemical Industries Company (PIC) annual reports. Table (6.2) shows the values for the supply and demand.

Table (6.2): Supply and Demand Data.

Feedstock Chemical	**Supply (10^3 tonne/year)**	**Final Product Chemical**	**Demand (10^3 tonne/year)**
Ammonia	575	ABS	20,000
Chlorine	16	Cumene	7,217
Naphtha	2,500	Polystyrene (Crystal Grade)	4,000
		Polyvinyl Chloride	6,803
		Vinyl Acetate Monomer	4,000

The constraint on the final products demand, Equation (6.2), uses a value for Kuwait's share in the petrochemical market. An overview of Kuwait's exports of some chemicals like methanol and fertilizers have shown that Kuwait's share is roughly 1% of the total world petrochemical market. However, Al-Sharrah et al. (2001) recommended that, after development, Kuwait must increase its share in the petrochemical market to at least 4%, to get a good economical utilization of the industry and its products. Therefore, $\boldsymbol{U}$ in Equation (6.2) was assigned the value of 4%. The next constraint, Equation (6.3), needs minimum economic production rates $\boldsymbol{B_j}$. These values were taken for all technologies in the models from SRI reports (1992). In the constraint, $\boldsymbol{H}$ is a valid upper limit for production rates $\boldsymbol{X_j}$. The importance of assigning a reasonable value for $\boldsymbol{H}$ came from its effect on the model solution. A low value for $\boldsymbol{H}$ resulted in excluding some good high production rates from the model solution. A high value for $\boldsymbol{H}$ will result in increasing the solution space and hence, the model will display greater computational difficulties.

The $\boldsymbol{P}$ in Equation (6.5) is the number of final products needed to be selected from a set of proposed final products. For this study, we have a case for selecting three products and therefore, $\boldsymbol{P}$ was assigned the value of three. The fixed capital for Equation (6.7) was estimated from SRI reports (1992) and updated to the current year using a plant cost index. The available budget was taken from the PIC annual report (2003/2004).

Data needed for the economic objective function in the model are prices of final products and cost of main feedstocks. Table (A.4) lists the price data. For the safety objective, data sources were discussed in Chapter 4. The list for the safety index that is used in the model listed in Table (A.3).The environmental risk index data base source was presented and discussed in chapter 5. The IRCHS and ERI indices are listed in Table (A.2). Most of the model data are listed with each technology in Appendix A.

6.4 Model Solution

The final form of the model is a MILP model with 70 continuous variables, 62 binary variables, 185 constraints and three objectives forming a moderately sized model. While binary variables are very useful in the model formulation, it is at a cost; computing time becomes very long. The complexity of the problem grows exponentially as the number of binary decision variables increase linearly. This situation can produce an intractable or unsolvable problem, even in a moderately sized model formulation. This is where a specialized solver algorithm is employed that can iterate to a near optimal solution in much less time by using algorithms and techniques to check only a small portion of the total problem.

When dealing with a model formulation of this complexity, the only option for solving it is the use of a computer. With the computing power available on a desktop PC, it is now a reality that a problem of this type can be solved conveniently. The petrochemical MILP model was solved using the commercial

optimization package GAMS (Brook et al., 1992); the acronym stands for General Algebraic Modelling System. A sample GAMS output is listed in Appendix B. The GAMS itself does not solve the model, but passes it to one of a number of separate solvers according to the selection of the modeller and the model type. The solver used mostly in this work was CPLEX; it is an optimization solver used for linear, network, integer programming, and mixed integer programming. It was originally developed by Robert E. Bixby and sold via CPLEX optimization Inc., which was bought by ILOG, Inc. in 1997.

CPLEX uses a branch-and-bond approach for problems containing integer variables. The optimization algorithm maintains a hierarchy of related linear programming sub-problems, known collectively as a *search tree*. At each node on the search tree, a sub-problem is created and evaluated using the branch-and-bond solving algorithm. This approach can create many combinations of sub-problems but the CPLEX algorithm employs a search mechanism that passes over (rejects) many of the sub-optimal solutions. It is extremely time consuming for the solver to check every possible sub-problem solution, so it uses algorithms and techniques such as cuts, heuristics and a variety of branching and node selection strategies that gains a very near optimal solution to the overall problem.

The three objective functions were tested with the model separately. The model was solved using a single objective function to get the industry bounding structure. Next the three objectives were combined and the model was solved.

Overall, the model solution gave the selected final products (three out of five chemicals), the corresponding petrochemical network of plants from the basic feedstocks to final products and plants production rates. The tables below show the results for different solution methods and indicate four values from the solution: the rejected final product chemical; the value of the economics the value of environmental risk and the safety. Note that the number of final products for the development of the petrochemical industry is five, but it is only desired to select three, i.e. to reject two chemical.

6.4.1 Solution with a Single Objective

1. The objective value and the rejected chemicals using single objective function for the petrochemical model:

a. Economic objective

The model was solved with a single economic objective, which is the plants added valued, using current prices as indicated in Equation (6.8). The objective function was maximized and the results are shown in Table (6.3) with the corresponding safety and environmental indices.

Table (6.3): Results with Single Economic Objective

Rejected Chemicals	Economic Objective (10^4 $/yr)	Corresponding Safety (people affected/yr)	Corresponding Environmental Index (IRCHS)
• Cumene • Polystyrene	**127,452**	32,154	373,625

b. Safety objective

The model was solved with a single safety objective. The objective is the safety index which was discussed in previous chapters as indicated in Equation (6.9). The objective function was minimized and the results are shown in Table (6.4) with the corresponding economics and the corresponding environmental risk index.

Table (6.4): Results with Single Safety Objective

Rejected Chemicals	Safety Objective (people affected/yr)	Corresponding Economics (10^4 $/yr)	Corresponding Environmental Index (IRCHS)
• ABS • PVC	**1,406**	11,958	54,678

c. Environmental objective

The model was solved with a single environmental objective; the objective uses the IRCHS indices. The objective was minimized and the results are shown in Table (6.5) with the corresponding economics, calculated using current prices, and the corresponding safety index.

Table (6.5): Results with Single Environmental Risk Objective

Rejected Chemicals	Environmental Objective Index (IRCHS)	Corresponding Safety (people affected/yr)	Corresponding Economics (10^4 $/yr)
• ABS • PVC	**50,859**	1,436	19,852

2. The recommended plants using single objective function for the petrochemical model:

a. Economic objective

Table (6.6): Plants Recommended by the Economical Objective Function of the Petrochemical Model*

Plant Index, ***j***	Plant	Production Rate (10^3 tonne/yr)
1	Acetaldehyde by one step oxidation from ethylene	88.3
5	Acetic acid by air oxidation of acetaldehyde	115.2
10	Acetylene by Pyrolysis of methane (partial oxidation)	624.3
14	Acrylonitrile by the cyanation/oxidation of ethylene	176
17	ABS by bulk/suspension polymerization	800
18	Benzene by the hydrodealkylation of toluene	438.2
28	Ethylbenzene by the alkylation of benzene	615.3
37	Ethylene by hydrogenation of acetylene	415.7
42	Hydrogen cyanide by the ammoxidatin of methane	105.6
49	(PVC) Polyvinyl chloride by bulk polymerization	272.2
52	Styrene by dehydrogenation of ethylbenzene	536
58	Vinyl acetate by reaction of acetylene and acetic acid	160
62	Vinyl chloride by the hydrochlorination of acetylene	279

*Shaded rows present the selected final products in the model solution

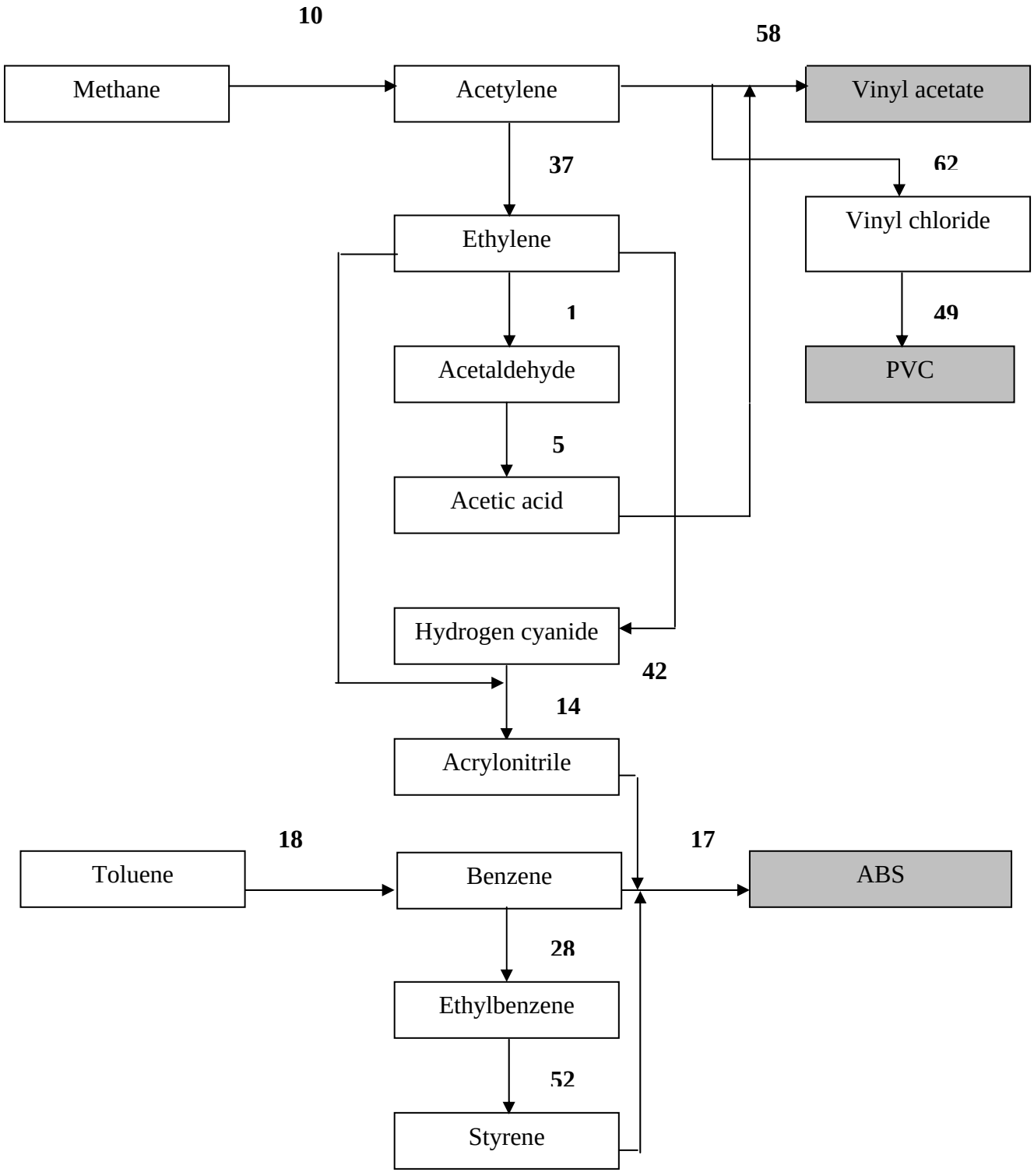

Figure (6.2): The Planned Petrochemical Network from Basic Feedstock to Final Product Chemicals (numbers indicate plant indices) Based on Economical Objective Function. (*Shaded boxes are the final products were selected in the model solution).

b. Safety objective

Table (6.7): Plants Recommended by the Safety Objective Function of the Petrochemical Model

Plant Index, *j*	**Plant**	**Production Rate (10^3 tonne/yr)**
1	Acetaldehyde by one step oxidation from ethylene	67.5
5	Acetic acid by air oxidation of acetaldehyde	88.1
9	Acetylene by hydration of calcium carbide	39.2
18	Benzene by the hydrodealkylation of toluene	121.9
26	Cumene by the reaction of benzene and propylene	83.9
28	Ethylbenzene by the alkylation of benzene	91.8
33	Ethylene by pyrolysis of propane	113.4
48	Polystyrene (crystal grade) by bulk polymerization	78.4
52	Styrene by dehydrogenation of ethylbenzene	80
58	Vinyl acetate by reaction of acetylene and acetic acid	122.4

