Development and Integration of Simple and Quantitative Safety, Pollution and Energy Indices into the Design and Retrofit of Process Plants

by

Mohammad Hossein Ordouei

A thesis

presented to the University of Waterloo

in fulfillment of the

thesis requirement for the degree of

Doctor of Philosophy

in

Chemical Engineering

Waterloo, Ontario, Canada, 2014

Author's Declaration

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.

I understand that my thesis may be made electronically available to the public.

Abstract

Currently, the main focus in a chemical process design is cost reduction and profitability. This approach results in high expenditure due to the generation of huge amounts of wastes, which in turn requires waste control stations such as wastewater treatment facility, incinerator and so on. In other words, in conventional design the waste reduction is carried out at the late stage of process design, sometimes referred to as the end of pipe treatment, which causes impacts on environment, inventory of hazardous chemicals, energy consumption as well as cost impacts on the process.

Due to all the above aspects, the impact of decision making is highest at the conceptual phase of a process design. However, this impact can be minimized by shifting the waste reduction from the late step of the process design to its early stage. There are several barriers for such shifting; the most important of which is the lacking of a methodology to be used as a screening tool at the conceptual design phase in order to select the inherently safer and the environmentally friendlier design.

The objective of this thesis is to develop simple and quantitative indices that can be employed in minimizing the adverse effects of material and energy emissions from chemical industries. Several improvements to existing methodologies for pollution minimization are given. These are based on waste reduction concepts and are applicable from the initial step of a process design to revamping of existing processes. A simple risk index for the evaluation of risks to the safety of chemical processes is also developed. The work provides indices for evaluation of potential environmental impacts as well as safety risks of a chemical process in order to reduce the hazardous wastes generation and energy consumptions as well as safety risks reduction while maintaining the process throughput and profitability.

This research offers new methodologies, which have significant contributions in sustainability development by providing new and simple indices to be employed at initial step of a chemical process design with minimum available process data for the evaluation of energy impacts of the process on the environment and at the same time for the assessment of the risks to the chemical process.

These new indices are combined with the well-known WAR algorithm to offer a composite index to help investors, regulators and also process designers to select the sustainable design from other process design array. The new methodology uses Key Process Index (KPI) for ranking purposes merely from technical point of view. Even when two or more sustainable processes are concerned, the composite index can find the inherently safest, environmentally friendliest process without trade off with process economy and profitability. So, the new indices can be renamed as "Must Know Composite Indices" for chemical process designers. These Must Know Composite Indices are illustrated on several case studies and are proven to be effective tools on several fronts such as:

1.   As screening tools for investors/owners who need not be experts in chemical, environmental or safety engineering. They usually receive a bunch of proposals after advertising a tender for a new project or retrofitting an existing chemical process plant. The utilization of the Must Know Composite Indices will allow them to enter the available process and economic and calculate all indices, rank the proposals and recommend the top ranked processes.

2.   As screening tools for process designers: A process engineer will get into the insight of design alternatives in terms of environmental protection, inherent safety and energy impacts of the alternative designs. Then, s/he will make necessary changes to make a sustainable design at minimum impacts of decision at conceptual design stage.

3.   As a coding system for process design similar to piping codes. For instance, KPI 1234 (234, 500, 500); where 234, 500 and 500 are the contribution of energy impacts, environmental impacts and safety risks to the process design, respectively.

4.   As an incentive/penalty tool for the government in order to penalize plants who are harmful to the environment and society or to, otherwise, provide stimulus programs.

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List of Symbols

a	Cost Estimation Parameter
A	Equipment Size for Cost Analysis
b	Cost Estimation Parameter
α	Kinetic Coefficients for the Intensity of Intermolecular Interactions
α_i	Weighting Factor (Site effective) the unit of PEI per mass
C	Total Capital Cost
C_A	Concentration of Compound A (mol/lit)
C_e	Equipment Cost (U$)
C_{H2}	Concentration of Hydrogen (mol/lit)
C_i	Concentration of Hydrocarbons and Oxygenates in a Blend
C_P	Equipment Cost (U$).
D^n	Dipole Moment (n = Empirical Kinetic Coefficient)
ΔH_{Comb}	Enthalpy of Combustion (kCal/kgmole Carbon)
E	Activation Energy (j/mol)
η_k	Efficiency of Equipment k (%)
f_i	Frequency of accident for component i (# of accidents/year)
H_i	Hazard effects of chemical i, (#people affected/ton of chemical)
I_{System}	Quantity of PEI Inside the Chemical Process System (PEI)
$I_{in}^{(t)}$	Rate of Total PEI Existing in the Input Streams (PEI/h)
$I_{in}^{(NP)}$	Rate of PEI Existing in the Input Waste Streams (PEI/h)
$I_{j,in}^{(t)}$	Rate of Total PEI Existing in Stream j in the Input Streams (PEI/h)
$I_{j,in}^{(NP)}$	Rate of PEI Existing in Stream j in the Input Waste Streams (PEI/h)

$\dot{I}_{out}^{(t)}$	Rate of Total PEI Existing in the Output Streams (PEI/h)
$\dot{I}_{out}^{(NP)}$	Rate of PEI Existing in the Output Waste Streams (PEI/h)
$\dot{I}_{j,out}^{(t)}$	Rate of Total PEI Existing in Stream j in the Output Streams (PEI/h)
$\dot{I}_{j,out}^{(NP)}$	Rate of PEI Existing in Stream j in the Output Waste Streams (PEI/h)
$\dot{I}_{gen}^{(t)}$	Rate of Total PEI Generated in the Process (PEI/h)
$\dot{I}_{gen}^{(NP)}$	Rate of PEI of Waste Generated in the Process (PEI/h)
$\dot{I}_e$	Emissions rate of carbon dioxide to the atmosphere ($kgCO_2$/h)
$\dot{I}_{J,k}$	Emission Rate of Gas j (CO_2, SO_2, NO_2) in Equipment k (kg j/h)
K	Al-Sharrah's Risk Index (# affected people/year)
K_1, K_2 and K_3	Correlation Parameters for Cost Estimation
k_{ref}	Frequency Factor at a Reference Temperature
λ	Eigenvalue
M_j	Maximum one Month Inventory of Stream j (tonne)
MW_C	Atomic Weight of Carbon (kg C/kgmole Carbon)
MW_{CO2}	Molecular Weights of Carbon Dioxide (kg CO_2/kgmole)
MWi	Atomic Weight of Atom i (kg i/kgmole i)
MW_j	Molecular Weights of Emitted Gas j (kg j/kgmole)
$\dot{M}_{j,out}$	Mass Flow Rate of Stream j in Output Streams (kg/h)
n	Cost Estimation Parameter
$\dot{P}_n$	Production Rate of Product n
$\dot{Q}$	Heat Flow or Energy Consumption (kCal/h)
$\dot{Q}_{i,k}$	Heat Flow/Energy Consumption by Equipment k Due to Combustion of Component i (kCal/h)
R	General Gas Constant
$(R.I)^W$	New Risk Index (superscript W denotes waste)- # affected people/year

$(R.I)^W$	New Risk Index (superscript P denotes product)- # affected people/year
S	Equipment Size for Cost Analysis
$(\text{Score})_{k,i}$	Relative Score of Component k for an Impact Category i
$\langle(\text{Score})_k\rangle_i$	Arithmetic Average Score of all Components for the Impact Category i
σ_i	Standard Deviation of all Component Scores in Impact Category i.
ψ_k	Overall PEI of Component k
ψ_{ki}^S	Specific PEI of Component k for an Impact Category i (PEI/kg)
T_{ref}	Reference Temperature (K)
x_c	Mass Fraction of Carbon Component in the fuel
x_i	Mass Fraction of Component i (C, S, N) in fuel
$x_{i,j}$	Mass Fraction of Hazardous Chemical i in Stream j (Safety Risk Index)
x_{kj}	Mass Fraction of Component k in Stream j (WAR Algorithm)

List of Abbreviations

AHP	Analytical Hierarchical Process Methodology
AP	Acidification Potential
ATP	Aquatic Toxicity Potential
ATR	Auto Thermal Reforming
B.L.	Battery Limit of a Process Plant
CFD	Cash Flow Diagram
CI	Consistency Index
CR	Consistency Ratio
CSTR	Continuous Flow Stirred Tank Reactor
EIA	Energy Information Administration
EIP	Eco-Industrial Park
EPA	US Environmental Protection Agency
FCI	Fixed Capital Cost
FTP	Fischer-Tropsch Process
FTS	Fischer-Tropsch Synthesis
GWP	Global Warming Potential
HEN	Heat Exchange Network
HFO	Heavy Fuel Oil
HTPE	Human Toxicity Potential by Exposure
HTPI	Human Toxicity Potential by Ingestion
HV	Heat Value of a Fossil Fuel (kCal/kg Fuel)
HYSYS	A Process Simulation Software from Hyprotech Company
IRCHS	Indiana Relative Chemical Hazard Score Methodology
ISD	Inherently Safer Design

KPI	Key Performance Indicators
LCA	Life Cycle Assessment
MEN	Mass Exchange Network
NREL	National Renewable Energy Library
ODP	Ozone Depletion Potential
ON	Octane Number
PCOP	Photochemical Oxidation Potential
PEI	Potential Environmental Impact
PFD	Process Flow Diagram
PFR	Plug Flow Reactor
POX	Partial Oxidation
RI	Random Index
SEE	Safety-Energy-Environment (New Sustainability Indices)
SMR	Steam Methane Reforming
Sp. Gr.	Specific Gravity
TCI	Total Capital Cost
TTP	Terrestrial Toxicity Potential
UTN	University of Tennessee Methodology
WAR	WAste Reduction Algorithm
WAR GUI	WAste Reduction Graphical User Interface Software
WCI	Working Capital Cost

Chapter 1

INTRODUCTION

Climate change, acid rain, global warming, and waste production are familiar to most families around the world as threats to environment. Protection of the environment has become one of the major concerns of scientists, engineers, environmentalists, governments and even every single member of the human society. The rationale underlying this trend mainly includes the improvement of human's and animal's health, reducing safety issue, preservation of clean environment and natural resources for the next generation, saving money and resources, and above all, following and respecting the law (or policy).

Due to huge consumption of raw materials and generation of new products in chemical plants and refineries, they are addressed as the main sources of pollution generation. Even a low percentage of non-products yield some tens of tonnes of wastes production, which are unwanted not only due to economic considerations, but also for depletion of natural resources, increasing of hazardous chemicals as disposal to the environment and so forth.

Many attempts have been made to address such waste materials in many different ways in order to reduce their impacts on the environment such as identification and classification of chemical wastes, source classifications, development of emission profiles, wastes segregation (inventory), the fates of pollutants, and finally pollutant treatment. The main focuses have been on chemical process plants. The wastes generated in such plants usually are referred to as hazardous wastes.