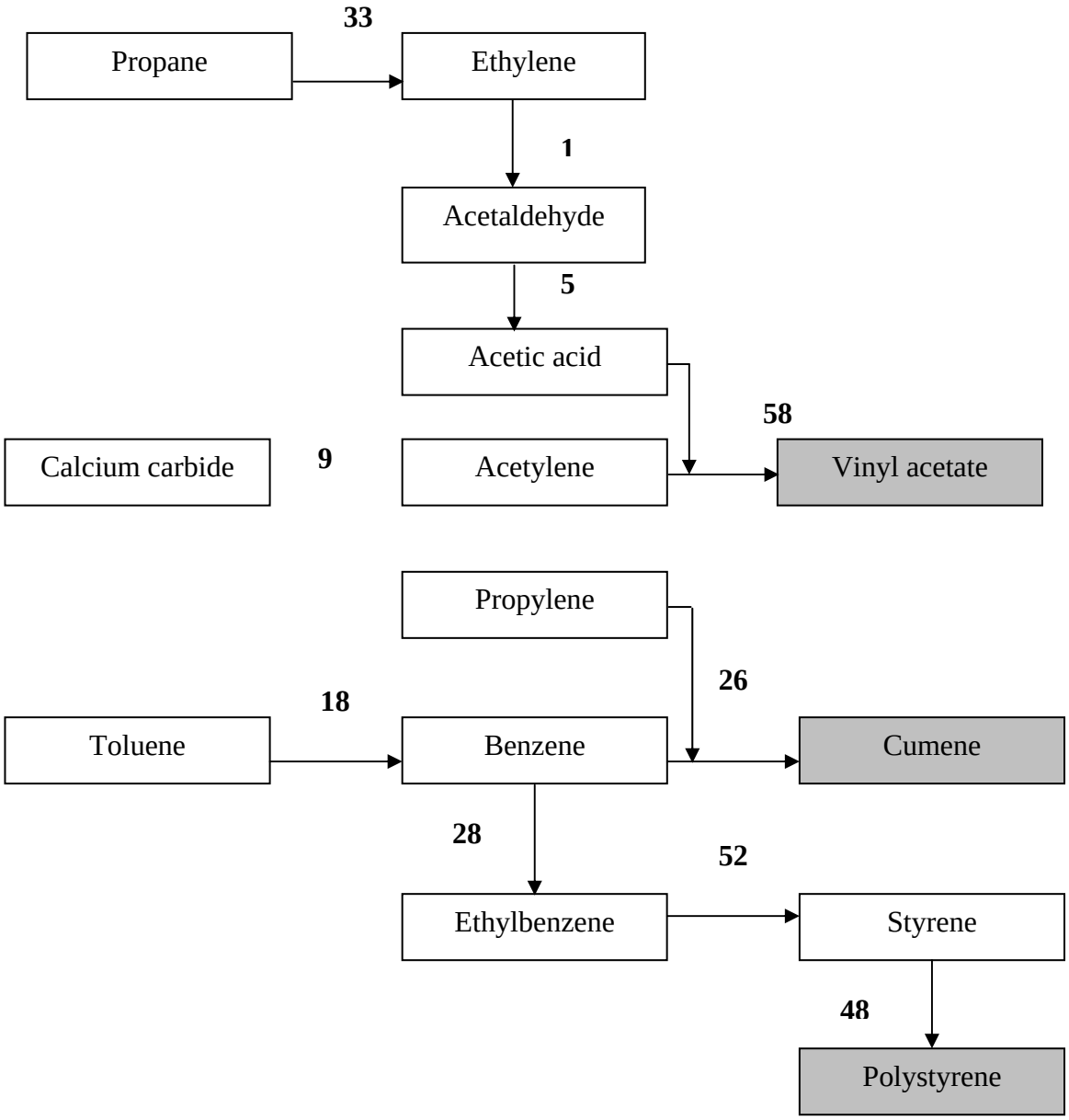

Figure (6.3): The Planned Petrochemical Network from Basic Feedstock to Final Product Chemicals (numbers indicate plant indices) Based on Safety Objective Function.

c. Environmental objective

Table (6.8): Plants Recommended by the Environmental Objective Function of the Petrochemical Model

Plant Index, *j*	**Plant**	**Production Rate (10^3 tonne/yr)**
2	Acetaldehyde by two oxidation from ethylene	87.7
5	Acetic acid by air oxidation of acetaldehyde	106.1
18	Benzene by the hydrodealkylation of toluene	105.8
26	Cumene by the reaction of benzene and propylene	60
28	Ethylbenzene by the alkylation of benzene	91.8
33	Ethylene by pyrolysis of propane	81
48	Polystyrene (crystal grade) by bulk polymerization	78.4
52	Styrene by dehydrogenation of ethylbenzene	80
59	Vinyl acetate by the reaction of ethane and acetic acid	139.6

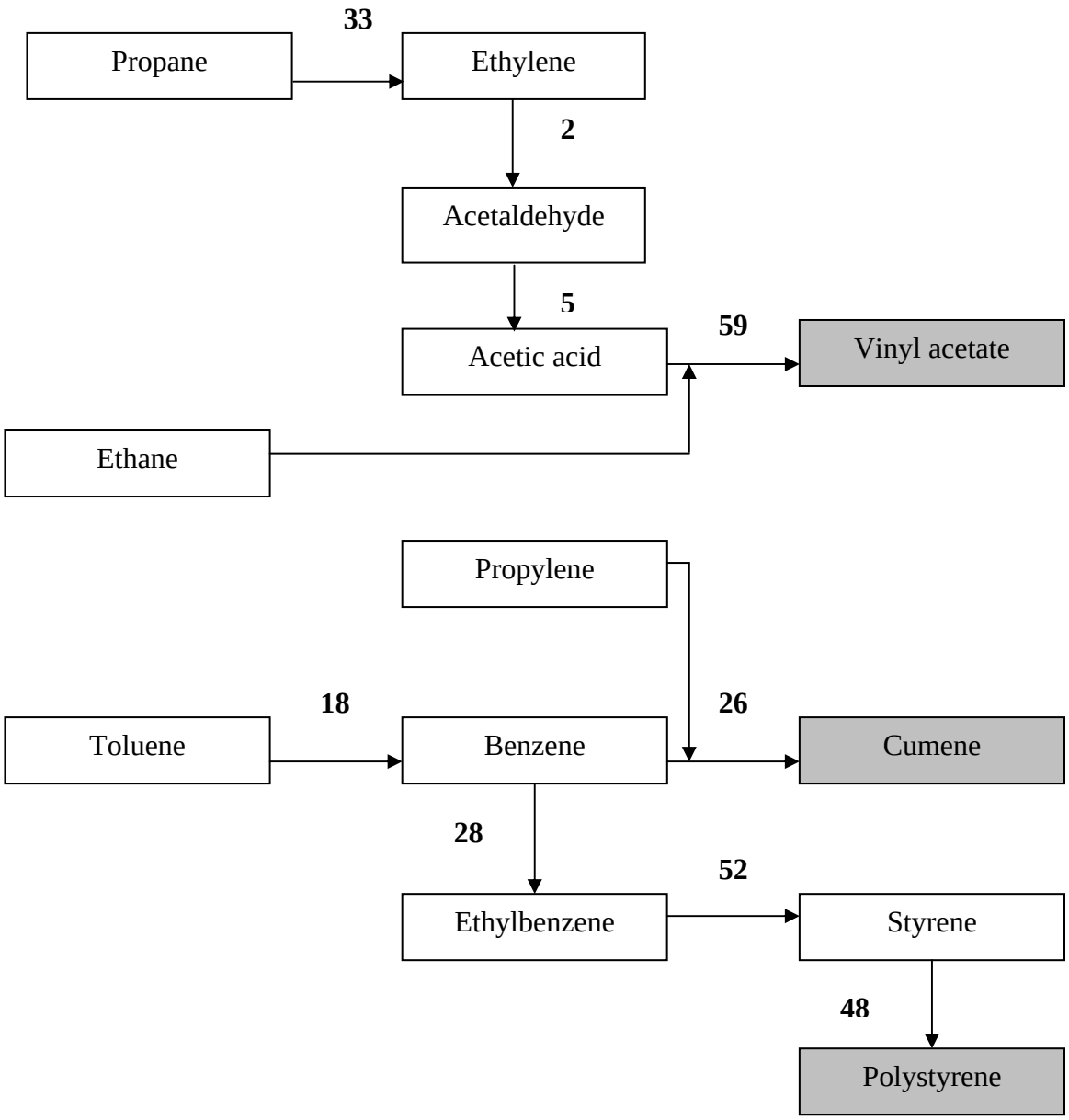

Figure (6.4): The Planned Petrochemical Network from Basic Feedstock to Final Product Chemicals (numbers indicate plant indices) Based on Environmental Objective Function.

6.4.2 Solution with Multiple Objectives

The model was solved with multiobjective method; the objective function has the form:

$$Min. \quad f = -\sum_j \frac{ADD_j}{ADD^*} X_j + \sum_j \frac{SI_j}{SI^*} X_j + \sum_j \frac{ERI_j}{ERI^*} X_j \tag{6.13}$$

where, ADD_j , SI_j and ERI_j are the economic, safety, and environmental indices for plant j calculated similar to Equation (6.11) and ADD^*, SI^* and ERI^* are the corresponding highest indices values for normalization. The indices are normalized using the highest index value to solve the incommensurable formats and units in the objectives. Results are shown below.

Table (6.9): Results with Multiobjective Functions

Rejected Chemical	Economics (10^4 $/yr)	Safety (people affected/yr)	Environmental Index (IRCHS)
• ABS • Polystyrene	35,479	1,734	85,877

Table (6.10): Plants Recommended by the Mulriobjective Solution of the Petrochemical Model

Plant Index, *j*	**Plant**	**Production Rate (10^3 tonne/yr)**
6	Acetic Acid by oxidation of N-butanol	122
12	Acetylene by the pyrolysis of ethane	447
18	Benzene by the hydrodealkylation of toluene	633
26	Cumene by the reaction of benzene and propylene	289
49	(PVC) Polyvinyl chloride by bulk polymerization	272
51	Propylene (chemical grade) from propylene refinery grade	109
57	Vinyl acetate by the reaction of ethylene and acetic acid	160
62	Vinyl chloride by the hydrochlorination of acetylene	279

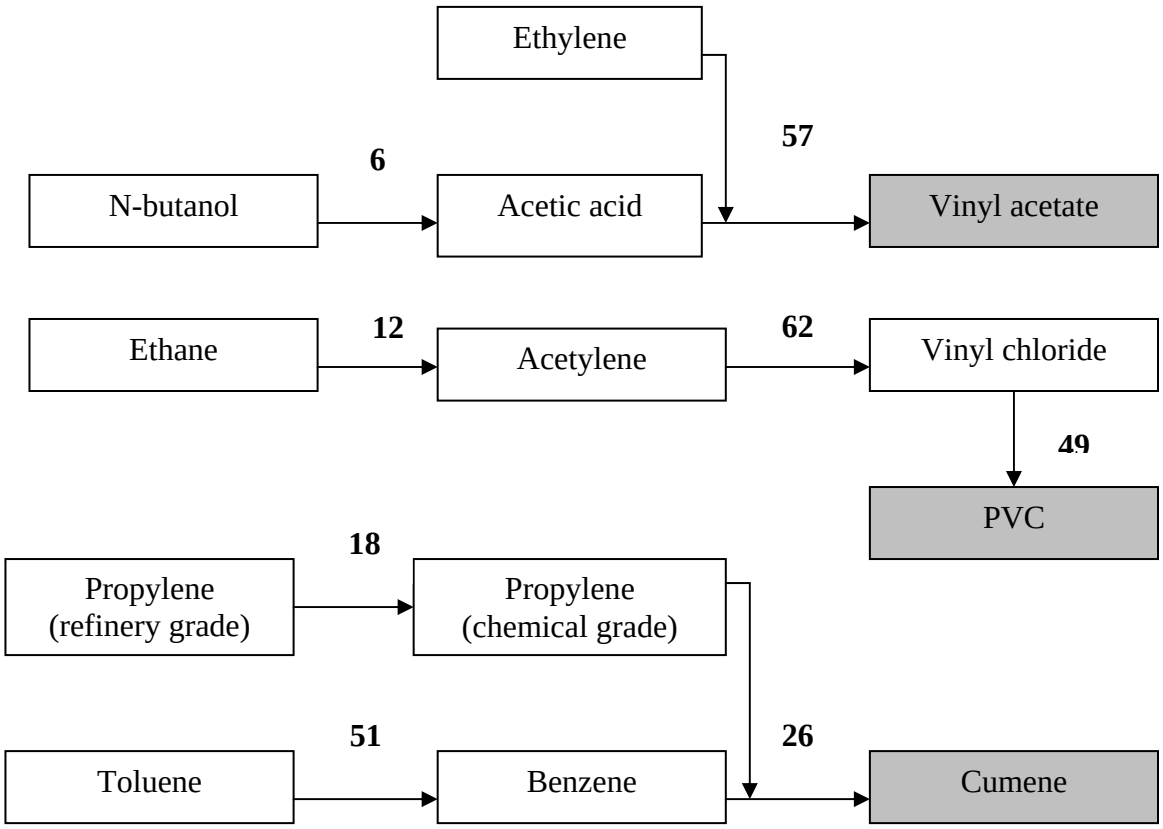

Figure (6.5): The Planned Petrochemical Network from Basic Feedstock to Final Product Chemicals Based on Multiobjective Function (numbers indicate plant indices).

6.5 Results Interpretation

Starting with single objective functions applied in the MILP model for the data related Kuwait petrochemical industry. For the economic objective, Table (6.3), presents the value of the objective, the corresponding values of the safety index and environmental risk index. Also it presents the two rejected final products, since the planning strategy of the petrochemical industry is based on producing three out of five final products. The selected chemical process routes and the three final products are represented in a more understandable way in Table (6.6) and Figure (6.2).

It can be observed that the value of the economical profit is extremely high, but at the same time the value of the corresponding safety and the environmental risk indices are also high. The selection of chemical process routes for planning a petrochemical industry was based on the economical factor only; the selected routes will be the one that leads to the highest possible profit, whatever the other factors. The model will not necessarily include the safer chemicals or even the less locally or globally environmental hazardous. Consequently, the corresponding safety and environmental risk indices were very high. Knowing that the environmental index represents the environmental risk of the whole petrochemical industry under planning and it considers each chemical in each chemical process route, the industry must expect negative environmental impacts on air, soil, water and on worker in the media of the plants. Also the corresponding safety index is very high and it implies that more than 32,000 people per year maybe affected from an incidental accident that can

happen in the petrochemical network and this includes people hospitalized, injured or dead.

Table (6.4) presents the results when the model was solved with a single safety objective. It shows the value of the safety objective function and the corresponding economics and the environmental index. When safety objective was used in the model to select chemical process routes, the value of the safety objective was slightly more than 1400 people rather than 32000 people affected per year in the case were an economical objective was selected. This means that the safety index (i.e. the affected people by incidental accidents per year in the petrochemical industry plants) was reduced by around 96%, between selecting economical and safety objectives. This type of planning of a petrochemical industry not only decreases the possible number of affected people per year, but also the corresponding environmental risk index (i.e. the negative environmental effect) which was reduced by around 85%. On the other hand, the corresponding economics were reduce by 91%, which is a big economical lose. It can be stated now that the safety objective and environmental risk assessment objective are mainly in the same directions of choices.

The focus of this work was on planning of the petrochemical industry in Kuwait under environmental risk considerations, and as explained before this can not establish the sustainability aim without taking into considerations two of the major forces that shape the industry in the world, namely economics and plant safety. That's why, in the previous paragraphs we discussed the effect of applying economics and safety factor, separately in the model and on the planning of the petrochemical

industry, before adding an extra planning factor. After choosing IRCHS as an environmental risk index, it was used to calculate the environmental risk of each chemical process (plant) using simple linear combinations of all the IRCHS of all chemicals in the process with the corresponding production/consumption coefficients. Values of IRCHS were used to solve the model with a single environmental risk objective function. Table (6.5) shows the value of the environmental risk index as an objective value and the corresponding values of the economics and plant safety. Also it represents the two rejected chemicals.

The value of the environmental risk was highly reduced, by around 86%, in comparison with its value when the model was solved with single economic objective. The value of the corresponding safety index was almost the same as that presented in Table (6.4) also; the corresponding economics shows a little increase. These final results give a good indication that when the environmental risk assessment factor was used in planning the industry and especially petrochemical industry, it can manage the selection of the chemical process routes toward the most environmental friendly and even safety chemicals.

Attention must be paid to the selected and rejected final products in the previous cases that were applied on the model for planning of the petrochemical industry. These observations support the understanding of the effect of solving the model with each single objective function, i.e., economic, safety and environmental objective. The rejected final products from the final five products, when the model was solved with a single economic objective are Cumene and Polystyrene (PS). Cumene

will not generate much economic gain due to its low price. PVC is slightly cheaper than PS, but PS was rejected because the major feedstocks and the chemicals in the intermediate stages of producing this product are more expensive (see Table A.4). The rejected final products, when the model was solved with a single safety objective and single environmental risk objective, are the same, as shown in Tables (6.4 and 6.5) and they were ABS and PVC. The production of ABS needs the production of Acrylonitrile, which is very hazardous since it has very high safety index and also high environmental risk index. Also, Table (A.4) shows that ABS and PVC have very high environmental index. This agreement about the rejected chemicals between safety and environmental objectives, proves that they are mainly in the same directions of chemicals hazardous evaluation and consequently toward chemical process routes selections.

By reviewing Tables (6.6-6.8) and Figures (6.2-6.4), in which they show the selected process chemical routes for each single objective applied on the model, many issues can be identified. The tables and the figure present the selected chemical process routes, which include the major feedstocks, chemicals in the intermediate stages, the final products and the production rates. The general simplified petrochemical network that was shown in Figure (6.1), which includes 62 chemical process routes, was reduced to be 11, 9, 8 routes in the cases of economic, safety, and environmental risk single objectives, respectively. Environmental risk objective has the characteristic of including the lowest number of routes in the planned petrochemical industry. Another observation is that the production rates of the plants were high when the economic objective was considered and low for the safety and environmental objectives. This is

an expected result since the economy is advanced by high products and sales while the environment and people suffer from the existence of huge chemical inventory and production.

The model was solved with a multiobjective function and results in Tables (6.9-6.10) and Figure (6.5) show the resulted values of economics, safety and the environmental risk indices related to the proposed plan together with the plants recommended by the model. Values of the environmental risk index and the safety index are acceptable since they are close to the optimum (low) values found, previously, by solving the model with a single objective function, i.e. environmental and safety objectives. On the other hand, the value of the economics was much less than the optimum (high) value also found by solving the model with a single economic objective. It is however, better than the values obtained from solving model with environmental and safety objectives. Obviously, this means that we are in the middle area between the choices of the three separate objectives. Also, it appears that since two objectives are mainly in the same directions toward the more environmental and safety chemical process routes selection, they are more powerful to direct these selections. Accepting low economics does not mean a big loses, since we are looking for a plan with long term safety and reduction of negative effects on the environment.

The previous discussion of the solved models with single objective function was helpful to examine and understand the selection criteria of the chemical process routes. Results indicate that processes selected by economic objective, safety objective, environmental objective and multiobjective function are different. These

differences are related to the selection criteria for each objective. Processes selected by the multiobjective function model were in the intermediate area between the three single objective functions. This proves the validity of the multiobjective function with its simple computation to present a good planning of the petrochemical industry under economic, environmental risk and safety consideration.

CHAPTER 7

DISCUSSION AND CONCLUSIONS

7.1 Discussion

The structure of the petrochemical industry is cross-linked and can be visualized as a network of chemical process connecting basic feedstock chemicals to the desired final products. The objective of this study is to develop a model that translates the network into mathematical relations and plans for the development of petrochemical industry in Kuwait. The objectives involve the planning of the petrochemical industry under economic, environmental risk and safety considerations.

As mentioned earlier in the study, the selection of the chemical process routes for industrial planning was mainly based on the economical factor and in the advanced planning safety factor was collaborated with the economical factor to insure the worker and work place safety. Also, the local and global environmental problems related to chemical emissions that were produced from burning fuel and chemical processing must be included. The aim of this work was directed to involve the environmental factor in the routine of the selection of the chemical process routes in addition to the economical and safety factors, while planning of the petrochemical industry. To

establish our aim, the IRCHS were selected as an environmental index that evaluates the environmental risk for the chemicals used in the industry. This index has the facility of ranking the chemicals by hazard to environment and workers, even though; there are no incidental accidents. Other specialty of the IRCHS index that it was calculated for a large number of chemicals that has never been done in other similar indices.

This index was used to calculate the environmental risk for the chemical plants that were selected for planning the petrochemical industry in Kuwait. These values were applied in the MILP model in addition to the economical values (added values) and the safety indices. This was done to identify the effect of involving the environmental risk factor on the selection of chemical process routes to produce the final required products and, therefore; on the overall planning of petrochemical industry.

Model results lead us to conclude that even if the plants recommended by the single economic objective were constructed, the expected sustainability is limited. Chemicals that are used in these plants are not with a high extent of safety, an incidental accident can have extremely hazardous effects and it will be difficult to control the situation since the chemicals are highly explosive or toxic. Therefore, the safety factor has to be included in any planning for petrochemical industry in addition to the economics. In the mean while, we can not include the safety and neglect the environmental risk factor. If there are no incidental accidents, this does not mean that we are far away from the dangerous effects of the chemical process on the

environment and the workers for the long and short terms. Environmental aspects include potential damage to the local and regional environment (including humans) caused by routine emissions.

An environmentally friendly chemical plant is one that has a small impact on the environment during normal operations. The earlier the environmental friendless of the proposed chemical process plant is considered the better. This is because decision made in the initial stages of the development and design processes have the most impact upon the final plant design and it is easier to make changes to a design in the early stages (Cave et .al., 1997). Therefore, the planning of petrochemical industry under safety and environmental considerations is of a pressing necessity.

Model results with environmental risk objective and the multiobjective function, explains the validity of the selection of IRCHS as an environmental index. IRCHS consists of two parts, the environmental hazard value and the worker exposure hazard value, combined to allow simple comparative ranking of environmental risk among chemicals. These scores of IRCHS can be used to evaluate the environmental risk for chemicals and process involved in a petrochemical network.

Although, the safety index was restricted to incidental accidents, its role can not be neglected in supporting the understanding of the environmental risk. The logic and the model results show those environmental and human wellnesses (objectives) are mainly moving towards the same targets.

We never claim that we have reached to the perfect overview of the planning of a petrochemical industry; mainly the selection of a simple and well designed environmental risk index was presented and used in a planning model. To complete the risk awareness in the petrochemical plants, safety index was important to complete the invisible dangerous of the incidental accidents. The combination of the economics, environmental risk and safety considerations in the planning of petrochemical industry is a step further towards the important concept of building up an environmental management system and sustainability, but it is not the end. These forces were used as a basis for planning leading to many possible acceptable ideas for development. The decision is not easy and it needs tools to assist in providing the confidence in the final decision.

In the following section we will brief the overall scope of our work and we will discuss some recommended ideas for development.

7.2 Conclusions and recommendations for future work

Petrochemical industries are the most feasible industries for development in the world and consequently in Kuwait. This country has the advantage of good oil resources and good international relations for marketing. If successful, the development of Kuwait petrochemical industry will support the steady state economic growth with decreasing dependence on crude oil exporting.

On the other hands, international institutes insure that petrochemical plants are one of the major sources of environmental risk and even safety problems to humans. If the petrochemical industry not well planned, it can cause harmful effects to the local and global environment and accordingly to the people. The ignorance of the environmental risk and safety considerations in the petrochemical industry planning will prevent future developments in the plants due to the predicted harmful effects. Also, it will not be a balanced sustainability plan since the economic factor is leading. Sustainability targets lead us to search for tools to evaluate the environmental risk and plant safety, so that they can be included in the planning of petrochemical industry. IRCHS index, which includes both an environmental hazard value and workers exposure hazard value, can be used effectively as an objective function within the planning model. Also, it can be easily combined with other objectives to give a more balanced plan.

Results indicate that high economic gain is usually accompanied with high risk to environment and people, and the balanced industry should have economics and

environmental risk and safety as important decision factors. It was shown also, that in cases of multiobjectives and single objective, the values of the objectives are not the only important issues. The selected or rejected chemicals, process routes and other variables have the same importance.

Although the model was applied to Kuwait, this work is planned to be modified to include development in any petrochemical industry. The three major forces of economics, safety and environmental risk when used as a basis for planning lead to many acceptable and applicable ideas for development. The planning and final decision is not easy and it needs tools to assist in providing the confidence in the final decision.

The following key recommendations are briefly described to illustrate a future view for the model modification and work improvement:

- Determining the acceptability of the environmental risk and plant safety are often the most challenging aspects of risk assessment. International standards can be used to emphasis whether the facility under study can insure operation less than the maximum risk levels.

- Any development in the petrochemical industry should take the growth of the products and its size into its strategic plan. In future plans for work modification, it is recommended to include such factors to insure long-term profit and sustainability. This implies the need for a wide and efficient strategy.

- The model can be modified to include a larger petrochemical network. This will provide an increase in the final products or feedstock and provide a more efficient search for more economical and environmentally friendly products.

- The simple form of the multiobjective function can be replaced by other forms used in the field of the muliobjective optimization such as the weighing method. Although, this will increase the computational difficulty of the model, it will generate more solutions (plans) and consequently more planning confidence.

- Another benefit of the use of multiobjective function in the MILP model is to extend the model by considering more objectives affecting the petrochemical industry such as fuel consumption, electricity….etc.

- The final decision of the best petrochemical plant is not easy and tools are needed to assist the confidence of the final decision. Strategic tools are recommended to be used in order to analyze different plants and products in terms of dimensions of value to the industry.

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APPENDIX A

Processes and Data Included in the Petrochemical Model

1. Plants Included in the Petrochemical Model

Table (A.1), shown in the following pages, summarizes the plants, which are included in the petrochemical model. The coefficients given for the chemicals in each plant are the tonnes of chemical produced or consumed per tonne of main product (the coefficient is 1.0 for the main product by definition). It is used in the model as o_{ij} the output coefficient of chemical ***i*** from plant ***j***. Materials consumed are differentiated from materials produced by negative coefficient. Reagents are not included in this tabulation. Also the minimum economic production rate and the fixed capital based on the year 1992 are listed for each plant. All the data in Table (A.1) were taken from SRI reports (1992).