The traditional approach to alleviate the waste reduction within a process plant contains four remedial actions based on the priority from a waste management point of view:

1. Source reduction including design or equipment modification and raw materials substitution.

2. Recycling and reusing solvents, process water, by-products and wastes inside the process plant. This task may need to employ separation techniques.

3. End-of-pipe treatment through addition of a new set of equipment as waste water treatment plant to reduce toxicity and/or the volume of downstream wastes. This new plant may employ biological treatment, chemical precipitation, incineration, flocculation, burning pit in refineries etc.

4. Disposal which is usually concerned with off-site waste handling and shipment facilities entitled under waste management facilities.

However, technological constraints remained the huge barriers to perform hazardous treatment satisfactorily. Hence, there is a need to minimize waste generation in the early design stage of a chemical process. The integration of pollution prevention into a chemical process in the design stage was first revealed by El-Halwagi and Manousiouthakis (1989) by introducing the concept of HENs (Heat Exchanger Networks) followed by the application of MENs (Mass Exchange Networks). Although in both techniques the wastes are minimized at the preliminary step of process design instead of utilizing end-of-pipe treatments, neither technique is concerned with the pollution impacts on the environment.

Hilaly and Sikdar (1994) introduced WAR (WAste Reduction) algorithm for the first time. They proposed the concept of pollution balance equation in a process flow sheet to introduce WAR algorithm as a systematic method of waste reduction of a process. Pollution balance equation is a methodology that enables a process engineer to follow a contaminant in an

entire process plant (similar to material balance). Chemical wastes can be produced in any steps of a chemical life cycle; e.g. raw material, production, product distribution, product transportation, disposal etc; however, only the manufacturing (process) step is concerned with the WAR algorithm. This methodology guarantees an inherently less polluting process design and eliminates or at least reduces the cost of pollution control devices used in conventional process designs.

Today, the approach in process systems engineering focuses on "inherently safer process design" (Heikkilä et al., 1996; Khan et al. 1998c; Khan and Amyotte, 2002; Shariff et al. 2006; Leong and Shariff, 2008; Cordella et al., 2009; Shariff and Leong, 2009; Hendershot, 2011), which means reducing or eliminating hazards associated with materials used and operations, and this reduction or elimination is a permanent and inseparable part of the process technology (Kletz, 2001).

Potential environmental impact (PEI) balance is an amendment to WAR algorithm methodology, which estimates the adverse influences of hazardous chemicals of a process on the environment (Cabezas and Young, 1999). One of the definite advantages of PEI compared to other methodologies is that it highlighted that the impacts of a substance at a low flow rate on the environment might be higher than the impacts of other chemicals at higher flow rate.

The initial stage of a chemical process design, including refinery and petrochemical plants, is crucial not just because of choosing right location, transportation system, raw material availability, the cost and the marketability of final products. Although these factors are all important to design a profitable process, there are other essential features which have to be considered at the conceptual design stage; i.e. protection of environment from the impacts of materials and energy used in a process plant and the risks associated with the process design.

Unfortunately, the last two issues have been overlooked in almost all of conventional process designs leading to the generation of large amounts of waste and pollutants (EPA, 2012a). It turns out that ignorance of these factors will increase the design expenditure due to needing control stations such as waste water treatment facilities, incinerators and so on. These control stations do not eliminate the pollutants or wastes but decrease/dilute pollutions generated in a process plant.

This is the reason why the impact of a decision is high at early stage of a chemical process design compared to the rest of a project stages (Figure 1.1). Basically, a process design consists of three main steps: "Basic Design", "Front End engineering" and "Detailed Design".

The first step in basic design (conceptual design) contains activities such as process root, material compositions, block flow diagram (BFD), and chemical reactions. This is followed by the design criteria where one aims at determining the standards and project specifications, project limitations, and process philosophy. Finally, for the basic design step the engineer produces process flow diagram, piping and instrument diagram and material and energy balances. In this thesis, we will focus on the first step in the design process and seek to incorporate sustainability metrics to improve the design methodology.

A chemical process plant is built in three distinctive steps before commissioning: Engineering, Procurement and Construction (EPC). All of these phases are accomplished on the basis of "conceptual design". A wisely conceptualized design has influence on waste minimization, prevention of pollution emission, risk reduction, and decreasing of capital costs. On the other hand, it results in an increase in profitability. Lewin (2004) has depicted the impacts of decisions and the percentage of total budget versus the project life time (Figure 1.1).

Industrial pollutants have adverse effects on both human health and the environment such as fish degeneration in lakes and devastation of trees in forest (NRC, 1989). For instance, CO_2 causes of greenhouse effects and global warming leading to a decline in agricultural productivity and coastal flooding.

On the other hand, heat and energy generation from fossil fuels to supply the energy demands in industrial and municipal sectors result in emissions of tons of pollutants to the environment in the forms of CO_2, NO_x, SO_x gases.

Above all, the catastrophic accidents in chemical and refinery plants; such as Bhopal factory in India in 1984 leaving tens of thousands of people dead or injured from toxic gases, as well as Louisiana oil spill in Gulf of Mexico in April 2010 resulting in killing of 11 workers and several months oil leaking unrestrained into the ocean, have made the public anxious about chemical industries. There are much more cases reported in public media or websites every day. The quest is to minimize these accidents specifically in chemical processes, but how? In this research an attempt will be made to answer to this very important question.
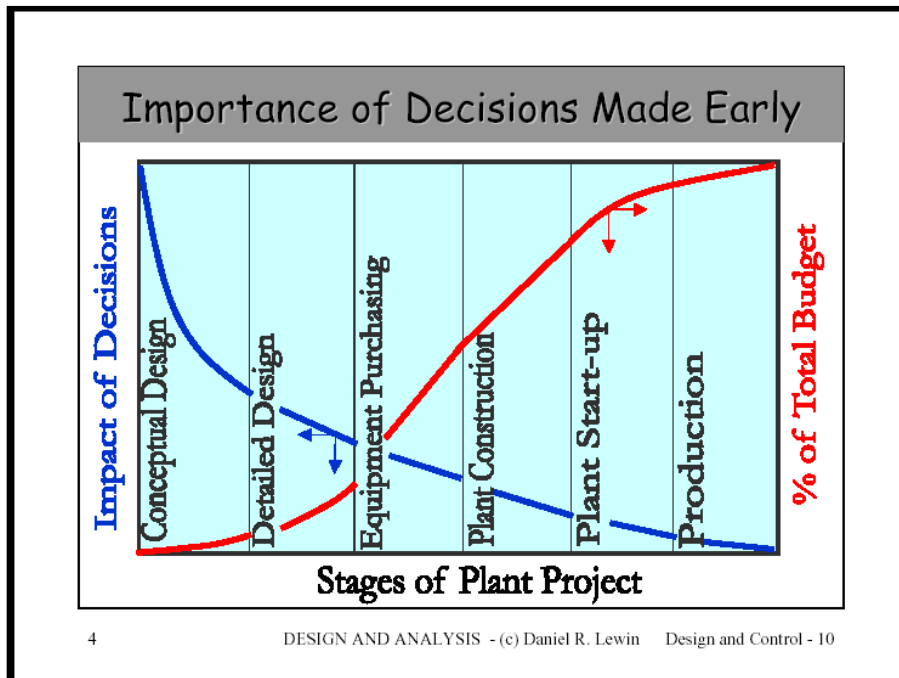
Figure 1.1. Process project progress vs. budget and project impacts diagram (Lewin, 2004).

The concepts of Potential Environmental Impacts (PEI), WAste Reduction (WAR) algorithm, and Inherently Safer Design (ISD) introduced earlier have been extensively used in this research.

This thesis introduces new composite indices as a new methodology, and integrates them into conceptual stage of chemical process design resulting in environmentally friendlier and inherently safer process design without compromising process profitability.

The new composite indices presented in this thesis have wide variety of applications including research, sustainable process design, operation, retrofitting, energy impacts evaluation, safety risks assessment to name a few.

The new sustainability indices consist of two categories and three fundamental methodologies, which require minimum available process data:

1) Environmental impacts assessment, which employs two methodologies:
    a) WAR algorithm, which estimates the PEI of materials used in chemical processes.
    b) New simple and quantitative methodology for the estimation of energy impacts on environment.

2) A developed new simple and quantitative methodology for Inherently Safer Design (ISD).

Several case studies have been provided in the present research to examine the afore-mentioned broad applicability; such as Product Design: Gasoline Blends (research), Eco-Industrial Park (Sustainable EIP design), Hydrogenation of Unsaturated Hydrocarbons and the Chlorination of Methane (Sustainable Process Design) and Solvent Recovery (Sustainable Development-Cradle-to-Cradle Design).

The organization of the present thesis is as follows:

In chapter 2, a literature review consisting of a historical approach to waste reduction and sustainability are provided. The most important sustainable methodologies used in chemical process industries including AIChE Sustainability Index, waste reduction and energy impacts on the environment as well as inherent safer process design methodologies are discussed in details.

In chapter 3, the waste reduction or WAR algorithm and its amendment Potential Environmental Impacts (PEI) are presented since they are used in this research as a strong sustainable method in early stage of a chemical process design.

In chapter 4, a new methodology for energy impacts assessment at early stage of a process design is developed and applied to two processes; i.e. the chlorination of methane and the hydrogenation of unsaturated hydrocarbons, to illustrate their screening capabilities in determining of sustainable design.

In chapter 5, a new methodology for inherently safer design (ISD) is introduced followed by above two case studies (chlorination and hydrogenation processes). The inherently safer design concept is new in process design. The new ISD is a strong tool to be used at conceptual design phase in lack of detailed process data.

Chapter 6 deals with the application of several metrics including new risk assessment methodology on new product design. In this chapter different gasoline blends have been simulated by HYSYS to examine octane number, mileage loss, PEI, risks to process safety (except energy impacts, which is set to zero) as the major factors of all blends, which affect process performance. This chapter illustrates how such integration can lead to a better product development by comparison of the metrics through Analytical Hierarchical Process (AHP), which is a multi-criteria decision-making methodology. The AHP is employed when metrics oppose one another meaning that each one favors to one design alternative so that it is difficult to select the best choice. The outcome of the application of the AHP on major metrics is called Key Performance Index (KPI) representing the technical evaluation of the process. Then, the case study is accomplished by cost-KPI (analogous to cost-benefit) analysis resulting in an economic, environmentally friendly, inherently safe and economic product (gasoline blend) design.