Table A.1: Plants Included in the Model

J	Plant	Output coefficient o_{ij}	Fixed Capital (10^6 $)	Minimum Eco. Prod. Rate (10^3 tonne/yr.)
1	Acetaldehyde # 1: One Step Oxidation from Ethylene		74	67.5
	Acetaldehyde	1		
	Ethylene	-0.68		
	Hydrogen Chloride	-0.0033		
2	Acetaldehyde # 2: Two Step Oxidation from Ethylene		74	67.5
	Acetaldehyde	1		
	Ethylene	-0.68		
	(Hydrogen Chloride)	-0.023		
3	Acetaldehyde # 3: Oxidation of Ethanol		74	67.5
	Acetaldehyde	1		
	Ethanol	-1.2		
4	Acetic Acid # 1: Low Pressure Carbonylation of Methanol		185.5	180
	Acetic Acid	1		
	Carbon monoxide	-0.61		
	Methanol	-0.57		
5	Acetic Acid # 2: Air Oxidation of Acetaldehyde		74.1	67.5
	Acetic Acid	1		
	Acetaldehyde	-0.78		
6	Acetic Acid # 3: Oxidation of n-Butanol		74.1	67.5
	Acetic Acid	1		
	n-Butanol	-0.83		
7	Acetic Acid # 4 : Direct Oxidation of n-Butylenes		74.1	67.5
	Acetic Acid	1		
	n-Butylenes (1- and 2-)	-1.01		

	Butenes -Mixed n-, iso-, dienes, …	0.09		
	Formic Acid	0.06		
8	Acetylene # 1 : Submerged Flame Process		32.2	22.5
	Acetylene	1		
	Fuel Oil (High Sulfur)	-8.34		
	Synthesis Gas 2:1	5.47		
	Fuel Gas	1.3		
	Ethylene	1.15		
9	Acetylene # 2 : Hydration of Calcium Carbide		32.2	22.5
	Acetylene	1		
	Coke	-1.86		
10	Acetylene # 3 : Pyrolysis of Methane (Partial Oxidation)		32.2	22.5
	Acetylene	1		
	Methane	-4.23		
	Synthesis Gas 2:1	4.01		
11	Acetylene # 4 : Pyrolysis of Naphtha (One-Stage Partial Oxidation)		32.2	22.5
	Acetylene	1		
	Naphtha	-4.31		
	Fuel Gas	0.84		
	Coke	-0.01		
12	Acetylene # 5 : Pyrolysis of Ethane (Regenerative Process)		32.2	22.5
	Acetylene	1		
	Ethane	-3		
	Fuel Gas	0.57		
	Fuel Oil (Low Sulfur)	0.18		
13	Acrylonitrile # 1: Ammoxiation of Propylene		364.6	90
	Acrylonitrile	1		
	Chemical Grade Propylene	-1.2		

	Ammonia	-0.428		
	Sulfuric Acid	-0.152		
14	Acrylonitrile # 2 : Cyanation/Oxidation of Ethylene		364.6	90
	Acrylonitrile	1		
	Ethylene	-0.76		
	Hydrogen Cyanide	-0.6		
	Hydrogen Chloride	-0.17		
15	Acrylonitrile-Butadiene-Styrene # 1:By Emulsion/Emulsion Polymerization		83.6	25
	Acrylonitrile-Butadiene-Styrene	1		
	Styrene	-0.5409		
	Butadiene	-0.2451		
	Acrylonitrile	-0.1937		
	Sodium Hydroxide	-0.0042		
16	Acrylonitrile-Butadiene-Styrene # 2: By Suspension/Emulsion Polymerization		70.8	25
	Acrylonitrile-Butadiene-Styrene	1		
	Styrene	-0.54		
	Butadiene	-0.25		
	Acrylonitrile	-0.19		
17	Acrylonitrile-Butadiene-Styrene # 3: Bulk/Suspension Polymerization		70.8	25
	Acrylonitrile-Butadiene-Styrene	1		
	Styrene	-0.67		
	Acrylonitrile	-0.22		
	Polybutadiene Rubber	-0.07		
18	Benzene # 1: Hydrodealkylation of Toluene		44.5	125
	Benzene	1		
	Toluene	-1.2		
	Methane	0.24		
	Hydrogen	-0.07		

19	Benzene # 2 : Disproportion of Toluene		44.5	100
	Benzene	1		
	Toluene	-2.69		
	Xylenes (Mixed)	1.16		
	Fuel Gas	0.01		
20	Butadiene # 1 : Dehydrogenation of n-Butylenes		61.1	25
	Butadiene	1		
	n-Butylenes (1- and 2-)	-1.46		
	Ammonia	-0.01		
	Sulfuric Acid	-0.01		
21	Butadiene # 2 : Oxidative Dehydrogenation of n-Butylenes		61.1	25
	Butadiene	1		
	n-Butylenes (1- and 2-)	-1.316		
22	Butadiene # 3 : Dehydrogenation of n-Butane		61.1	25
	Butadiene	1		
	n-Butane	-1.793		
23	Butadiene # 4 : By Extractive Distillation		61.1	25
	Butadiene	1		
	C-4 fraction - Mixed butanes , -enes, …	-2.374		
	Butenes- Mixed n-, iso-, dienes, …	1.3		
24	Carbon monoxide # 1 : Steam Reforming of Natural Gas		160	27.3
	Carbon monoxide	1		
	Methane	-0.635		
	Hydrogen	0.23		
25	Carbon monoxide # 2 : From Naphtha		160	27.3
	Carbon monoxide	1		
	Naphtha	-0.8		
	Hydrogen	0.25		

26	Cumene # 1 : Reaction of Benzene and Propylene		33.7	60
	Cumene	1		
	Benzene	-0.6733		
	Chemical Grade Propylene	-0.3783		
27	Ethanol # 1 : Hydration of Ethylene		191.3	125
	Ethanol	1		
	Ethylene	-0.7477		
	Fuel Gas	0.06		
	Hydrogen	-0.0031		
	Sodium Hydroxide	-0.0026		
28	Ethylbenzene # 1: Alkylation of Benzene		69.6	250
	Ethylbenzene	1		
	Benzene	-0.74		
	Ethylene	-0.27		
	Fuel Oil (Low Sulfur)	0.01		
29	Ethylene # 1 : Steam Cracking of Ethane-Propane (50-50wt%)		501	250
	Ethylene	1		
	Ethane	-0.815		
	Propane	-0.815		
	Fuel Gas	0.36		
	Chemical Grade Propylene	0.1697		
	C-4 fraction - Mixed butanes , -enes, …	0.0601		
30	Ethylene # 2 : Steam Cracking of Gas Oil (High Severity)		839.2	250
	Ethylene	1		
	Gas Oil	-3.9042		
	Gasoline	0.6426		
	Chemical Grade Propylene	0.6032		
	Fuel Oil (Low Sulfur)	0.5361		
	C-4 fraction - Mixed butanes , -enes, …	0.3461		
	Sodium Hydroxide	-0.0022		

31	Ethylene # 3 : Steam Cracking of Naphtha (High Severity)		762	250
	Ethylene	1		
	Naphtha	-3.17		
	Gasoline	0.7061		
	Fuel Gas	0.5		
	Chemical Grade Propylene	0.4539		
	C-4 fraction - Mixed butanes , -enes, …	0.307		
	Fuel Oil (Low Sulfur)	0.1008		
	Sodium Hydroxide	-.00035		
32	Ethylene # 4 : Pyrolysis of Ethane		519.4	250
	Ethylene	1		
	Ethane	-1.22		
	Fuel Gas	0.14		
	C-4 fraction - Mixed butanes , -enes, …	0.04		
	Chemical Grade Propylene	0.02		
	Gasoline	0.02		
	Sodium Hydroxide	-0.01		
33	Ethylene # 5 : Pyrolysis of Propane		636.2	250
	Ethylene	1		
	Propane	-2.12		
	Fuel Gas	0.6		
	Chemical Grade Propylene	0.28		
	C-4 fraction - Mixed butanes , -enes, …	0.11		
	Gasoline	0.1		
	Fuel Oil (Low Sulfur)	0.03		
34	Ethylene # 6 : Pyrolysis of Naphtha (Low Severity)		108	250
	Ethylene	1		
	Naphtha	-3.9		
	Gasoline	1.3		
	Fuel Gas	0.58		

	Chemical Grade Propylene	0.42		
	Fuel Oil (Low Sulfur)	0.3		
	C-4 fraction - Mixed butanes , -enes, …	0.3		
35	Ethylene # 7 : Pyrolysis of Gas Oil (Low Severity)		108	250
	Ethylene	1		
	Gas Oil	-6.02		
	Fuel Oil (Low Sulfur)	2.16		
	Gasoline	1.1		
	Chemical Grade Propylene	0.85		
	C-4 fraction - Mixed butanes , -enes, …	0.53		
	Fuel Gas	0.39		
36	Ethylene # 8 : Steam Cracking of Gas Oil (Medium Severity)		108	250
	Ethylene	1		
	Gas Oil	-4.8		
	Fuel Oil (Low Sulfur)	1.45		
	Gasoline	0.73		
	Chemical Grade Propylene	0.63		
	C-4 fraction - Mixed butanes , -enes, …	0.55		
	Fuel Gas	0.43		
37	Ethylene # 9 : Hydrogenation of Acetylene		108	250
	Ethylene	1		
	Fuel Gas	1.24		
	Acetylene	-1.09		
	Hydrogen	-0.31		
38	Ethylene # 10 : Dehydration of Ethanol		108	250
	Ethylene	1		
	Ethanol	1.75		
39	Ethylene # 11 : Pyrolysis of Butane		108	250
	Ethylene	1		
	n-Butane	-2.5		
	Fuel Gas	0.58		

	Chemical Grade Propylene	0.43		
	C-4 fraction - Mixed butanes , -enes, …	0.26		
	Gasoline	0.2		
	Fuel Oil (Low Sulfur)	0.04		
40	Ethylene Dichloride # 1 : Chlorination of Ethylene		22.7	180
	Ethylene Dichloride	1		
	Chlorine	-0.7		
	Ethylene	-0.36		
41	Ethylene Dichloride # 2 : Oxychlorination of Ethylene	73.4	73.4	180
	Ethylene Dichloride	1		
	Hydrochloric Acid	-0.94		
	Ethylene	-0.34		
42	Hydrogen Cyanide # 1: Ammoxidation of Methane		101.6	30
	Hydrogen Cyanide	1		
	Methane	-1.02		
	Ammonia	-0.75		
43	Methanol # 1 : From Methane (Low Pressure)		345.4	410
	Methanol	1		
	Methane	-0.49		
44	Methanol # 2 : From Methane (Medium Pressure)		345.4	410
	Methanol	1		
	Methane	-0.49		
45	Methanol # 3 : From Methane (High Pressure)		345.4	410
	Methanol	1		
	Methane	-0.5		
46	Methanol # 4 : From Syn. Gas (High Pressure)		345.4	410
	Methanol	1		
	Synthesis Gas 3:1	-0.923		
	Carbon Dioxide	-0.32		

47	Methanol # 5 : From Syn. Gas (Low Pressure)		345.4	410
	Methanol	1		
	Synthesis Gas 3:1	-0.89		
	Carbon Dioxide	-0.36		
	Sulfuric Acid	-0.02		
48	Polystyrene (Crystal Grade) # 1 : By Bulk Polymerization		18.4	15
	Polystyrene (Crystal Grade)	1		
	Styrene	-1.02		
49	Polyvinyl Chloride # 1 : Bulk Polymerization		91	50
	Polyvinyl Chloride	1		
	Vinyl Chloride	-1.025		
	Sodium Hydroxide	-0.0005		
50	Polyvinyl Chloride # 2 : Suspension Polymerization		164.3	90
	Polyvinyl Chloride	1		
	Vinyl Chloride	-1.025		
	Sodium Hydroxide	-0.0041		
	Hydrogen Chloride	-0.0033		
	Toluene	-0.0023		
	Polyvinyl Alcohol	-.00015		
51	Chemical Grade Propylene # 1 : Chemical Grade Propylene from Refinery Grade		49.1	90
	Chemical Grade Propylene	1		
	Refinery Grade Propylene	-1.33		
	Propane	0.33		
52	Styrene # 1 : Dehydrogenation of Ethylbenzene		216	225
	Styrene	1		
	Ethylbenzene	-1.148		
	Toluene	0.052		
	Benzene	0.032		

53	Styrene # 2 : From Ethylbenzene by Hydroperoxide Process		216	225
	Styrene	1		
	Ethylbenzene	-1.139		
	Propylene Oxide	0.408		
	Chemical Grade Propylene	-0.3248		
	Sodium Hydroxide	-0.013		
54	Sulfuric Acid # 1 : Double Absorption Process		80.8	320
	Sulfuric Acid	1		
	Sulfur	-0.328		
55	Synthesis gas 3:1 # 1 : Partial Oxidation of Residual Oil		167.1	937
	Synthesis gas 3:1	1		
	Fuel Oil (High Sulfur)	-0.91		
56	Synthesis gas 3:1 # 2 : Methane Reforming		167.1	937
	Synthesis gas 3:1	1		
	Methane	-0.49		
57	Vinyl Acetate # 1 : Reaction of Ethylene and Acetic Acid		126.2	67.5
	vinyl Acetate	1		
	Acetic Acid	-0.704		
	Ethylene	-0.393		
58	Vinyl Acetate # 2 : Reaction of Acetylene and Acetic Acid		91.8	67.5
	Vinyl Acetate	1		
	Acetic Acid	-0.72		
	Acetylene	-0.32		
	Acetaldehyde	0.01		
59	Vinyl Acetate # 3 : Reaction of Ethane and Acetic Acid		91.8	67.5
	Vinyl Acetate	1		

	Acetic Acid	-0.76		
	Ethane	-0.44		
60	Vinyl Chloride # 1 : Chlorination and Oxychlorination of Ethylene		218.7	250
	Vinyl Chloride	1		
	Chlorine	-0.606		
	Ethylene	-0.475		
	Sodium Hydroxide	-0.007		
61	Vinyl Chloride # 2 : Dehydrochlorination of Ethylene Dichloride		95.9	125
	Vinyl Chloride	1		
	Ethylene Dichloride	-1.66		
	Hydrogen Chloride	0.61		
62	Vinyl Chloride # 3 : Hydrochlorination of Acetylene		95.9	200
	Vinyl Chloride	1		
	Hydrogen Chloride	-0.6		
	Acetylene	-0.43		
	Sodium Hydroxide	-0.01		

2. Plants Included in the Petrochemical Model

Table (A.2), shown in the following pages, summarizes the plants, which are included in the petrochemical model. It also presents the IRCHS value for each chemical i and the ERI value for each plant j in the plants included in the model. IRCHS values were taken from (Scorecord, 2007) and the ERI values are calculated using Equation (6.11). The coefficients given for the chemicals in each plant are the tonnes of chemical produced or consumed per tonne of main product (the coefficient is 1.0 for the main product by definition). It is used in the model as o_{ij} the output coefficient of chemical ***i*** from plant ***j***.

Table A.2: (IRCHS) and Environmental Risk Index (ERI) Corresponding to the Plants Included in the Model

j	Plant	Output coefficient o_{ij}	Chemicals IRCHS	Plants ERI
1	Acetaldehyde # 1: One Step Oxidation from Ethylene			51.04
	Acetaldehyde	1	38	
	Ethylene	-0.68	19	
	Hydrogen Chloride	-0.0033	37	
2	Acetaldehyde # 2: Two Step Oxidation from Ethylene			51.77
	Acetaldehyde	1	38	
	Ethylene	-0.68	19	
	(Hydrogen Chloride)	-0.023	37	
3	Acetaldehyde # 3: Oxidation of Ethanol			53.6
	Acetaldehyde	1	38	
	Ethanol	-1.2	13	
4	Acetic Acid # 1: Low Pressure Carbonylation of Methanol			62.55
	Acetic Acid	1	30	
	Carbon monoxide	-0.61	30	
	Methanol	-0.57	25	
5	Acetic Acid # 2: Air Oxidation of Acetaldehyde			59.64
	Acetic Acid	1	30	
	Acetaldehyde	-0.78	38	
6	Acetic Acid # 3: Oxidation of n-Butanol			45.77
	Acetic Acid	1	30	
	n-Butanol	-0.83	19	
7	Acetic Acid # 4 : Direct Oxidation of n-Butylenes			48.8
	Acetic Acid	1	30	
	n-Butylenes (1- and 2-)	-1.01	13	
	Butenes -Mixed n-, iso-, dienes, …	0.09	41	
	Formic Acid	0.06	33	

8	Acetylene # 1 : Submerged Flame Process			335
	Acetylene	1	18	
	Fuel Oil (High Sulfur)	-8.34	15	
	Synthesis Gas 2:1	5.47	30	
	Fuel Gas	1.3	15	
	Ethylene	1.15	19	
9	Acetylene # 2 : Hydration of Calcium Carbide			49.62
	Acetylene	1	18	
	Coke	-1.86	17	
10	Acetylene # 3 : Pyrolysis of Methane (Partial Oxidation)			159.45
	Acetylene	1	18	
	Methane	-4.23	5	
	Synthesis Gas 2:1	4.01	30	
11	Acetylene # 4 : Pyrolysis of Naphtha (One-Stage Partial Oxidation)			78.4
	Acetylene	1	18	
	Naphtha	-4.31	13	
	Fuel Gas	0.84	5	
	Coke	-0.01	7	
12	Acetylene # 5 : Pyrolysis of Ethane (Regenerative Process)			53.55
	Acetylene	1	18	
	Ethane	-3	10	
	Fuel Gas	0.57	5	
	Fuel Oil (Low Sulfur)	0.18	15	
13	Acrylonitrile # 1: Ammoxiation of Propylene			77.4
	Acrylonitrile	1	48	
	Chemical Grade Propylene	-1.2	13	
	Ammonia	-0.428	22	
	Sulfuric Acid	-0.152	29	

14	Acrylonitrile # 2 : Cyanation/Oxidation of Ethylene			101.13
	Acrylonitrile	1	48	
	Ethylene	-0.76	19	
	Hydrogen Cyanide	-0.6	54	
	Hydrogen Chloride	-0.17	37	
15	Acrylonitrile-Butadiene-Styrene # 1:By Emulsion/Emulsion Polymerization			74.45
	Acrylonitrile-Butadiene-Styrene	1	0	
	Styrene	-0.5409	33	
	Butadiene	-0.2451	41	
	Acrylonitrile	-0.1937	48	
	Sodium Hydroxide	-0.0042	13	
16	Acrylonitrile-Butadiene-Styrene # 2: By Suspension/Emulsion Polymerization			37.19
	Acrylonitrile-Butadiene-Styrene	1	0	
	Styrene	-0.54	33	
	Butadiene	-0.25	41	
	Acrylonitrile	-0.19	48	
17	Acrylonitrile-Butadiene-Styrene # 3: Bulk/Suspension Polymerization			65.83
	Acrylonitrile-Butadiene-Styrene	1	0	
	Styrene	-0.67	33	
	Acrylonitrile	-0.22	48	
	Polybutadiene Rubber	-0.07	7	
18	Benzene # 1: Hydrodealkylation of Toluene			84
	Benzene	1	48	
	Toluene	-1.2	29	
	Methane	0.24	5	
	Hydrogen	-0.07	0	
19	Benzene # 2 : Disproportion of Toluene			156.22
	Benzene	1	48	
	Toluene	-2.69	29	

	Xylenes (Mixed)	1.16	26	
	Fuel Gas	0.01	5	
20	Butadiene # 1 : Dehydrogenation of n-Butylenes			60.49
	Butadiene	1	41	
	n-Butylenes (1- and 2-)	-1.46	13	
	Ammonia	-0.01	22	
	Sulfuric Acid	-0.01	29	
21	Butadiene # 2 : Oxidative Dehydrogenation of n-Butylenes			58.108
	Butadiene	1	41	
	n-Butylenes (1- and 2-)	-1.316	13	
22	Butadiene # 3 : Dehydrogenation of n-Butane			64.309
	Butadiene	1	41	
	n-Butane	-1.793	13	
23	Butadiene # 4 : By Extractive Distillation			125.16
	Butadiene	1	41	
	C-4 fraction - Mixed butanes , -enes, …	-2.374	13	
	Butenes- Mixed n-, iso-, dienes, …	1.3	41	
24	Carbon monoxide # 1 : Steam Reforming of Natural Gas			33.18
	Carbon monoxide	1	30	
	Methane	-0.635	5	
	Hydrogen	0.23	0	
25	Carbon monoxide # 2 : From Naphtha			40.4
	Carbon monoxide	1	30	
	Naphtha	-0.8	13	
	Hydrogen	0.25	0	
26	Cumene # 1 : Reaction of Benzene and Propylene			69.2
	Cumene	1	32	
	Benzene	-0.6733	48	
	Chemical Grade Propylene	-0.3783	13	

27	Ethanol # 1 : Hydration of Ethylene			27.54
	Ethanol	1	13	
	Ethylene	-0.7477	19	
	Fuel Gas	0.06	5	
	Hydrogen	-0.0031	0	
	Sodium Hydroxide	-0.0026	13	
28	Ethylbenzene # 1: Alkylation of Benzene			64.8
	Ethylbenzene	1	24	
	Benzene	-0.74	48	
	Ethylene	-0.27	19	
	Fuel Oil (Low Sulfur)	0.01	15	
29	Ethylene # 1: Steam Cracking of Ethane-Propane (50-50wt%)			41.71
	Ethylene	1	19	
	Ethane	-0.815	10	
	Propane	-0.815	12	
	Fuel Gas	0.36	5	
	Chemical Grade Propylene	0.1697	13	
	C-4 fraction - Mixed butanes , -enes, …	0.0601	13	
30	Ethylene # 2 : Steam Cracking of Gas Oil (High Severity)			112.01
	Ethylene	1	19	
	Gas Oil	-3.9042	13	
	Gasoline	0.6426	34	
	Chemical Grade Propylene	0.6032	13	
	Fuel Oil (Low Sulfur)	0.5361	15	
	C-4 fraction - Mixed butanes , -enes, …	0.3461	13	
	Sodium Hydroxide	-0.0022	13	
31	Ethylene # 3 : Steam Cracking of Naphtha (High Severity)			98.13
	Ethylene	1	19	
	Naphtha	-3.17	13	

	Gasoline	0.7061	34	
	Fuel Gas	0.5	5	
	Chemical Grade Propylene	0.4539	13	
	C-4 fraction - Mixed butanes , -enes, …	0.307	13	
	Fuel Oil (Low Sulfur)	0.1008	15	
	Sodium Hydroxide	-.00035	13	
32	Ethylene # 4 : Pyrolysis of Ethane			33.7
	Ethylene	1	19	
	Ethane	-1.22	10	
	Fuel Gas	0.14	5	
	C-4 fraction - Mixed butanes , -enes, …	0.04	13	
	Chemical Grade Propylene	0.02	13	
	Gasoline	0.02	34	
	Sodium Hydroxide	-0.01	34	
33	Ethylene # 5 : Pyrolysis of Propane			56.36
	Ethylene	1	19	
	Propane	-2.12	12	
	Fuel Gas	0.6	5	
	Chemical Grade Propylene	0.28	13	
	C-4 fraction - Mixed butanes , -enes, …	0.11	13	
	Gasoline	0.1	34	
	Fuel Oil (Low Sulfur)	0.03	15	
34	Ethylene # 6 : Pyrolysis of Naphtha (Low Severity)			130.66
	Ethylene	1	19	
	Naphtha	-3.9	13	
	Gasoline	1.3	34	
	Fuel Gas	0.58	5	
	Chemical Grade Propylene	0.42	13	
	Fuel Oil (Low Sulfur)	0.3	15	
	C-4 fraction - Mixed butanes , -enes, …	0.3	13	
35	Ethylene # 7 : Pyrolysis of Gas Oil (Low Severity)			186.95
	Ethylene	1	19	

	Gas Oil	-6.02	13	
	Fuel Oil (Low Sulfur)	2.16	15	
	Gasoline	1.1	34	
	Chemical Grade Propylene	0.85	13	
	C-4 fraction - Mixed butanes , -enes, …	0.53	13	
	Fuel Gas	0.39	5	
36	Ethylene # 8 : Steam Cracking of Gas Oil (Medium Severity)			145.46
	Ethylene	1	19	
	Gas Oil	-4.8	13	
	Fuel Oil (Low Sulfur)	1.45	15	
	Gasoline	0.73	34	
	Chemical Grade Propylene	0.63	13	
	C-4 fraction - Mixed butanes , -enes, …	0.55	13	
	Fuel Gas	0.43	5	
37	Ethylene # 9 : Hydrogenation of Acetylene			44.82
	Ethylene	1	19	
	Fuel Gas	1.24	5	
	Acetylene	-1.09	18	
	Hydrogen	-0.31	0	
38	Ethylene # 10 : Dehydration of Ethanol			41.75
	Ethylene	1	19	
	Ethanol	1.75	13	
39	Ethylene # 11 : Pyrolysis of Butane			70.77
	Ethylene	1	19	
	n-Butane	-2.5	13	
	Fuel Gas	0.58	5	
	Chemical Grade Propylene	0.43	13	
	C-4 fraction - Mixed butanes , -enes, …	0.26	13	
	Gasoline	0.2	34	
	Fuel Oil (Low Sulfur)	0.04	15	