In chapter 7, the new methodology (composite indices) consisting of the main metrics; i.e. the material and energy impacts as well as the safety risk indices, are integrated into the conceptual design step. Two case studies have been provided: "Sustainable Development" (Cradle-to-Cradle design) through thinner recovery process design and the hydrogenation of unsaturated hydrocarbons. The case studies probe that the composite indices are strong screening tool for choosing the best design among other alternatives. The case studies probe how the new composite indices help a process designer design/choose sustainable processes among other alternatives.

Chapter 8 deals with an Industrial Park design where the presented new indices are not only applicable to chemical process design, but also to industrial parks. A set of standalone industrial and agricultural wastes are considered for the calculations of the impacts of wastes

on the environment as well as the evaluation of associated safety risks. Then, the individual wastes are used to design an eco-industrial park (EIP) for the waste recovery followed by the calculation of associated potential environmental impacts and safety risks, the results have been compared in order to measure the pollution prevention and risk reduction quantitatively through EIP design and to demonstrate how the new indices facilitate such quantification and decision-making.

Chapter 9 concerns with the necessary conclusions and future work and summarizes the benefits of the new composite indices and future opportunity to take more benefits out of the new methodology.

There are also two appendices at the end of the thesis: A. Profitability Analysis; B. PEI classification.

Chapter 2

Up to the 1970s, the end-of-pipe treatment was the only solution to meet environmental protection demands. This task was carried out by installation of pollution control systems such as waste water treatment and incinerator in chemical manufacturing plants. The incinerator is still widely being used in chemical industries in order to transform pollutants to benign compounds.

There has been little attention to hazardous wastes until 1976 when the Resource Conservation and Recovery Act (RCRA) was endorsed by the US congress and after detection of severe damages to underground water as a source of drinking water. The Act briefly states that the operating and construction companies have to handle their hazardous wastes at their job site facilities. RCRA largely covers the waste discharge requirements introduced by "Clean Air Act" (CAA) and "Clean Water Act" (CWA) such as removal of hazardous species from air emissions and also from water disposal; however, neither of CAA or CWA guarantees that the final disposals are not ailing to the environment. Moreover, RCRA was not directly concerned with hazards already discharged to the environment or stored in abandoned sites. Therefore, Comprehensive Environmental Response, Compensation, and Liability Act (CERCLA, sometimes referred to as Superfund) was elaborated to overcome the issues concerned with these sites (Davis and Masten, 2004a). Other in-process compounds, which are not covered by RCRA, have been addressed by other

Acts such as Toxic Substances Control Act, regulated pesticides under Federal Insecticide, Fungicide, etc.

In the 1980s, therefore, the main focus was on procedures for recycling or recovering of hazardous wastes to reuse in the plants or to sell. This task was fulfilled by employing separation methods; these technologies have constraints as shown in Table 2.1.

Due to lack of achievements in fulfillment of RCRA, in 1984 US Congress enacted an amendment to augment the scope of RCRA called as HSWA (Hazardous and Solid Waste Amendment). The scope includes (Davis and Masten, 2004a):

- Waste minimization as a preferable method of hazardous waste management.
- Prohibition of hazardous wastes disposal to the land. The United States Environmental Protection Agency (EPA or USEPA, established in 1970) was responsible for preparation of land disposal standards.
- Providing standards for land disposal facilities including new technologies.
- Preparation of prerequisite for small scale waste producers.
- Preparation of standards for underground storage facilities by EPA.
- Assessment of the standards for urban solid trashes landfills as well as improvement of monitoring prerequisites by EPA.

The approach of the US federal government to hazardous waste management is based on the following five foremost activities whose necessary guidelines are disseminated by EPA (Davis and Masten, 2004a):

- Hazardous waste classification.
- Recording (manifesting) system.
- The afore-mentioned federal standards to be ensued by relevant sectors; e.g. generators, transporters, treatment facilities, store, or hazardous waste disposal.
- Putting the federal standards for facilities into effect via a permit program.
- Allowing the state programs to operate instead of federal program.

Table 2.1: Classification of pollution treatment, constraints and required technologies (adopted from Cohen and Giralt, 1996).

Classification of Pollution	Required Technologies	Constraints
Fugitive emissions	Identification of low leak rates	Dispersed sources Complex mixtures Measurement of low leak rates
Stack emission	Source reduction Improved gas cleanup (e.g. catalytic treatment, reactive membranes, ESP) Remote detection of pollutants	Removal of trace quantities of pollutants Online monitoring
Aqueous streams	Selective separation and recovery	Complex mixtures Low concentration
Chemical processes (reactors, feed treatment units, furnaces, etc.)	Use of alternative non-hazardous raw materials and catalysts Selective reaction pathways Plant optimization with environmental constraints	Byproducts Excessive use of water
Separation units	Alternate non-hazardous solvents Optimize separation sequences	Hazardous chemical solvents Excessive use of water
Sorption processes	Selective separation Cost-effective regeneration Recovery	Competitive sorption High regeneration cost
Membrane processes	Selective separation and recovery Reactive membranes	Membrane fouling
Destruction		
Thermal treatment		Generation of air toxics, sludge and ashes Operational upsets
Wet oxidation		Generation of byproducts Limited catalyst life
Biodegradation		VOC emissions Environmental stress on microorganisms

Environmental laws in the USA are enacted by the US federal officials. They instruct the dedicated organizations to prepare regulations in order to fulfill the requirements by law. The EPA is a major organization who develops and implements environmental regulations.

Federal laws are referred to as Congress' "Acts" and have titles and codes. The EPA develops rules and regulations based on the Acts (Davis and Masten, 2004a).

In this work, we follow the EPA's standards for environmental protection since its regulations are globally accepted and its databases are regularly updated.

2.1 METHODOLOGIES FOR WASTE REDUCTION AND SUSTAINABLE DEVELOPMENT

Waste reduction or minimization has more limiting applications than pollution prevention. The former encompasses **avoidance, reduction or elimination** of waste generation by on-site process; e.g. recovering or recycling in the plant (OTA, 1987), while the latter has a wider definition and includes both on-site and off-site recovering and recycling processes (Lave et al., 1994). A process is more desirable for investors when it produces fewer wastes and accomplishes with cheaper waste treatment schemes (El-Halwagi, 1997). The main concern of the traditional approach to waste management is waste control techniques including end-of-pipe treatment (usually by separation techniques) and disposal. However, recently the waste reduction is accomplished by "source reduction", "recycling" and preferably in early stage of process design.

The integration of pollution prevention into a chemical process in the design stage was first revealed by El-Halwagi and Manousiouthakis (1989) by introducing the concept of HENs (Heat Exchanger Networks). The HENs technique is employed for designing of total and individual heat exchange surfaces in a process design in order to minimize energy consumption. The idea behind HENs design is network temperature pinch, which represents a bottleneck to heat recovery. They also introduced MENs (Mass Exchange Networks) methodology for pollution prevention within a process during design step. Then, optimization techniques were utilized for HENs and MENs in order to optimize waste reduction efficiency (El-Halwagi, 1997).

Although in both techniques the wastes are minimized at the early design stage of a chemical process instead of utilizing end-of-pipe treatment, neither technique was concerned with the pollution impacts on the environment. For instance, the emission of methane at 400 kg/h and carbon dioxide at 1,000 kg/h is both undesirable, but the question is which one is worse in terms of detrimental effects on the environment?

Other methodologies, which are important at the initial step of a process design, are the methodology provided by the University of Tennessee (UTN) and Indiana Relative Chemical Hazard Score (IRCHS) methodologies (Davis, 1994). The former emphasizes on aquatic ecosystem and is less concerned with the potential impacts on air such as global warming or ozone depletion. This disadvantage makes UTN an imperfect method. IRCHS team has developed the UTN methodology. The IRCHS algorithm includes hazard towards the environment such as air quality, potential for soil and groundwater contamination, and stratospheric ozone depletion. IRCHS has also expanded the algorithm to assign a hazard value for the chemicals based on the chemical hazards towards the factory workers. The two environmental and workplace employee's hazard values are then combined and the average of the two becomes the combined hazard value for the chemical (for more information please refer to the Clean Manufacturing Technology Institute (CMTI) website: www.ecn.purdue.edu/CMTI/IRCHS).

Despite several advantages mentioned above, IRCHS methodology has also considerable disadvantages that make it inappropriate to be used in conceptual design such as:

- Comprehensive

- Score based

- Both safety and environmental impacts are evaluated as environmental issues

- Hazard based (not risk) based. So, it doesn't say how likely an accident may happen?

2.2 SUSTAINABLE DEVELOPMENT

Sustainable development is defined by Microsoft Encarta (2004) as: "economic development maintained within acceptable levels of global resource depletion and environmental pollution". It is also defined as the development, which satisfies the existing and forthcoming demands without compromising impending needs (Xu, 2004).

AIChE Institute for Sustainability has defined sustainability as (Cobb et al., 2007): "The path of continuous improvement, wherein the products and services required by society are delivered with progressively less negative impacts upon the Earth."

As mentioned earlier, over decades the trend of regulators has been the prevention of pollution emissions to protect the environment. Today, the main objective of environmental protection strategy is to inspire sustainable development (Heijungs et al., 1992). Hence, the sustainable development can be achieved only when economic design and environmental protection are coined closely.

Chemical engineering has a substantial talent to achieve sustainability (Batterham, 2006). Thus, the objective of a sustainable chemical process is to satisfy stakeholders, regulators and society by its profitability and social responsibility while generating lower potential environmental impacts and wastes without compromising products quality. Such designs use minimum raw materials and minimum energy.

There are several methods for sustainability measurement. Below, the most important methods and a brief explanation for each one are presented:

2.2.1 Dow Jones Sustainability Indices:

Dow Jones (2013) has introduced corporate sustainability in order to guarantee long term benefits for stakeholders based on economic, environmental and social developments. The corporate sustainability encompasses indices with business approach to integrate company's

policy and management to sustainability products and services as well as sustainability reduction in costs and risks in a quantifiable manner.

These indices result in high levels of aptitude in different areas such as strategy, financial, customer and product, governance and shareholders, and human resources.

2.2.2   FTSE4Good Environmental Leaders Europe 40 Index:

FTSE4Good Environmental Leaders Europe 40 is a European-based index which ascertains leading companies involved in environmental practices and has the following characteristics:

- It is used for retail and institutional investment products

- It is a guideline for investors who look for European companies demonstrated for best practice environmental management

- It provides environmental risk reduction within portfolios of those companies

- It gets the most out of strong environmental management, examples include eco-efficiencies and also improved brand image

- Actively encourage companies to be more responsible

2.2.3   AIChE Sustainability Index (SI):

The above mentioned sustainability indices have several advantages; however, they are either concerned with society or have a business approach. There are some missing key sustainability considerations in those indices, which limits their applications to chemical processes.

In order to overcome this gap, AIChE's Work Group has set new metrics to form their Sustainability Index or SI (Cobb et al., 2007). SI has the following advantages:

- Application to chemical process industries; i.e. operation, engineering, research etc., unlike conventional sustainability indices.