40	Ethylene Dichloride # 1 : Chlorination of Ethylene			68.24
	Ethylene Dichloride	1	39	
	Chlorine	-0.7	32	
	Ethylene	-0.36	19	
41	Ethylene Dichloride # 2 : Oxychlorination of Ethylene			80.24
	Ethylene Dichloride	1	39	
	Hydrochloric Acid	-0.94	37	
	Ethylene	-0.34	19	
42	Hydrogen Cyanide # 1: Ammoxidation of Methane			66.18
	Hydrogen Cyanide	1	54	
	Methane	-1.02	5	
	Ammonia	-0.75	22	
43	Methanol # 1 : From Methane (Low Pressure)			27.45
	Methanol	1	25	
	Methane	-0.49	5	
44	Methanol # 2 : From Methane (Medium Pressure)			27.45
	Methanol	1	25	
	Methane	-0.49	5	
45	Methanol # 3 : From Methane (High Pressure)			27.5
	Methanol	1	25	
	Methane	-0.5	5	
46	Methanol # 4 : From Syn. Gas (High Pressure)			53.97
	Methanol	1	25	
	Synthesis Gas 3:1	-0.923	30	
	Carbon Dioxide	-0.32	4	
47	Methanol # 5 : From Syn. Gas (Low Pressure)			53.72
	Methanol	1	25	
	Synthesis Gas 3:1	-0.89	30	
	Carbon Dioxide	-0.36	4	
	Sulfuric Acid	-0.02	29	

48	Polystyrene (Crystal Grade) # 1 : By Bulk Polymerization			33.66
	Polystyrene (Crystal Grade)	1	0	
	Styrene	-1.02	33	
49	Polyvinyl Chloride # 1 : Bulk Polymerization			86.2
	Polyvinyl Chloride	1	36	
	Vinyl Chloride	-1.025	49	
	Sodium Hydroxide	-0.0005	13	
50	Polyvinyl Chloride # 2 : Suspension Polymerization			86.47
	Polyvinyl Chloride	1	36	
	Vinyl Chloride	-1.025	49	
	Sodium Hydroxide	-0.0041	13	
	Hydrogen Chloride	-0.0033	37	
	Toluene	-0.0023	29	
	Polyvinyl Alcohol	-.00015	0	
51	Chemical Grade Propylene # 1 : Chemical Grade Propylene from Refinery Grade			34.25
	Chemical Grade Propylene	1	13	
	Refinery Grade Propylene	-1.33	13	
	Propane	0.33	12	
52	Styrene # 1 : Dehydrogenation of Ethylbenzene			63.6
	Styrene	1	33	
	Ethylbenzene	-1.148	24	
	Toluene	0.052	29	
	Benzene	0.032	48	
53	Styrene # 2 : From Ethylbenzene by Hydroperoxide Process			80.23
	Styrene	1	33	
	Ethylbenzene	-1.139	24	
	Propylene Oxide	0.408	38	
	Chemical Grade Propylene	-0.3248	13	
	Sodium Hydroxide	-0.013	13	

54	Sulfuric Acid # 1 : Double Absorption Process			29.98
	Sulfuric Acid	1	29	
	Sulfur	-0.328	3	
55	Synthesis gas 3:1 # 1 : Partial Oxidation of Residual Oil			
	Synthesis gas 3:1	1	30	
	Fuel Oil (High Sulfur)	-0.91	15	
56	Synthesis gas 3:1 # 2 : Methane Reforming			32.45
	Synthesis gas 3:1	1	30	
	Methane	-0.49	5	
57	Vinyl Acetate # 1 : Reaction of Ethylene and Acetic Acid			65.6
	vinyl Acetate	1	37	
	Acetic Acid	-0.704	30	
	Ethylene	-0.393	19	
58	Vinyl Acetate # 2 : Reaction of Acetylene and Acetic Acid			64.7
	Vinyl Acetate	1	37	
	Acetic Acid	-0.72	30	
	Acetylene	-0.32	18	
	Acetaldehyde	0.01	38	
59	Vinyl Acetate # 3 : Reaction of Ethane and Acetic Acid			64.2
	Vinyl Acetate	1	37	
	Acetic Acid	-0.76	30	
	Ethane	-0.44	10	
60	Vinyl Chloride # 1 : Chlorination and Oxychlorination of Ethylene			77.5
	Vinyl Chloride	1	49	
	Chlorine	-0.606	32	
	Ethylene	-0.475	19	

	Sodium Hydroxide	-0.007	13	
61	Vinyl Chloride # 2 : Dehydrochlorination of Ethylene Dichloride			136.3
	Vinyl Chloride	1	49	
	Ethylene Dichloride	-1.66	39	
	Hydrogen Chloride	0.61	37	
62	Vinyl Chloride # 3 : Hydrochlorination of Acetylene			79.07
	Vinyl Chloride	1	49	
	Hydrogen Chloride	-0.6	37	
	Acetylene	-0.43	18	
	Sodium Hydroxide	-0.01	13	

3. Safety Index

Table (A.3), shown in the following page, presents the safety index that was established by Al-Sharrah, G.K., et.al. (2007). This index was explained in detail in chapter 4 and it was used in the multiobjective function of the model to present the safety index for all plants included in the models and therefore to present the safety objective function.

Table A.3: Safety Index*

Chemical	*Freq* Accidents/process, yr	*Haz* People affected/tonne	*Inv* Tonne/accident	*Size* No. of process /plant	*K* People affected / plant . yr
Acetaldehyde	0.008	0.1202*	5625	3	11.2
Acetic acid	0.038	0.0229	5625	3	14.7
Acrolein	0.064	0.5763*	12.5	3	1.4
Acrylic acid	0.038	0.0561	7500	3	47.9
Acrylonitrile	0.042	0.4224*	7500	3	399.2
Ammonia	0.016	0.1357	8750	3	57
Benzene	0.008	0.1465	8333	3	293
Butadiene	0.013	0.1233*	2083	3	10.0
Carbon tetrachloride	0.056	0.1827	1875	3	57.6
Chlorine	0.022	0.8105	7500	3	401.2
Cumene	0.008	0.0742*	5000	3	8.9
Ethane	0.014	0.1526	4366	3	28
Ethyl benzene	0.008	0.0451*	15000	3	16.2
Formaldehyde	0.009	1.8414	1250	3	62.1
Hydrogen chloride	0.06	0.4273	1666	3	128.1
Hydrogen cyanide	0.064	5.9972	2500	3	2878.7
Hydrogen fluoride	0.064	0.0116	1458	3	3.2
Nitric acid	0.038	0.2298	1875	3	49.1
Pentane	0.013	0.1515*	417	3	2.5
Phenol	0.008	0.0002	3750	3	0.02
Phosphoric acid	0.038	0.0133	14400	3	21.8
Styrene	0.008	0.4484	18750	3	201.78
Sulfuric acid	0.038	0.0149	26666	3	45.3
Toluene	0.008	0.0747	5833	3	10.5
Vinyl acetate	0.042	0.1866	5625	3	132.3
Vinyl chloride	0.042	0.0337	10417	3	44.2
Xylene	0.008	0.2348	5000	3	28.2

*source: Al-sharrah, G.K., et.al. (2007). calculated from LD_{50}

4. Price Data

Table (A.4), shown in the following page, presents the price data for the chemicals included in the model. These values were used to calculate the profit added value for the plants that was include in the model and consequently, these data were used in the multiobjective function in the model to present the economical objective function. These data values were taken from Al-Sharrah, G.K., et.al. (2001).

Table (A.4): Price Data*

NO.	Chemicals	($/ton)	NO.	Chemicals	($/ton)
1	Acetaldehyde	657	34	Isopropyl alcohol	527
2	Acetic acid	644	35	Methane	134
3	Acetone	443	36	Methanol	113
4	Acetylene	1820	37	Methyl acrylate	1450
5	Acrylic fibers	744	38	Methayl methacrylate	1910
6	Acrylonitrile	822	39	Naphtha	203
7	ABS	2300	40	n-Butane	185
8	Ammonia	152	41	n-Butylenes (1- and 2-)	245
9	Benzene	407	42	Pentane	456
10	Butadiene	322	43	Phenol	688
11	Butenes (mixed)	869	44	Polybutadiene rubber	1900
12	C-4fraction (mixed)	179	45	Polystyrene (crystal grade)	1100
13	Carbon dioxide	104	46	Polystyrene (expandable beads)	1650
14	Carbon monoxide	17.6	47	Polystyrene (impact grade)	1150
15	Chlorine	104	48	Poly(vinyl acetate)	1060
16	Clorobenzene	514	49	Poly(vinyl alcohol)	3040
17	Hydrogen fluoride	727	50	Poly(vinyl chloride)	789
18	Cumene	507	51	Propane	172
19	Ethane	147	52	Propylene (chemical grade)	381
20	Ethanol	631	53	Propylene (refinery grade)	280
21	Ethyl benzene	547	54	Propylene oxide	1020
22	Ethylene	461	55	Sodium carbonate	192
23	Ethylene dichloride	282	56	Sodium hydroxide	368
24	Formic acid	666	57	Styrene	697
25	Fuel gas	109	58	Sulfuric acid	60
26	Fuel oil	103	59	Sulfur	27.9
27	Gas oil	188	60	Synthesis gas of 3:1	80
28	Gasoline	212	61	Synthesis gas of 2:1	80
29	Hydrochloric acid	485	62	Toluene	321
30	Hydrogen	575	63	Vinyl acetate	1020
31	Hydrogen chloride	172	64	Vinyl chloride	500
32	Hydrogen cyanide	507	65	Xylene	292
33	Hydrogen peroxide	1330	------	----------	------

APPENDIX B

Sample Model Program Output File

This appendix contains one output list file from the model's program. The output file is the solution obtained from GAMS commercial optimization package.

THESIS

C o m p i l a t i o n

```
 4
 5
 6  SETS
 7  I   constraints  /1*26/
 8  J   process    /1*70/
 9
10
11   TABLE A(I,J)      constraints coefficints
12         1    2    3    4    5    6    7    8    9    10   11   1
     2   13   14   15   16   17   18   19   20
13     1  1    1    1    0  -0.78  0    0    0    0    0    0    0
       0    0    0    0    0    0    0    0
14     2  0    0    0    1    1    1    1    0    0    0    0    0
       0    0    0    0    0    0    0    0
15     3  0    0    0    0    0    0    0    1    1    1    1    1
       0    0    0    0    0    0    0    0
16     4  0    0    0    0    0    0    0    0    0    0    0    0
       1    1  -.1937  -.19  -.22  0    0    0
17     5  0    0    0    0    0    0    0    0    0    0    0    0
       0    0    1    1    1    0    0    0
18     6  0    0    0    0    0    0    0    0    0    0    0    0
       0    0    0    0    0    1    1    0
19     7  0    0    0    0    0    0    0    0    0    0    0    0
       0    0  -.2451 -.25   0    0    0    1
20     8  0    0    0  -.61   0    0    0    0    0    0    0    0
       0    0    0    0    0    0    0    0
21     10 0    0  -1.3   0    0    0    0    0    0    0    0    0
```

0 0 0 0 0 0 0 0

22 12 -.6 -.68 0 0 0 0 0 1.15 0 0 0 0

0 -.76 0 0 0 0 0 0

23 14 0 0 0 0 0 0 0 0 0 0 0 0

0 -.6 0 0 0 0 0 0

24 15 0 0 0 -.57 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0

25 18 0 0 0 0 0 0 0 0 0 0 0 0

-1.2 0 0 0 0 0 0 0

26 19 0 0 0 0 0 0 0 0 0 0 0 0

0 0 -.5409 -.54 -.67 0 0 0

27 20 0 0 0 0 0 0 0 0 0 0 0 0

-.152 0 0 0 0 0 0 -.01

28 24 0 0 0 0 0 0 0 0 0 0 0 0

0.428 0 0 0 0 0 0 0.01

29 26 0 0 0 0 0 0 0 0 0 0 4.31 0

0 0 0 0 0 0 0 0

30 + 21 22 23 24 25 26 27 28 29 30 31 3

2 33 34 35 36 37 38 39 40

31 3 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 -1.09 0 0 0

32 6 0 0 0 0 0 -.6733 0 -.74 0 0 0 0

0 0 0 0 0 0 0 0

33 7 1 1 1 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0

34 8 0 0 0 1 1 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0

35 9 0 0 0 0 0 1 0 0 0 0 0 0

0 0 0 0 0 0 0 0

36 10 0 0 0 0 0 0 1 0 0 0 0 0

0 0 0 0 0 -1.75 0 0

37 11 0 0 0 0 0 0 0 1 0 0 0 0

0 0 0 0 0 0 0 0

38 12 0 0 0 0 0 0 -.7477 -.27 1 1 1 1

1 1 1 1 1 1 1 -.36

39 13 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 1

40 18 0 0 0 0 0 -.3783 0 0 .1697 .6032 .4539 .0

4 .28 .42 .85 .63 0 0 .43 0

41 25 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 .7

42 26 0 0 0 0 0.8 0 0 0 0 0 3.17 0

0 3.9 0 0 0 0 0 0

43 + 41 42 43 44 45 46 47 48 49 50 51 52

53 54 55 56 57 58 59 60

44 1 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0.01 0 0

45 2 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 -.704 -.72 -0.76 0

46 3 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 -.32 0 0

47 6 0 0 0 0 0 0 0 0 0 0 0 .0

32 0 0 0 0 0 0 0 0

48 11 0 0 0 0 0 0 0 0 0 0 0 -1.1

48 -1.139 0 0 0 0 0 0 0

49 12 -.3 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 -.393 0 -.475

50 13 1 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0

51 14 0 1 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0

52 15 0 0 1 1 1 1 1 0 0 0 0 0

0 0 0 0 0 0 0 0

53 16 0 0 0 0 0 0 0 1 0 0 0 0

0 0 0 0 0 0 0 0

54 17 0 0 0 0 0 0 0 0 1 1 0 0

0 0 0 0 0 0 0 0

55 18 0 0 0 0 0 0 0 0 0 0 1 0

-.3248 0 0 0 0 0 0 0

56 19 0 0 0 0 0 0 0 -1.02 0 0 0 1

1 0 0 0 0 0 0 0

57 20 0 0 0 0 0 0 -.02 0 0 0 0 0

0 1 0 0 0 0 0 0

58 21 0 0 0 0 0 -.923 -.89 0 0 0 0 0

0 0 1 1 0 0 0 0

59 22 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 1 1 1 0

60 23 0 0 0 0 0 0 0 0 -1.025 -1.025 0 0

0 0 0 0 0 0 0 1

61 24 0 0.75 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 0

62 25 0 0 0 0 0 0 0 0 0 0 0 0

0 0 0 0 0 0 0 .606

63 + 61 62 63 64 65 66 67 68 69 70

64 3 0 -.43 0 0 0 0 0 0 0 0

65 5 0 0 -1 0 0 0 0 0 0 0

66 9 0 0 0 0 0 0 -1 0 0 0 0

67 13 -1.66 0 0 0 0 0 0 0 0 0 0

68 16 0 0 0 0 0 0 0 -1 0 0 0

69 17 0 0 0 0 0 -1 0 0 0 0 0

70 19 0 0 0 0 0 0 0 0 0 0 0

71 22 0 0 0 0 -1 0 0 0 0 0 0

72 23 1 1 0 0 0 0 0 0 0 0 0

73 24 0 0 0 0 0 0 0 0 -1 0 0

74 25 0 0 0 0 0 0 0 0 0 -1 0

75 26 0 0 0 0 0 0 0 0 0 0 -1

```
76
77   SCALAR F,w1,w2;
78   PARAMETER B(J)    lower limit /1 67.5,2 67.5,3 67.5,4 180,5 67.5,6 67.5
     ,7 67.5,8 22.5,9 22.5,10 22.5,
79   11 22.5,12 22.5,13 90,14 90,15 25,16 25,17 25,18 80,19 100,20 25,21 25,22,
     25,23  25,24  27.5,25  27.5,26  60,27  125,28,80,29  250,30  250,31  250,32
     250,33 80,34 250,35 250,36 250,37 250,38   250,39 250,40 180,
80   41 180,42 30,43 410,44 410,45 410,46 410,47 410,48 15,49 50,50 90,51
     90,52  80,53  225,54  320,55  937,56  937,57  20,58,67.5,59  67.5,60  250,61
     125,62 200,63 5,64 67.5,65 50,66 60,67 15/;
81
82
83   PARAMETER ERI(J) environmental risk index /1 51.04,2 51.77,3 53.6,4
     ,62,55,5 59.64,6 45.77,7 48.8,8 335.55,9 49.62,10 159.45,
84   11 78.4,12 53.55,13 77.4,14 101.13,15 74.4
     5,16 37.19,17 65.83,18 84,19 156.22,20 60.49,
85   21 58.108,22 64.31,23 125.16,24 33.18,25 4
     0.4,26 69.2,27 27.54,28 64.8,29 41.72,30 112.01,
86   31 98.13,32 33.7,33 56.36,34 130.66,35 186.95
     ,36 145.46,37 44.82,38 41.75,39 70.77,40 68.24,
87   41 80.24,42 66.18,43 27.45,44 27.45,45 27.5,
     ,46 53.97,47 53.72,48 33.66,49 86.2,50 86.47,
88   51 34.25,52 63.6,53 80.23,54 29.984,55 43.65,
     56 32.45,57 65.6,58 64.7,59 64.2,60 77.5,
89   61 136.3,62 79,63 0,64 0,65 0,66 0,67 0/;
90   PARAMETER SI(J) safety index /1 0.341,2 0.4672,3 0.4803,4 0.3926,5 0.40
     5,6 0.4458,7 1.35625,8 0.6068,9 0.108,10 3.0635,
91   11 14.7103,12 1.2578,13 5.0832,14 62.8868,
     15 1.4425,16 1.5609,17 1.5766,18 0.6343,19 1.4527,20 0.579,
92   21 0.57182,22 0.8941,23 1.20595,24 0.5286,
     25 2.7831,26 0.4682,27 0.3325,28 4.1889,29 0.9898,30 1.2033,
93   31 11.1914,32 0.7301,33 0.6785,34 13.7448,
```

```
      35 1.8524,36 1.5042,37 0.4517,38 0.467,39 1.2261,40 3.5125,
 94   41 1.2804,42 97.0508,43 0.5308,44 0.5308,45
      0.5308,46 0.2231,47 0.2258,48 0.9147,49 0.4275,50 0.4490,
 95   51 0.8044,52 5.3735,53 5.70199,54 0.17727,
      55 0.025,56 0.3558,57 2.1584,58 2.1528,59 2.2786,60 3.1741,
 96   61 4.9079,62 4.3092,63 0,64 0,65 0,66 0,67
      0/;
 97   PARAMETER ADD(J) Added value /1 0,2 0,3 0,4 0,5 0,6 0,7 -25.351,8 -
      85.904,9 -135.222,10 0,
 98   11 0,12 0,13 0,14 0,15 0,16 0,17 0,18 -34.
      635,19 -86.349,20 -36.646,
 99   21 -33.032,22 -33.17,23 -42.049,24 -8.509,
      25 0,26 0,27 0,28 0,29 -24.922,30 -67.195,
100   31 5.495,32 -17.214,33 -34.495,34 5.37,35
      -103.689,36 -82.543,37 0,38 0,39 -41.596,40 0,
101   41 0,42 -13.668,43 -6.566,44 -6.566,45 -6.7,46 0,47 0,48 0,49 0,50 -0.074,
102   51 -19.95,52 0,53 0,54 -0.886,55 -9.373,56
      -6.566,57 0,58 0,59 0,60 0,
103   61 0,62 0,63 132,64 110.2,65 79.6,66 40.6,
      67 108.3,68 -10.4,69 -15.2,70 -20.3/;
104
105   PARAMETER CAP(J) Fixed capital /1 74,2 74,3 74,4 185.5,5 74.1,6 74.1,7
      74.1,8 32.2,9 32.2,10 32.2,11 32.2,12 32.2,
106   13 364.6,14 364.6,15 83.6,16 70.8,17 70.8,
      ,18 44.5,19 44.5,20 61.1,21 61.1,22 61.1,23 61.1,
107    24 160,25 160,26 33.7,27 191.3,28 69.6,
      29 561,30 839.2,31 762,32 519.4,33 636.2,
108   34 108,35  108,36 108,37 108,38 108,39
      108,40 22.7,41 73.4,42 101.6,43 345.4,
109   44 345.4,45 345.4,46 345.4,47 345.4,48
      18.4,49 91,50 164.3,51 49.1,52 216,53 216,54 80.8,55 167.1,56 167.1,
110   57 126.2,58 91.8,59 91.8,60 218.7,61 95.9,62 95.9,63 0,64 0,65 0,66 0,67 0/;
```

```
111
112
113
114     VARIABLES X(J),Y(J),Z;
115    POSITIVE VARIABLES X(J);
116     BINARY VARIABLES Y(J);
117
118
119

120              EQUATIONS
       ASSI(I),LIM1(J),LIM2(J),LIM3,S1,S2,S3,S4,S6,S7,S8,S9,S10,
121    S11,S12,S13,S14,S15,S16,S17,S19,S20,
122    S21,S22,S23,S27,S29,S30,OBJ;
123    ASSI(I).. SUM(J,A(I,J)*X(J))=E=0;
124    LIM1(J).. X(J)-B(J)*Y(J)=G=0;
125    LIM2(J).. X(J)-1000*Y(J)=L=0;
126    LIM3.. SUM(J,Y(J)*CAP(J))=L=10000;
127
128
129
130
131     S1.. Y("1")+Y("2")+Y("3")=L=1;
132     S2.. Y("7")+Y("4")+Y("5")+Y("6")=L=1;
133     S3.. Y("8")+Y("9")+Y("10")+Y("11")+Y("12")=L=1;
134     S4.. Y("14")+Y("13")=L=1;
135     S6.. Y("16")+Y("17")+Y("15")=L=1;
136     S7.. Y("18")+Y("19")=L=1;
137     S8.. Y("20")+Y("21")+Y("22")+Y("23")=L=1;
138     S9.. Y("25")+Y("24")=L=1;
139     S10.. Y("26")=L=1;
140     S11.. Y("27")=L=1;
```

```
141     S12.. Y("28")=L=1;
142     S13..Y("29")+Y("30")+Y("31")+Y("32")+Y("33")+Y("34")+Y("35")+
              Y("36")+Y("37")+Y("38")+Y("39")=L=1;
143     S14.. Y("40")+Y("41")=L=1;
144     S15.. Y("42")=L=1;
145     S16.. Y("43")+Y("44")+Y("45")+Y("46")+Y("47")=L=1;
146     S17.. Y("48")=L=1;
147     S19.. Y("49")+Y("50")=L=1;
148     S20.. Y("51")=L=1;
149     S21.. Y("52")+Y("53")=L=1;
150     S22.. Y("54")=L=1;
151     S23.. Y("55")+Y("56")=L=1;
152     S27.. Y("57")+Y("58")+Y("59")=L=1;
153     S29.. Y("60")+Y("61")+Y("62")=L=1;
154     S30.. Y("63")+Y("64")+Y("65")+Y("66")+Y("67")=E=3;
155     w1=1;
156     w2=1;
157
158    OBJ..Z=E=SUM(J,w2*SI(J)*X(J)/97,w1*ADD(J)*X(J)/135
         +ERI(J)*X(J)/335);
159    *OBJ.. Z=E=SUM(J,w2*SI(J)*X(J)/2210-w1*ADD(J)*X(J)/140159);
160    *OBJ.. Z=E=SUM(J,-w1*ADD(J)*X(J)/140159+ERI(J)*X(J)/85172);
161    *OBJ.. Z=E=SUM(J,-1*ADD(J)*X(J));
162    *OBJ.. Z=E=SUM(J,ERI(J)*X(J));
163    *OBJ.. Z=E=SUM(J,SI(J)*X(J));
164
165    F=4;
166    X.UP("63")=200*F;
167    X.UP("64")=40*F;
168    X.UP("65")=68.039*F;
169    X.UP("66")=72.165*F;
170    X.UP("67")=40*F;
```

```
171    X.UP("68")=575.765;
172    X.UP("69")=16.371;
173    X.UP("70")=2500;
174
175
176    MODEL   THESIS   /ALL/;
177
178    OPTION LIMROW=0;
179    OPTION LIMCOL=0;
180     OPTION MIP=CPLEX;
181      OPTION ITERLIM=60000;
182    SOLVE THESIS USING MIP MINIMIZING Z;
183

184     PARAMETER
              environmental
185           economy
186           safety;
187     environmental = SUM(J, ERI(J)*X.L(J));
188     economy = SUM(J, ADD(J)*X.L(J));
189     safety= SUM(J,SI(J)*X.L(J));
190     DISPLAY environmental    , economy,safety;


COMPILATION TIME     =        0.000 SECONDS      3 Mb  WIN222-145 Dec 21,
2007
```

THESIS

Model Statistics SOLVE THESIS Using MIP From line 182

MODEL STATISTICS

BLOCKS OF EQUATIONS	29	SINGLE EQUATIONS	192
BLOCKS OF VARIABLES	3	SINGLE VARIABLES	141
NON ZERO ELEMENTS	613	DISCRETE VARIABLES	70

GENERATION TIME = 0.000 SECONDS 4 Mb WIN222-145 Dec 21, 2007

EXECUTION TIME = 0.000 SECONDS 4 Mb WIN222-145 Apr 21, 2006

THESIS

Solution Report SOLVE THESIS Using MIP From line 182

S O L V E S U M M A R Y

MODEL THESIS OBJECTIVE Z

TYPE MIP DIRECTION MINIMIZE

SOLVER CPLEX FROM LINE 182

**** SOLVER STATUS 1 NORMAL COMPLETION

**** MODEL STATUS 1 OPTIMAL

**** OBJECTIVE VALUE 11.4207

RESOURCE USAGE, LIMIT	0.140	1000.000
ITERATION COUNT, LIMIT	265	60000

GAMS/Cplex Dec 21, 2007 WIN.CP.CP 22.2 031.034.041.VIS For Cplex 10.0

Cplex 10.0.1, GAMS Link 31

Cplex licensed for 1 use of lp, qp, mip and barrier, with 2 parallel threads.