- Rather determined to data-collection in order to improve innovation than checklist motivated.

- An effective tool for monitoring a company's total business lines.

The main objectives of AIChE index include:

- Empower internal chemical and other engineering skills to technically maintain sustainability.

- Contribution to both the wider role of engineering skill and the sustainability

- Recording the sustainability data.

AIChE SI has used data from the world's largest chemical companies identified in Fortune Global 500 for the initial calculations of their index. The index determines the operation of a delegate set of international chemical companies compared to the similar plants in the US. It provides a tool for the measurement of plant overall sustainability performance. AIChE SI has seven elements:

- Strategic commitment to sustainability,
- Safety performance,
- Environmental performance,
- Social responsibility,
- Product stewardship,
- Value-chain management, and
- Innovation

Each element contains some sub metrics. For instance, safety performance has two metrics; "process safety" and "employee safety" while environmental performance has three metrics; "resource use", "waste and emissions" and "compliance history". Each metric has a weight based on the industry under investigation. Also, each index has either a quantitative score

such as US$/sales for greenhouse gas emissions or a qualitative one such as reported sustainability in R&D.

The data sources include company's annual sustainability report, industrial performance rankings, government's pamphlet and newsletters. The metrics are scaled from 0~7 and depicted on a spider chart as shown in Fig. 2.1 (Cobb et al., 2007).

Figure 2.1 AIChE sustainability Index and its benchmarks for comparison of chemical companies in Global Fortune 500 (Cobb et al., 2007).

As said earlier AIChE SI has seven elements for the assessment of a company performance and uses the open sources of representative companies for the evaluation. Two elements among the others are concerned with the objective of my thesis; i.e. (a) Environmental performance and (b) Safety performance (Cobb et al., 2009):

(a) Environmental performance: It is based on the following metrics (Figure 2.2):

Resource use: Energy intensity, chemicals consumption, usage of renewable energy, water and materials.

Greenhouse Gas Emissions (GGE) and Other Emissions: GGE intensity, other emissions include: air, wastewater and hazardous wastes.

Compliance Management: Environmental capital venture and management.

Figure 2.2 shows the metrics associated with environmental performance element by bars ranging from 0 for worst case to 7 for ideal situation, asterisks denote the average scores for each factor.
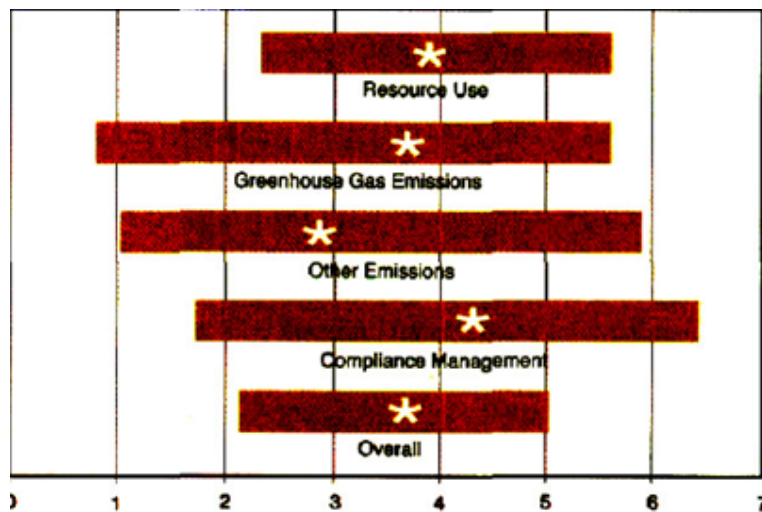
Figure 2.2 Environmental Performances (Cobb et al., 2009).

(b) Safety performance: This includes (Figure 2.3):

Employee Safety such as injury rates including day away from work.

Process Safety including accident trend, normalized values based on the number of employees, the number of incidents, etc.

Plant Security: It encompasses security management system proposed by Responsible Care Program.
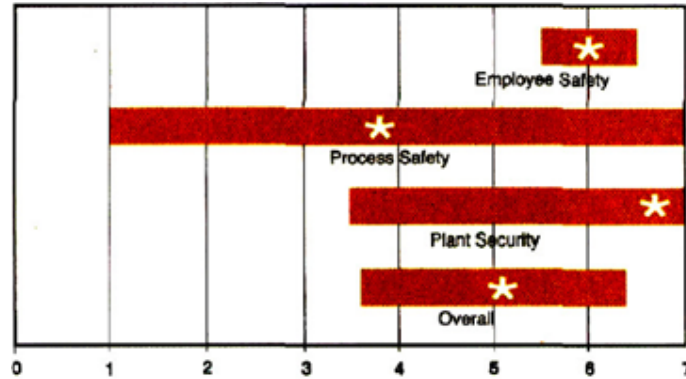
Figure 2.3 Safety Performances (Cobb et al., 2009).

Other elements are treated in the same manner as mentioned above. As an interesting conclusion, the more the company's revenue is, the higher score the company gains. The rationale behind this is that the largest companies are more committed to sustainability development.

Originally, the companies participated in AIChE SI were: Air Products, Akzo Nobel, Ashland, BASF, Celanese, Dow, DuPont, Eastman, Praxair, and Rohm & Haas.

2.2.4   Life-cycle analysis (LCA) methodology:

Life-cycle analysis (LCA), sometimes referred to as Cradle-to-Grave analysis, is one of the most commonly used methodologies developed to estimate the impacts of goods, processes or services on the environment within its entire lifetime. It is used as an effective tool to improve the sustainability and quality of the products within a company and also to compare alternative processes to determine which one has the least life cycle impact on the environment.

LCA is a method of evaluation of environmental aspects and the potential impacts of a product, process or service on the environment. This is carried out by collecting the record of material and energy input and emissions to the environment, assessment of the potential

environmental impacts of the identified inputs and released and finally, construing the outcomes for decision-making (EPA, 2012b).

2.2.5   Waste reduction (WAR) algorithm (history and theory):

Hilaly and Sikdar (1995) proposed the concept of pollution balance equation of a process in a process flow sheet. They introduced WAR (WAste Reduction) algorithm as a systematic method of waste reduction in a process. Pollution balance equation (similar to material balance) is a methodology that enables a process engineer to track and follow a contaminant in an entire process plant. They also presented "pollution index" to make a quantitative measurements of pollutions generated in a chemical process and defined it as the pollution mass generated in a process per unit mass of product. The principle of pollution balance equation is similar to the conservation law and is valid for a process unit as well as an entire flow sheet. The pollution balance is calculated by using the process flow sheet in addition to thermodynamic data and kinetic data and then, a pollution index is determined. Other process alternatives are evaluated based on the determination of pollution indices. The calculations are repeated for other alternatives to find the least index. Thus, one typical usage of WAR algorithm is to compare alternative process designs to find out which one has the least impacts on the environment.

This method guarantees an inherently less polluting process design and eliminates or at least reduces the cost of pollution control devices used in conventional process designs.

WAR algorithm is a methodology developed to account for the evaluation of chemical waste generation and/or energy consumptions within a process plant as emissions into the air, water or land. It can be considered as a tool for environmental management system (EMS) in order to improve the quality of the practices within a company with respect to sustainable development.

2.3 POTENTIAL ENVIRONMENTAL IMPACT (PEI) THEORY

The concept of pollution balance was the foundation of potential environmental impact (PEI) balance. PEI balance was first developed by Young and Cabezas (1999) as an amendment to WAR algorithm. It indicates the quantitative impact of a contaminant in a process and determines the level of friendliness of the process to the environment. They also incorporated the energy used in a process into the environmental assessment and then calculated the PEI of materials and energy and related the indices to the level of environmental friendliness of a chemical process. The PEI of a known amount of material and energy are defined as "the negative consequences on the environment in case the material were to be disposed into the environment" (Young et al., 2000). This definition implies that the PEI has a probabilistic character as it refers to an incident or accident that has not happened yet. That means PEI of a dedicated material or energy waste is an estimation of the influence that the waste have on average. (Young and Cabezas, 1999)

As a matter of fact, energy cannot be measured directly but can only be calculated when the measurable quantities such as temperature, pressure etc. are known. Similarly, the potential environmental impacts (PEI) as the effects of energy and material streams of a chemical process on the environment are conceptual values and can only be calculated from other measurable quantities (Cabezas et al., 1997). Like material and energy balance of a flow sheet, PEI balance relates PEI entered to (and generated in) a process system into the PEI left and accumulated in the system. Thus, the study of the potential environmental impact should be divided into two categories: the impacts of the non-product streams as well as the impacts of the energy streams within the process.

Since the main objective of this work is to reduce the wastes and to increase the production rates, the non-product streams are considered as waste only and therefore, the impact of product streams are set to zero, as suggested by Hilaly and Sikdar (1995).

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The PEI theory employs eight environmental impact classifications for the assessment of the PEI indices. The units of the Potential Environmental Impact values are in PEI/kg for chemicals and in PEI/MWh for energy. Thus, the values are not directly comparable. For detailed information about PEI classifications, please refer to Appendix B.

2.4 ENERGY IMPACTS ON THE ENVIRONMENT

Climate change, acid rain, global warming and the emission of pollutant gas are of great concerns of scientists, engineers, environmentalists, governments and our today's society. The rationale behind this concern includes the improvement of human's and animal's health, societal awareness of threads to people and environment, preservation of a clean environment and natural resources for the next generation, saving money and resources, and above all, following and respecting the law or policy. Many attempts have been made to address waste materials and energy to reduce their effects on the environment in many different ways.

Energy generation particularly from fossil fuels such as coal, natural gas and oil has adverse effects on the environment. Fossil fuels are mainly used in industries to generate heat and electricity resulted in the intervention of gas pollutants to the environment.

Industrial sector such as chemical complexes and fossil-fueled power plants have a great interest in finding a simple and accurate relationship between energy generation and gas pollutant emissions to the atmosphere, so do environmentalists and regulators. Such a relationship encourages the regulators to offer stimulus programs to protect the environment from gas emissions. The industrial investors are restricted by environmental regulations such as banned disposals, manifesting of chemical wastes, mandated cost impact for the exposure of chemical and hazardous wastes to the environment. So, in order for them to devise and to follow up effective strategies for pollution prevention, incentives such as tax reduction,

subsidies and loans or credits for on-site recycling of wastes, R&D assistance etc. seem to be necessary (Cohen and Giralt, 1996).

Currently, most researchers, engineers and environmentalists use the annual reports made by Energy Information Administration (EIA) or by U.S. Environmental Protection Agency (EPA) in order to relate the energy generated or consumed in manufacturing industries and power plants to CO_2 emissions to the atmosphere.

This research offers a new methodology in order to relate thermal and electrical energy (in kJ/h) to CO_2, NO_2, and SO_2 emission rates (in kg/h) to the environment, given the characteristics of fossil fuel used for heat/power generation. This methodology provides a simple index to estimate the emission rates of gas pollutants when the heat or power consumption is known; e.g. from a tag of an electromotor.

Chemical manufacturing industries are concerned with energy in the following ways:

- Boilers for steam generation to initiate reactions in reactors, to heat-up reboilers, heaters and to use in steam turbines to generate electricity.
- Cooling towers to provide cooling water (CW) for removing of heat from reactors, coolers, condensers, etc.
- Electric power for running rotary equipment such as pumps, fans, compressors, blowers, agitators, etc.

Coal, natural gas and oil are known as main fossil fuels with relatively high energy contents. The combustion of fossil fuels results in gas emission such as CO_2, NO_x and SO_x to atmosphere. In steam turbine power plants, the heat of steam is transformed into electricity. The conversion efficiency of a steam turbine is 35% (EPA, 1997a) and that of a boiler is 75% (Coulson and Richardson, 2001). The generation of heat and electricity in a plant requires high-tech equipment and huge expenditures, while depleting natural energy resources.

So, the fewer the electricity or the steam in industries is used, the more economical and environmentally friendlier process is designed, and the global energy resources are preserved.

Methodologies for energy impacts assessment

There are few important methodologies for the estimation of the energy impacts of a stream or process on the environment such as:

2.4.1   EPA's Methodology (Potential Environmental Impacts or PEI)

EPA has developed standalone software for the evaluation of material and energy impacts on the environment called WAR GUI (2008), a program based on waste reduction (WAR) algorithm for the estimation of Potential Environmental Impacts (PEI) of a chemical processes. The PEI of a hazardous chemical and energy is defined as the influence of such material and energy on the environment if they were discharged to the environment (Young and Cabezas, 1999). The PEI theory is an amendment to "waste reduction (WAR) algorithm", which employs eight environmental impact categories such as global warming, ozone depletion, acidification potential etc. for the assessment of the impacts of a chemical substance on the environment (Young et al., 2000). The impact of the energy on the environment is reported in PEI/h by WAR GUI (2008).

The methodology is based on the available air emissions data for the fossil fueled electric power generation such as coal, oil and gas. These data are collected from the energy and waste inventories of utility and non-utility electric generation plants. The primary business of a utility power producer includes retail or wholesale of electricity, exchange, transmission and distribution of electricity. A non-utility power producer primarily generates electricity and other businesses than electricity sale (EPA, 1997a).

These data are classified into different categories based on industry size, geographic distribution of utilities and non-utilities, their capacity by prime movers, fossil fuel energy source (i.e. gas, coal, oil), type of producer (e.g. small power producer, cogenerator), waste and pollutant generation, wastes release profile, emissions to the atmosphere, annual air pollutant releases, emission factors for gas-fired, coal-fired and oil-fired power generators, inorganic and organic HAPs (Hazardous Air Pollutant) emissions, etc. The detailed information and related tables have been published by EPA (1997a).

Air quality management is carried out by different parties such as federal, state, and local agencies, consultants and industry via emission inventories. The emission inventory can be done by using emission factor (EF) as a cost effective tool. EPA (1997b) has published AP-42 document for development of the emission factors (EFs) for over 200 source categories by different methods such as source test data, material balance and engineering estimates. The following general equation shows how EFs can be used to estimate a source's emissions (EPA, 2011b):

$$E = A \times EF \times (1 - ER / 100) \tag{2.1}$$

where E is emissions, A is activity rate, EF is emission factor and ER is overall emission reduction efficiency (%). ER is the efficiency of control device used to mitigate pollutants. The EF relates the pollutant quantity released to the atmosphere to the corresponding pollutant activity.

The presented EFs are usually the averages of the existing data of acceptable quality and can be employed as long-term averages for all facilities in the source category. This data are generated by measurements and collected from survey within power plants, which use fossil fuels (EPA, 1997a). The survey consists of two waste categories (i.e. process wastes and pollutants) for three fossil fuel type (i.e. gas, coal, oil). The wastes are expanded into three

types: "Air Emissions", "Combustion Wastes" and "Non-Combustion Wastes". The examples for air emissions are flue gas, SO_x, CO_2, NO_x, etc. The example for combustion wastes consist of remaining solids such as fly ash, heavy metals etc. The example for non-combustion wastes is blow down of boilers.

EPA has presented and employed several test methods for the development of the EF (EPA, 1997b) such as New Source Performance Standard (NSPS), National Emission Standard for Hazardous Air Pollutant (NESHAP) or Maximum Achievable Control Technology (MACT).

Despite of plenty of benefits accredited to the EFs, they have the following limitations:

- EFs are average emission rates so; they cannot be considered as standards or emission limits.
- For a specific source category, the source type and age, technology, control systems, raw materials etc. make between-factors variability since they vary from one source to another.
- Estimation of short-term emissions from a specific source encompasses uncertainty, since the emissions vary over the time due to changes in operation conditions (within-source variability).
- The EFs for controlled sources (the sources with air pollution control device) does not necessarily represent the best emissions control device, instead, it shows the available emissions level at the time the tests were carried out.
- Material balance is a method for estimating of EFs when there is a risk of wasting high percentage of the materials to the atmosphere. Otherwise, it may be inappropriate.
- There is also between-source variability due to variations in average emission factors from source to source.

The EPA's method (WAR GUI, 2008) provides impact rates for each fossil fuel in "PEI per unit energy" for each impact category, which is multiplied by the energy generated in the plants in unit energy per hour to give the energy impact in "PEI per hour". The assumption made by EPA to validate this calculation is that the rate of pollution emission has a direct

dependency on the amount of energy required (WAR GUI Tutorial, 2008). Table 2.2 represents the impacts of four sample categories in PEI /MJ for different types of fossil fuels.

Table 2.2: The impact rates for each fossil fuel (PEI/MJ) for each impact category (WAR GUI Tutorial, 2008).

Category	Coal	Gas	Oil
HTPI [a]	7.83E-05	4.76E-08	9.14E-05
GWP [b]	1.93E-04	9.57E-05	1.52E-04
ODP [c]	2.03E-09	3.63E-10	0.00E+00
AP [d]	5.98E-03	9.92E-04	3.74E-03

[a] Human toxicity potential by ingestion
[b] Global warming potential
[c] Ozone depletion potential
[d] Acidification potential

Total PEI/MJ associated with coal, gas and oil for all categories are 6.59 x 10^{-3}, 1.10 x 10^{-3} and 4.299 x 10^{-3}, respectively.

EPA (2013) has also provided several conversion factors for the estimation of CO_2 emissions from electricity consumption to fuels burning in vehicles as well as the combustion of natural gas, oil, coal etc. For instance, to relate electricity reduction (kWh) eGRID (Emission & Generation Resource Integrated Database) is used. For such relationship, the Greenhouse Gas Equivalencies Calculator uses a non-baseload emission rate, which is emission from power plants that are brought to operation when required to meet demand. The rationale behind it is that the most energy-related emissions seekers look for emission reduction from energy efficiency or renewable energy program, which are not supposed to affect baseload emissions; i.e. continuous running power plants. This Emission Factor follows:

7.0555 × 10^{-4} metric tons CO_2 / kWh" OR "196 mg CO_2/kJ

There are several disadvantages for this method:

- Lack of other gas emissions; e.g. NO_2, SO_2 etc.
- Restricted to non-baseload power plants.
- Inventory based conversion factor.
- There is a significant difference between this method and EIA's (both interconnected governmental organization), which is discussed in succeeding section.

2.4.2   Energy Information Administration (EIA) data:

In lack of the afore-mentioned data in previous case, the data prepared by Energy Information Administration (EIA) may be used. EIA is a U.S. governmental organization who prepares annual report for energy consumption from clean and fossil fuel sources, pollution emissions etc. in different countries around the world. In case of using EIA's data, boiler or turbine efficiency factors should not be applied.

The energy content of a fuel can also be roughly calculated when total fuel consumption and CO_2 generation is available. The necessary data can be collected from U.S. Energy Information Administration (EIA). The following data about fossil fuels, energy consumptions as well as CO_2 emissions in Canada in 2006 have been obtained from EIA's website (EIA, 2009):

- Total Energy Consumption: 13.9×10^{15} Btu (oil, 32%; hydro, 25%; natural gas, 24%; nuclear, 7%; coal, 10%; other renewable, 1%).
- Energy-Related Carbon Dioxide Emissions: 614 million metric tons.

The total contribution of fossil fuels to energy consumption is about 66%. Other sources of energy are solar, nuclear, hydro, which are called clean energy, have no direct contributions to CO_2 emission from energy source. Thus, the total carbon dioxide emissions reported above by EIA are solely from fossil fuels and can be related to energy consumption in kJ as follows:

$$\left(614 \times 10^6 \text{ tons CO}_2 \big/ 13.95 \times 10^{15} \times 0.66 \text{ Btu}\right) \times (1.055 \text{ kJ/ Btu}) \times \left(10^6 \text{ gr} \big/ 1 \text{ ton}\right) = 63 \text{ mg}$$

$$\text{CO}_2 / \text{kJ} \tag{2.2}$$

Hence, 1kJ energy consumption in the form of heat or electricity releases 63 mg CO_2 gas as pollutant to environment.

This method only gives an approximate figure for the CO_2 emission rate to the atmosphere. It has two disadvantages: (1) EIA's methodology does not reveal the contribution of fossil fuel types on CO_2 emissions. And (2) the data for NO_x and SO_x emissions are unavailable. Thus, no relationships between emissions from particular fossil fuel; i.e. oil, gas and coal, and energy consumptions can be established.

There is a significant difference between this method and EPA's one in previous section (both interconnected governmental organization).

2.4.3   Other methodologies

a.   Exergy methodology

In thermodynamic expression, "exergy" is simply defined as the maximum available useful work and formulated as follows (Yantovski, 2004):

$$A = \Delta U - T_o \, \Delta S + P_o \, \Delta V = \Delta \, (U - T_o \, S + P_o \, V) \tag{2.3}$$

The term A was originally called "Availability" or "Available Energy", but since 1956 it has been addressed as "Exergy". ΔU is the difference in internal energy, $T_o \, \Delta S$ is the entropy loss or heat loss and $P_o \, \Delta V$ is the available PV work. Unlike energy that changes from one form to another, the exergy is irreversible and destroyed in a close system due to the friction and due to an increase in entropy according to the second law of thermodynamics. The exergy is calculated by the following equation (Fan and Zhang, 2012):

[Partial molar exergy at T and P, $\bar{\varepsilon}$] = [Partial molar chemical exergy, $\bar{\varepsilon_0}$] + [Partial molar thermal exergy, $\bar{\varepsilon_T}$] + [Partial molar pressure exergy, $\bar{\varepsilon_P}$] $\qquad$ (2.4)

And in mathematical form the above equation can be rewritten as:

$$\bar{\varepsilon} = \bar{\varepsilon_0} + \int_{T_0}^{T} \overline{C_p}\,(1 - T_0/T)dT + \int_{P_0}^{P}[\bar{V} - (T - T_0)(\partial V/\partial T)_P]\,dP \qquad (2.5)$$

$\bar{\varepsilon_0}$ in kCal/gmol can be found in thermodynamic handbooks; for instance $\bar{\varepsilon_0}$ for water in liquid and gas states are 0 and 56.23 kCal/gmol, respectively.