Proven optimal solution.

MIP Solution:	11.420681	(265 iterations, 5 nodes)
Final Solve:	11.420681	(0 iterations)

Best possible:	11.420681
Absolute gap:	0.000000
Relative gap:	0.000000

---- EQU ASSI

	LOWER	LEVEL	UPPER	MARGINAL
1	.	.	.	.
2	.	.	.	0.141
3	.	.	.	0.173
4	.	.	.	.
5	.	.	.	.
6	.	.	.	0.514
7	.	.	.	.
8	.	.	.	.
9	.	.	.	0.301
10	.	.	.	.
11	.	.	.	.
12	.	.	.	.
13	.	.	.	.
14	.	.	.	.
15	.	.	.	.
16	.	.	.	.
17	.	.	.	0.590
18	.	.	.	-0.678
19	.	.	.	.
20	.	.	.	.
21	.	.	.	.
22	.	.	.	0.317
23	.	.	.	0.320
24	.	.	.	.
25	.	.	.	.
26	.	.	.	.

---- EQU LIM1

	LOWER	LEVEL	UPPER	MARGINAL
1	.	.	+INF	.
2	.	.	+INF	.
3	.	.	+INF	.
4	.	.	+INF	.
5	.	.	+INF	.
6	.	45.140	+INF	.
7	.	.	+INF	.
8	.	.	+INF	.
9	.	.	+INF	.
10	.	.	+INF	.
11	.	.	+INF	.
12	.	63.500	+INF	.
13	.	.	+INF	.
14	.	.	+INF	.
15	.	.	+INF	.
16	.	.	+INF	.
17	.	.	+INF	.
18	.	80.182	+INF	.
19	.	.	+INF	.
20	.	.	+INF	.
21	.	.	+INF	.
22	.	.	+INF	.
23	.	.	+INF	.
24	.	.	+INF	.
25	.	.	+INF	.
26	.	177.906	+INF	.

27	.	.	+INF	.
28	.	.	+INF	.
29	.	.	+INF	.
30	.	.	+INF	.
31	.	.	+INF	.
32	.	.	+INF	.
33	.	.	+INF	.
34	.	.	+INF	.
35	.	.	+INF	.
36	.	.	+INF	.
37	.	.	+INF	.
38	.	.	+INF	.
39	.	.	+INF	.
40	.	.	+INF	.
41	.	.	+INF	.
42	.	.	+INF	.
43	.	.	+INF	.
44	.	.	+INF	.
45	.	.	+INF	.
46	.	.	+INF	.
47	.	.	+INF	.
48	.	.	+INF	.
49	.	145.122	+INF	.
50	.	.	+INF	.
51	.	.	+INF	0.937
52	.	.	+INF	.
53	.	.	+INF	.
54	.	.	+INF	.
55	.	.	+INF	.
56	.	.	+INF	.
57	.	140.000	+INF	.
58	.	.	+INF	.

59 . . +INF .

60 . . +INF .

61 . . +INF .

62 . . +INF 0.035

63 . . +INF .

64 . 92.500 +INF .

65 . 145.122 +INF .

66 . 177.906 +INF .

67 . . +INF .

68 . . +INF .

69 . . +INF .

70 . . +INF .

---- EQU LIM2

LOWER LEVEL UPPER MARGINAL

1 -INF . . .

2 -INF . . .

3 -INF . . .

4 -INF . . .

5 -INF . . .

6 -INF -887.360 . .

7 -INF . . .

8 -INF . . .

9 -INF . . .

10 -INF . . .

11 -INF . . .

12 -INF -914.000 . .

13 -INF . . -0.531

14 -INF . . .

15 -INF . . .

16	-INF	.	.	.
17	-INF	.	.	.
18	-INF	-839.818	.	.
19	-INF	.	.	.
20	-INF	.	.	.
21	-INF	.	.	.
22	-INF	.	.	.
23	-INF	.	.	.
24	-INF	.	.	.
25	-INF	.	.	.
26	-INF	-762.094	.	.
27	-INF	.	.	.
28	-INF	.	.	.
29	-INF	.	.	.
30	-INF	.	.	.
31	-INF	.	.	.
32	-INF	.	.	.
33	-INF	.	.	.
34	-INF	.	.	.
35	-INF	.	.	.
36	-INF	.	.	.
37	-INF	.	.	.
38	-INF	.	.	.
39	-INF	.	.	.
40	-INF	.	.	.
41	-INF	.	.	.
42	-INF	.	.	.
43	-INF	.	.	.
44	-INF	.	.	.
45	-INF	.	.	.
46	-INF	.	.	.
47	-INF	.	.	.

48	-INF	.	.	.
49	-INF	-804.878	.	.
50	-INF	.	.	.
51	-INF	-910.000	.	.
52	-INF	.	.	.
53	-INF	.	.	.
54	-INF	.	.	.
55	-INF	.	.	.
56	-INF	.	.	.
57	-INF	-840.000	.	.
58	-INF	.	.	.
59	-INF	.	.	.
60	-INF	.	.	-0.056
61	-INF	.	.	.
62	-INF	-800.000	.	.
63	-INF	.	.	-0.978
64	-INF	-840.000	.	.
65	-INF	-804.878	.	.
66	-INF	-762.094	.	.
67	-INF	.	.	-0.802
68	-INF	-1000.000	.	.
69	-INF	-1000.000	.	.
70	-INF	-1000.000	.	.

	LOWER	LEVEL	UPPER	MARGINAL
---- EQU LIM3	-INF	546.700	10000.000	.
---- EQU S1	-INF	.	1.000	.
---- EQU S2	-INF	1.000	1.000	.
---- EQU S3	-INF	1.000	1.000	.
---- EQU S4	-INF	.	1.000	.
---- EQU S6	-INF	.	1.000	.
---- EQU S7	-INF	1.000	1.000	.
---- EQU S8	-INF	.	1.000	.
---- EQU S9	-INF	.	1.000	.
---- EQU S10	-INF	1.000	1.000	.
---- EQU S11	-INF	.	1.000	.
---- EQU S12	-INF	.	1.000	.
---- EQU S13	-INF	.	1.000	.
---- EQU S14	-INF	.	1.000	.
---- EQU S15	-INF	.	1.000	.
---- EQU S16	-INF	.	1.000	.
---- EQU S17	-INF	.	1.000	.
---- EQU S19	-INF	1.000	1.000	.
---- EQU S20	-INF	1.000	1.000	.
---- EQU S21	-INF	.	1.000	.
---- EQU S22	-INF	.	1.000	.
---- EQU S23	-INF	.	1.000	.
---- EQU S27	-INF	1.000	1.000	.
---- EQU S29	-INF	1.000	1.000	.
---- EQU S30	3.000	3.000	3.000	.
---- EQU OBJ	.	.	.	1.000

---- VAR X

	LOWER	LEVEL	UPPER	MARGINAL
1	.	.	+INF	0.156
2	.	.	+INF	0.159
3	.	.	+INF	0.165
4	.	.	+INF	0.050
5	.	.	+INF	0.041
6	.	112.640	+INF	.
7	.	.	+INF	0.206
8	.	.	+INF	1.471
9	.	.	+INF	0.978
10	.	.	+INF	0.335
11	.	.	+INF	0.213
12	.	86.000	+INF	.
13	.	.	+INF	.
14	.	.	+INF	0.950
15	.	.	+INF	0.237
16	.	.	+INF	0.127
17	.	.	+INF	0.213
18	.	160.182	+INF	.
19	.	.	+INF	0.607
20	.	.	+INF	0.458
21	.	.	+INF	0.424
22	.	.	+INF	0.447
23	.	.	+INF	0.698
24	.	.	+INF	0.168
25	.	.	+INF	0.149
26	.	237.906	+INF	.
27	.	.	+INF	0.086
28	.	.	+INF	0.617

29	.	.	+INF	0.434
30	.	.	+INF	1.254
31	.	.	+INF	0.676
32	.	.	+INF	0.263
33	.	.	+INF	0.621
34	.	.	+INF	0.777
35	.	.	+INF	1.922
36	.	.	+INF	1.489
37	.	.	+INF	0.327
38	.	.	+INF	0.129
39	.	.	+INF	0.824
40	.	.	+INF	0.240
41	.	.	+INF	0.253
42	.	.	+INF	1.299
43	.	.	+INF	0.136
44	.	.	+INF	0.136
45	.	.	+INF	0.137
46	.	.	+INF	0.163
47	.	.	+INF	0.163
48	.	.	+INF	0.110
49	.	195.122	+INF	.
50	.	.	+INF	0.002
51	.	90.000	+INF	.
52	.	.	+INF	0.229
53	.	.	+INF	0.078
54	.	.	+INF	0.098
55	.	.	+INF	0.200
56	.	.	+INF	0.149
57	.	160.000	+INF	.
58	.	.	+INF	0.055
59	.	.	+INF	0.005
60	.	.	+INF	.

61 . . +INF 0.138
62 . 200.000 +INF .
63 . . 800.000 .
64 . 160.000 160.000 -0.499
65 . 195.122 272.156 .
66 . 237.906 288.660 .
67 . . 160.000 .
68 . . 575.765 0.077
69 . . 16.371 0.113
70 . . 2500.000 0.150

---- VAR Y

LOWER LEVEL UPPER MARGINAL

1 . . 1.000 EPS
2 . . 1.000 EPS
3 . . 1.000 EPS
4 . . 1.000 EPS
5 . . 1.000 EPS
6 . 1.000 1.000 EPS
7 . . 1.000 EPS
8 . . 1.000 EPS
9 . . 1.000 EPS
10 . . 1.000 EPS
11 . . 1.000 EPS
12 . 1.000 1.000 EPS
13 . . 1.000 -530.579
14 . . 1.000 EPS
15 . . 1.000 EPS
16 . . 1.000 EPS
17 . . 1.000 EPS

18	.	1.000	1.000	EPS
19	.	.	1.000	EPS
20	.	.	1.000	EPS
21	.	.	1.000	EPS
22	.	.	1.000	EPS
23	.	.	1.000	EPS
24	.	.	1.000	EPS
25	.	.	1.000	EPS
26	.	1.000	1.000	EPS
27	.	.	1.000	EPS
28	.	.	1.000	EPS
29	.	.	1.000	EPS
30	.	.	1.000	EPS
31	.	.	1.000	EPS
32	.	.	1.000	EPS
33	.	.	1.000	EPS
34	.	.	1.000	EPS
35	.	.	1.000	EPS
36	.	.	1.000	EPS
37	.	.	1.000	EPS
38	.	.	1.000	EPS
39	.	.	1.000	EPS
40	.	.	1.000	EPS
41	.	.	1.000	EPS
42	.	.	1.000	EPS
43	.	.	1.000	EPS
44	.	.	1.000	EPS
45	.	.	1.000	EPS
46	.	.	1.000	EPS
47	.	.	1.000	EPS
48	.	.	1.000	EPS
49	.	1.000	1.000	EPS

50	.	.	1.000	EPS
51	.	1.000	1.000	84.300
52	.	.	1.000	EPS
53	.	.	1.000	EPS
54	.	.	1.000	EPS
55	.	.	1.000	EPS
56	.	.	1.000	EPS
57	.	1.000	1.000	EPS
58	.	.	1.000	EPS
59	.	.	1.000	EPS
60	.	.	1.000	-55.845
61	.	.	1.000	EPS
62	.	1.000	1.000	6.929
63	.	.	1.000	-977.778
64	.	1.000	1.000	EPS
65	.	1.000	1.000	EPS
66	.	1.000	1.000	EPS
67	.	.	1.000	-802.222
68	.	1.000	1.000	EPS
69	.	1.000	1.000	EPS
70	.	1.000	1.000	EPS

	LOWER	LEVEL	UPPER	MARGINAL
---- VAR Z	-INF	11.421	+INF	.

**** REPORT SUMMARY : 0 NONOPT

0 INFEASIBLE

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THESIS

E x e c u t i o n

---- 190 PARAMETER environmental = 85877.291

PARAMETER economy = 35479.291

PARAMETER safety = 1734.372

EXECUTION TIME = 0.000 SECONDS 3 Mb WIN222-145 Dec 21, 2007

USER: CS/IE 635, UW-Madison (Wright) G060329/0001AS-WIN

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**** FILE SUMMARY

Input C:\Documents and Settings\C O M P\Desktop\gh11safety_env_econ_F3.gms

OutputC:\Documents and Settings\C O M P\My Documents\gamsdir\projdir\gh11safety_env_econ_F3.lst