The exergy is employed for the evaluation of sustainable design performance by the estimation of the design efficiency. The applications include building lighting, cooling and ventilation, home electrical appliances and so forth (Canadian Architect's website, 2012).

The efficiency is defined as:

$$\eta = \frac{available\ energy\ transfer\ of\ the\ desired\ kind\ achieved\ by\ the\ system}{available\ energy\ input\ into\ the\ system} \qquad (2.6)$$

Although the concept of the exergy has provided improvements in sustainable design, it neither gives information on the impacts of energy on the environment nor is it used in chemical processes.

b. Ricardo-AEA

Carbon Trust (2013) has provided a factsheet containing a number of conversion factors for carbon emissions from energy use within a business and public energy consumption. These factors are based on an annual report published by the UK government's website of Department of Environment, Food & Rural Affairs (2013). The conversion factors are calculated on the basis of Ricardo-AEA (2013). The user can select the fuel type from following website (Oct. 26, 2013):

Then, a list of questions appears and the user must answer to them correctly in order to make the calculations precisely followed by clicking on "Download" button. An excel file will be open when the calculation is finished by solver. For fuel oil the Net CV (calorific value) is 40.70 (compared to natural gas: 47.73) GJ/tonne fuel oil in 2013. The database is collected on inventory basis and therefore, subject to change each year; for instance, Net CV for fuel oil used to be 40.72 GJ/tonne in 2012 and dropped by 0.02 GJ/tonne fuel oil. Although this website provides several conversion factors for transportation, fossil fuels & biofuels consumptions, there is no relationship between heat flow and gas emissions.

c. Energy Usage Index (EUI)

The EUI is a methodology used for calculation of energy consumption in a premise in Btu per unit area. The corresponding database can be downloaded from the website of Oregon Department of Energy (2013). EUI requires following data for calculation;

1. 12 month utility bills,
2. Square footage,
3. Hours of operation.

An example for Energy Use Index is SID or School Interactive Database where the above data is entered to the spreadsheet and it calculates the energy consumption in Btu/sq. ft.

Apparently, the EUI methodology cannot be used in chemical process plants.

d. Energy Index Calculation

This is a software package developed by Texas Instrument (1999, 2013) for calculation of the energy index per unit area of building per unit temperature; e.g. Btu/sq. ft, degree day (BTUDD), the lower the index, the more efficient the premise is. Similar to EUI, this index is out of scope of this research.

e. Energy Efficiency Index (ODEX)

Energy efficiency index (ODEX) considers 10 industrial categories; i.e. chemical, steel, paper, non-ferrous, cement, food, machinery, transport equipment, textile and other non-metallic, for energy saving index, which is a weighted average of the contribution of each category in the total energy consumptions of all categories in year t. In the first three industries the specific consumption per tonne production is used, while for the rest the ratio of energy consumption per production index is employed.

The ODEX methodology only deals with energy savings in specific industries and gives no information about the gas emissions to the atmosphere.

f. Energy Development Index (EDI)

IEA has presented four indicators for the evaluation of the energy function in human development as a tool to help estimate UNDP's Human Development Index:

- Per capita commercial energy consumption as an indicator of country's economic development.
- Per capita electricity consumption in residential zones
- The contribution of modern fuels in total residential zone
- The population portion who have access to electricity

The following ratio is used for calculation of above indicators to track countries' transitions toward the use of modern fuel:

$$Indicator = \frac{Actual\ Value - Minimum\ Value}{Maximum\ Value - Minimum\ Value} \quad (2.7)$$

The World Energy Outlook is annually publishing the Energy Development Index (EDI) for the international awareness and monitoring of countries' progress from energy poverty to modern energy access.

g. Energy Efficiency Design Index (EEDI)

Energy efficiency design index (EEDI) is a complex index developed by Germanischer Lloyd SE (2013) to be used for improvement of energy efficiency of ships and maritime activities. EEDI index is a method of the calculation of CO_2 emissions and a function of ship type, fuel type and specific fuel oil consumption by main and auxiliary engines, power take-off devices such as shaft generator, propulsion power etc.

EEDI = CO_2 emissions / Transport work (2.8)

Global f_i Factor:

$$f_i = \prod_{i=1}^{x} f_i \tag{2.9}$$

from shaft generator using different fuels; e.g. fossil fuels, LNG etc.

h. Energy Performance Index (EPI) Calculation

Energy performance index is the ratio of annual primary energy consumption to aggregate product output.

http://www.seai.ie/Your_Business/Large_Energy_Users/Special_Initiatives/Special_Working_Groups/Commercial_Buildings_Special_Working_Group_Spin_I/Commercial_Buildings_Benchmarking_Irish_Context.pdf

Any changes in energy performance result in a change in EPI. The EPI is calculated by the following equation:

EPI = (Energy/Output) x F (2.10)

where F is a factor used to set the EPI to 100 for the first year the company joins the program. Then, F will be set for successive years. For example, for energy usage and production of 2,500 GWh and 100 weighted output units, respectively:

F = (Output / Energy) x EPI = 100 x 100 / 2,500 = 4

For subsequent year given energy usage and output of 2,750 GWh and 112 weighted output units, respectively, EPI equals to 98.21 and so forth.

EPI is a 5 page report containing the following information: Primary energy per unit of output, estimated CO_2 emissions, relationship between emission changes with energy performance. The total CO_2 emissions in present year is then calculated (based on fuel types and electricity consumption in GWh) and then multiplied by the EPI difference between present and previous years.

For instance, the available data for heavy fuel oil (HFO) contains:

- HFO consumption   47.04 GWh,
- Conversion   274
- CO_2 emissions   12,888.876 tonnes

Thus, the conversion factor for HFO is 274 tonnes CO_2 emissions/GWh or 76 mg/kJ.

The general conversion factor from EIA is 63 mg/kJ (Eq., 2.2).

The existing methods have several advantages and can be used in a number of different situations; however, they have also quite a few disadvantages that prevent them to provide accurate results. For example, both EPA and EIA methods provide no information about NO_X and SO_X gas emissions; the EIA methodology does not reveal the contribution of fossil fuel types to CO_2 emissions. The exergy methodology gives neither information on the impact of energy on the environment nor is it applied to chemical processes. Ricardo–AEA provides no relationship between heat flow and gas emissions. Both Energy Usage Index (for houses) & Energy Index calculation cannot apparently be used for chemical process plants. ODEX deals only with energy savings in specific industries and needs detailed operation data. In addition, it gives no information about gas emissions to the atmosphere. Energy Development Index

(EDI) is used for monitoring of the progress of individual countries from energy poverty towards modern energy access. The energy efficiency design index (EEDI) is a complex index for application to improvement of the energy efficiency of ships and other maritime activities. The energy performance index (EPI) is the ratio of annual primary energy consumption to aggregate product output. EPI needs detailed operational data from company's energy consumptions and product output over a range of years.

Hence, there is still a need for a simple and quantitative index to be preferably applicable (but not limited) to the initial stage of the process design at minimum available data. One of the key objectives of the present research is to provide such essential index. In this thesis, new indices are introduced and discussed why it is better than the existing methods (Chapter 4). The new energy indices estimate the impacts of energy generation/consumption in terms of unit mass of gas emissions to the environment per unit time and also per plant production rate.

2.5 SAFETY RISKS REDUCTION IN INITIAL DESIGN STEP OF CHEMICAL PROCESS
Safety aspects comprise the accidents as the causes of adverse consequences on people and process plant (Koller et al., 1999 and 2000). Safety is; therefore, a strategy to prevent an accident or loss to happen. It is based on hazard evaluation and therefore, an important part of a chemical process design. Hazard is an intrinsic chemical or physical property of a material or system or process, which can be detrimental to human, process plant, equipment, and environment. Chemical manufacturing industries are the main source of risks to process safety. Thus, a process is inherently safer when it handles less hazardous chemicals.

The word "inherent" is defined as "Unable to be considered separately from the nature of something because of being innate or characteristic" (Microsoft Encarta Dictionary, 2004). Hence, a chemical process is inherently safer when it is naturally safer, and an inherently

safer design means the process involved handles less quantity of hazardous chemicals instead of controlling them and/or deals with less number of risky operations (Heikkilä, 1999). Dangerous operation implies processes engaged inventory, high temperature, high pressure and equipment safety.

An optimum chemical process design by incorporating process integration, control and operation, safety and economy is still a struggling research work (Seferlis and Georgiadis, 2004); however, in grace of regulations and incentives for pollution prevention as well as the public awareness of the environmental issues, it is not so challenging to plead the investors with the incorporation of the environmental waste reduction and inherent safety into process design in early design phase.

Several attempts have been made to present methodologies for risk assessment at conceptual design stage of a chemical process, but the majority of them need detailed process data, which is unavailable at this phase. Such methodologies have been of great interest to regulators, process designers and investors. The idea behind this is that a process design is more economic when it is inherently safer. Inherent safety is known as the safety intrinsic to a process; the spirit of which is to mitigate hazards within the process. It is also possible to achieve inherently safer design by diminishing the hazards in multi-component streams during process design. Hazards reduction during design phase is a challenging task. A decrease in hazards in a process design not only improves process safety, it also protects environment from potential impacts of the process.

This research presents simple indices demanding minimum data for the evaluation of risks to chemical processes at conceptual design phase. As an important result, total capacity of a process among other design array does not suffice for decision making unless the mass fraction of hazards in product streams are appreciably low.

2.5.1 Chemical process design is tied to risk assessment

An accident in a chemical manufacturing plant is not only harmful to the plant; it can also be an irreparable spoil for the reputation of licensing company who has designed the chemical process. This fact reveals that it is imperative to alleviate possible risks to process safety during design phase. The tie between process design and the risk to process safety is not new; any kinds of design modifications and/or the development of operation instructions results in risk reduction within the process plant; e.g. purification of raw material, centralization of hazardous chemicals in safe containers or bags and transformation of the hazardous chemicals to benign materials (Carson et al., 2002). There are several qualitative and quantitative methods to estimate the risks associated with a chemical process; however, few of them can be used in conceptual design.

Chemicals, in general, are the main source of fire, explosion, toxicity and corrosion hazards. About two third of impacts were initiated mainly by explosion compared to fire (Lees, 1996); however, toxicity is more influential on the number of affected people compared to fire and explosion (Belke, 2000). Thus, it is vital to pay close attention to the chemical toxicity for the risk assessment during primitive step of the process design, especially in the absence of detailed process data.

2.5.2 Potential risk assessment

Hazard is an intrinsic chemical or physical property of a material or a system or a process, which can be detrimental to human, plant, equipment, and environment. Hazard and risk have two distinctive concepts (Canadian Centre for Occupational Health and Safety, 2009): A "hazard" refers to the potential of negative consequences on personnel's health or company's equipment and property, while a "risk" is defined as the probability of the hazard, which

results in adverse effects on the human, the property or the equipment. Hence, the risk is generally a function of two factors; frequency and consequences:

Risk Assessment = f (frequency, consequences)   (2.11)

This relationship has persuaded Marhavilas et al. (2011) to develop a model called decision matrix risk assessment (DMRA). It is widely being used by other researchers and engineers (Reniers et al., 2005; Woodruff, 2005; Henselwood et al., 2006; Marhavilas et al., 2008).

2.5.3   The constraints of existing methodologies for risk assessment

Researchers have made several attempts to provide simple methodologies for risk evaluation. A simple risk index is a mathematical model to be employed in the initial stage of planning in chemical plants, easily applicable in process plants, include industrial experience and require general plant (Al-Sharrah et al., 2007). The review of such methodologies is out of the scope of this paper; however, a list of most common used methodologies, their formulations, parameters, applications, advantages and disadvantages is provided in Table 2.3. Examples include (but not limited to) STEP, HAZOP, What-If Analysis, PRA, Checklist Analysis, SA, TA, FTA, DMRA, The Measure of Societal Risk (Marhavilas et al., 2011).

These risk analysis methods have one or a combination of several disadvantages such as qualitative, comprehensive, time consuming, dependant on the quality of either of training data collectors receive or experience of safety/production managers, require detailed process data, which is unavailable at the early stage of process design. The detailed study of available methodologies has been made by Koller et al. (2001), Tixier et al. (2002), Al-Sharrah et al. (2007) and Marhavilas et al. (2011).

Koller et al. (2001) have reviewed and classified the major characteristics of 13 index methods and made the following recommendations to be applied at early design stage:

- The combination of different methods.

- Possible risk evaluation in lack of detailed process data; e.g. equipment and plant.

- The advantage of history of previous incidents and accidents are constructive.

Tixier et al. (2002) have identified 62 safety risk analysis methods in industrial plants and pointed out the lack of human risk analysis in classical risk evaluations as the disadvantage of most of these methodologies.

Table 2.3: Comparison of Major Hazard and Risk Assessment Techniques (Marhavilas et al., 2011).

No	Techniques	Formulation	Safety Parameters	Application	Advantages	Disadvantages
1	Checklists		1) Historical record 2) Field inspection 3) Experienced individuals 4) Pre-established criteria	Equipment issues and human factors	1) A systematic approach based on questionnaire and checklist 2) Ensures that organizations are complying with standard practices 3) Easy application of the technique	1) Quality dependency on individual experts 2) Complex hazard sources identification 3) A supplement to another method 4) Qualitative information
2	What-If Analysis		1) Boundaries of risk related information 2) Problem identification (e.g. risk type, environmental impacts, economy) 3) Determination of subdivision of item 2 (e.g. location, tasks, subsystems) 4) Asking what-if questions	Equipment issues and human factors	1) Identifies hazards, hazardous situations or specific accident events 2) Relatively easy to use/not expensive 3) Applicable to any activity or system 4) Most often is used to supplement techniques	1) Quality dependency on individual experts, documentation, and the experience of the review teams 2) Determines only hazard consequences 3) A loosely structured assessment 4) Qualitative
3	Safety Audits (SA)		Operational safety programs	Administrative	1) Cheap 2) User friend 3) Diagnoses equipment conditions or process procedures, which results in casualties, environmental impacts or property loss	1) Not useful for the detection of hazard sources for technical installation 2) The outcome is a suggestion to management for various safety aspects of options 3) Qualitative
4	Task Analysis (TA)		1) Worker's tasks 2) Interpersonal interaction 3) Human-machine interaction	Administrative	1) A detailed information can be provided 2) A well-structured picture of the work process can be built. 3) Safety critical tasks can be identified	1) Time consuming 2) Dependency on safety experts or production engineers 3) Qualitative

5	Sequentially Timed Event Plotting (STEP)		Sequence of events	Operation	1) A valuable overview of timing and sequence of events that contributed to the accident. 2) Plotting the sequence of events that contributed to the accident	1) Time-consuming 2) qualitative
6	HAZOP		1) Pressure 2) Temperature 3) Flow rate 4) Equipment 5) Interlocks	Detailed engineering, operation, retrofitting	1) A systematic, documentary, imaginative methodology 2) Identifies deviations and causes of undesirable consequences 3) Recommends countermeasures to mitigate frequency & consequences of the deviations 4) Determines hazard causes & consequences 5) Very popular 6) Applicable to any system or procedure 7) Highly structured assessment relying on guide words to generate a comprehensive review	1) Expensive 2) Difficult to use 3) Requires multidisciplinary team of experts 4) Time-consuming 5) Qualitative
7	Proportional-Risk Assessment (PRA)	R=P.S. FR=Risk P=Probability S=Severity F=Frequency	1) Probability 2) Severity 3) Frequency	Operation, Construction	1) User friend 2) Quantitative 3) Mathematical risk evaluation 4) Safe results, based on the recorded data of undesirable events or accidents 5) Incorporated in databases 6) Can be used in other risk-assessment techniques 7) Predicts hazards, unsafe conditions and also prevents fatal accidents	1)Dependency on precisely recording the undesirable events 3) Time-consuming 3) Cannot be used at early design stage 4) Dependency on safety experts or production engineers 5) Hard to find probability function

8	Decision Matrix Risk Assessment (DMRA)	$R=S.P$ $R=$Risk $P=$Probability $S=$Severity	1) Probability 2) Severity	Operation	1) User friend 2) Good data quality 3) Combination of risk analysis and risk evaluation 4) Predicts hazards, unsafe and undesirable conditions 5) Prevents fatal accidents 6) Quantitative and graphical method 7) Facilitates prioritization and managing key risks	Dependency on safety experts or production engineers
9	Quantitative risk measure of societal risk	$R=\{(Sk,Fk,Nk)\}$ $Ski=$k-th accident scenario $Fu=$Frequency $No=$Consequence	1) Frequency 2) Severity	Operation	1) User friend 2) Considers both public and worker risk 3) Contains historical record of incidents 4) A quantitative and graphical technique 5) Encompasses criteria for judging the tolerability of risk	1) Needs qualified safety managers to document the undesirable events 2) Time-consuming
10	Fault-Tree Analysis (FTA)		1) Equipment failures 2) Human errors 3) External events 4) Constructed from even & gates (AND/OR)	Operation	1) Models combinations of equipment failures, human errors, and external conditions causing of an accident 2) Dependency on experts 3) Requires brainstorming meetings 4) Field inspections 5) Quantitative & 6) A highly structured method 7) Applicable for all type of risk-assessment 8) An effective root cause analysis	1) Very complicated 2) Difficult to use 3) Time-consuming 4) Expensive 5) A system-level risk-assessment technique

Al-Sharrah et al. (2007) have implemented the above-mentioned shortcomings to their risk index for use in petrochemical planning as follows:

$$K = Freq \times Haz \times Inv \times Size \qquad (2.12)$$

The index (K) expresses the risks to human life in maximum affected people per year (including fatalities, injuries and people hospitalized) if the plant chemical inventory were released in an accident. *Freq* is the frequency of accidents in number of accidents per process per year, *Haz* stands for hazard effects in number of people affected per ton of chemical released, *Inv* designates the inventory in tons of chemical released per accident, and the term *Size* is the number of major processes in plant, which is most probably equal to three since chemical plants are usually divided into three main process sections; reaction, purification and finished product storage facilities. It is important to note that most plants have purification and storage facilities for both reactants and products and they both share the reaction section.

Marhavilas et al. (2011) have classified the main risk assessment methods into three main categories: qualitative, quantitative and hybrid techniques and concluded that current methods have not been fully shared. Hence, the researchers encounter issues such as duplication and cohesion from one field to another.

The equation (2.12) has been used as a multi-objective tool in petrochemical industries (Al-Sharrah et al., 2006). It can also be used as a sustainability indicator for decision-making and optimization in process plants (Al-Sharrah et al., 2010).

2.5.4   Inherent safer design

The equation (2.11) represents the dependency of the risk on frequency (probability, likelihood) and consequences. The fundamental question is: which process should a process

engineer opt for, when two processes with the same potential risks are concerned? The process, which has higher likelihood of accidents but lower consequences? Or the one, which has lower likelihood of accidents but severe consequences?

Engineering design is based on codes and standards, which provide consistent tools for material selection, reliable procedures for fabrication, tests and installation of piping and equipment used for handling of hazardous and non-hazardous chemicals and facilities. Unlike hazardous materials, which escalate further costs due to safety reasons, the codes allow the engineers to use mild materials when benign chemicals (meaning low consequences) are concerned resulting in cheaper expenditure. This is the core of the inherent safety in a chemical process; i.e. hazards alleviation instead of employing protective devices (Heikkilä et al., 1999). Consequently, the question of the severity and the likelihood of an accident can be addressed when hazards have been identified.

Inherently safer design (ISD) is highly supported by the availability of simple indices that can be used at early stages of design. ISD is an approach to address the risks of hazardous chemicals to human, environment and process plant during design and manufacturing phases of a process (Hendershot, 2011a). The term ISD was first introduced in the 1970s after the big disaster in Flixborough, UK, in 1974; however, the concept of inherent safer design (ISD) is not new. It has been used since Stone Age when cave inhabitants decided to move up to a higher level of the cave to diminish the risk of flood, while they could reduce the risk by either of dike (engineering control) and monitoring the level of river (administrative control).

Today, more researchers and engineers are becoming familiar with ISD through new publications and training such as the relevant course provided by AIChE:

https://www.aiche.org/ccps/resources/education/courses/ch800/inherently-safer-design

Together with engineering and administrative controls, ISD is able to manage the risks of a process efficiently. There are four strategies to design an inherently safer process (CCCP, 2009):

1. Substitution of hazardous chemicals with benign materials.

2. Minimization of hazardous materials.

3. Moderating the process by dilution, refrigeration etc.

4. Simplification of operation by reducing the potential errors such as using interlocking commands for process control equipment.

It is now possible to replace toxic chemicals in off-shore oil and gas facilities during conceptual design in order to design an inherently safer process at optimum cost and minimum acceptable risk (Khan and Amyotte, 2002). The concept of inherent risk assessment has been used for the integration of risk quantification into HYSYS process simulator (Leong and Shariff, 2008; Shariff and Leong, 2009). Cordella et al. (2009) have submitted a comprehensive method for screening the design of inherently safer processes based on categorization of hazards with respect to human, ecosystem, and environmental media contamination.

The inherent safety is being used in practical situations by a number of researchers (Heikkilä et al., 1996; Khan and Abbasi, 1998; Khan and Amyotte, 2002; Shariff et al. 2006; Leong and Shariff, 2008; Cordella et al., 2009; Shariff and Leong, 2009; Hendershot, 2011a, b). The rationale underlying that is firstly, inherent safety helps to reduce the hazards associated with chemical manufacturing processes at design stage and secondly, there is a belief that it is possible to use simple cheap ways to design inherently safer processes (Kletz, 2001) by the elimination or the reduction of the size of protective and control devices.

2.5.5 The importance of inherent safety in conceptual design stage

Unfortunately, the risks of chemical hazards in design phase have been overlooked in almost all of conventional process design leading to generation of large amounts of wastes as pollutant source (EPA, 2012), whilst the most convenient time for effective source reduction falls in process design phase (Tchobanoglous, 2009). Traditionally, the safety and environmental considerations were left to designer experience at the initial phase of the design (Koller et al., 1999).

A process design is performed in three steps: basic (e.g. conceptual) design, front end engineering and detailed design. In each step, several technical documents are generated by corresponding departments, but risk assessment is usually accomplished at final step of process design.

In effect, conceptual design plays a decisive role in minimizing the risks of a process since all other design steps are based on this phase, it turns out that the impact of decisions is extremely high at conceptual design stage as shown in Figure 1.1 (Lewin, 2004) but can be minimized if the process is inherently (internally) safe and well conceptualized since protective and control devices (external safety) would be either eliminated or have smaller sizes. In other words, a conceptual design encompasses less decision making impacts when it comes to inherently safer processes (Kletz, 2001) due to selection of cheaper materials for piping and equipment. Thus, inherent safety at low expenditure can be achieved during conceptual design.

The present risk analysis methods have one or a combination of several disadvantages such as qualitative, comprehensive, time consuming, dependant on the quality of either of training data collectors receive or experience of safety/production managers, require detailed process data, which is unavailable at the early stage of process design. The objective of this research is to

develop simple and new indices for the evaluation of risks associated with hazards in process

streams to be implemented at conceptual design stage with minimum available data.

Chapter 3

METHODOLOGY FOR POTENTIAL ENVIRONMENTAL IMPACTS ASSESSMENT: MATERIAL

In this chapter, distinctive methodologies for the evaluation of potential environmental impacts (PEI) of materials and energy in a chemical process are reviewed. Today, an optimum chemical process design by incorporating process integration, control and operation, safety and economy is still a challenging research work (Seferlis and Georgiadis, 2004). Some methodologies mix-up safety and environment and introduce a hazard index for both to estimate the impacts of a process to the environment, property and staffs such as University of Tennessee (UTN) and Indiana Relative Chemical Hazard Score (IRCHS) methodology, which have been discussed in preceding chapter.

In this research, the impacts of a process on the environment have been divided into the impacts of materials handled and energy used within the process design. Thus, this research employs an existing methodology for the evaluation of the material impacts on the environment (WAR algorithm and PEI theory) and introduces two new simple and quantitative indices for the assessment of the energy impacts on the environment and the risks to the process safety. Finally, these three fundamental methodologies will be consolidated as the most important objective of the present research (introducing new composite metrics) to be used during conceptual design step (Chapter 7).

When the new composite indices underlie trade-offs between design alternatives and process profitability, a multi-criteria decision-making tool (Analytical Hierarchical Process; AHP) is employed for ranking and cost-benefit analyses purposes (Chapter 6).

This chapter introduces WAR algorithm and PEI methodology for the calculation of material impacts on the environment.

3.1 POTENTIAL ENVIRONMENTAL IMPACTS (PEI) AND WASTE REDUCTION (WAR) ALGORITHM

The approach to pollutant prevention or waste reduction in manufacturing companies has been made by regulators, investors, scientists and engineers since long time ago. The majority of the works and researches have been done to reduce the wastes by a process called end-of-pipe treatment as well as waste disposal whereby an additional unit or a package unit is installed in the plant for waste treatments.

Although these techniques are still very useful to reduce the wastes to significant levels in a chemical company, a process is more desirable for investors and regulators when it produces fewer wastes and accomplishes the preferential production output with cheaper waste treatment schemes (El-Halwagi, 1997). Therefore, in recent approach the most convenient time for effective source reduction falls in design phase of a product/process (Tchobanoglous, 2009).

Researchers have suggested several methodologies for waste reduction at the primitive step of a process design such as Heat Exchanger Networks (HENs), Mass Exchange Networks (MENs). Even though these methods have made significant improvements in chemical hazardous waste reduction, the main issue here is that none of them addresses the pollution impacts on the environment.

Methods such as the University of Tennessee (UTN) and Indiana Relative Chemical Hazard Score (IRCHS) are either limited to aquatic ecosystem (they have little concerns about other

environmental issues such as air pollution) or they are comprehensive and mixed up with safety risks of chemicals. Life Cycle Assessment (LCA) is another methodology, which has become popular due to its significant contribution on Environmental Management System (EMS) improvements. LCA is a method of the evaluation of environmental aspects and the potential impacts of a product, process or service, which is carried out by collecting a record of material and energy input and emissions to the environment, assessment of the potential environmental impacts of the identified inputs and released and finally, construing the outcomes for decision-making (EPA, 2012b).

Waste Reduction (WAR) algorithm is also another methodology for environmental protection. The WAR algorithm is not only a methodology for verifying the potential environmental impact of a chemical process in terms of both the impacts of material waste and the energy impacts on the environment; it is also a tactic to decrease the undesired species in the process (Hilaly and Sikdar, 1995). Chemical wastes can be produced in any step of a chemical life cycle such as raw material, manufacturing, product distribution, product transportation and disposal, which is concerned with LCA. However, only the manufacturing step is concerned with the WAR algorithm as shown in Figure 3.1 (Young and Cabezas, 1999).

Both LCA and WAR algorithm are recognized by EPA. Young and Cabezas (1999) have developed an amendment to the WAR algorithm, called PEI (Potential Environmental Impacts) balance, as a means to evaluate environmentally friendliness of a process design and alternatives. Adverse effects on the environment are not limited to material wastes especially as hazardous chemicals, energy in the form of heating medium, cooling water and electric power has also destructive influences on the environment.

In this research work, the PEI method has been used for material impacts assessment but developed new energy indices in order to convert energy generation and/or consumption in a process plant in either of kJ/r and kWh units to the energy impacts in terms of kg/h CO_2, NO_2 and SO_2 emissions to the environment. The new energy impacts indices can be extended to other industrial and business applications. In other words, given the energy consumption of an electromotor; for instance, one can easily calculate the above mentioned gas interventions to atmosphere.
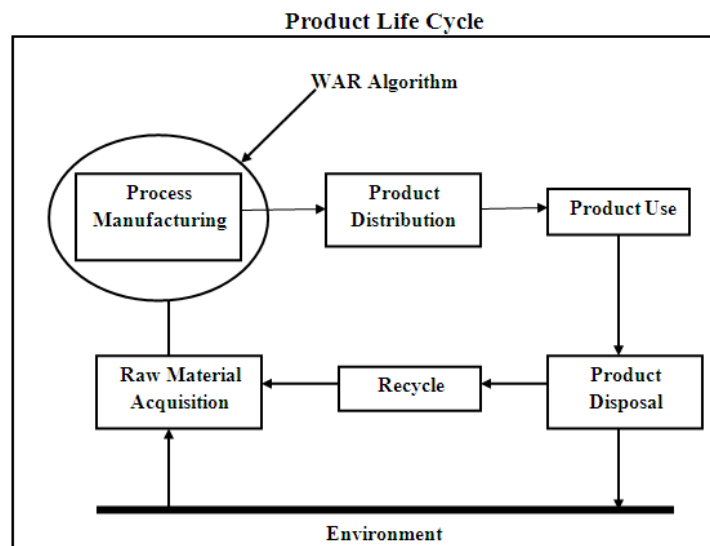
Figure 3.1 The WAR algorithm is concerned only with the processing step of a complete Life Cycle Analysis (LCA), (Young and Cabezas, 1999).

3.2 ENVIRONMENTAL IMPACTS CATEGORIES

The economic and environmental impacts perspectives are two major constraints for process engineers who intend to propose enviable chemical processes to investors, regulators and environmentalists. The WAR algorithm encompasses waste minimization and increasing the production rate and thus, it accounts for an economic design.

The WAR algorithm theory employs eight environmental impact categories for the assessment of PEI indices (Young et al., 2000). These categories are classified into two general areas of concerns; each one is associated with four categories:

- **Global atmospheric impacts:** The global atmospheric impacts contain Global warming potential (GWP), Ozone depletion potential (ODP), Photochemical oxidation potential (PCOP), and Acidification potential (AP).

- **Local toxicological impacts:** The local toxicological impacts contain Human toxicity potential by ingestion (HTPI), Human toxicity potential by exposure both dermal and inhalation (HTPE), Terrestrial toxicity potential (TTP), Aquatic toxicity potential (ATP).

3.3 METHODOLOGY FOR POTENTIAL ENVIRONMENTAL IMPACT (PEI) ASSESSMENT

The PEI of a hazardous chemical and energy is defined as the influence of such material and energy on the environment if they were discharged to the environment (Young and Cabezas, 1999).

Unlike temperature and pressure, which are the properties of a substance, PEI is a theoretical property and cannot be detected directly. Therefore, PEI has to be calculated from other measurable quantities as we do for the calculation of heat content of a substance or a stream from its temperature.

3.3.1 Total potential environmental impact indices

Cabezas et al. (1999) and Young et al. (2000) described the potential environmental impact balance by an equation similar to the following:

$$\frac{dI_{System}}{dt} = \dot{I}_{in}^{(t)} - \dot{I}_{out}^{(t)} + \dot{I}_{gen}^{(t)} \qquad (3.1)$$

where I_{System} represents the quantity of potential environmental impact inside the chemical process system, $\dot{I}_{in}^{(t)}$ and $\dot{I}_{out}^{(t)}$ are the rate of total potential environmental impact existing in the input streams to/and the output streams from the chemical process system, respectively. The term $\dot{I}_{gen}^{(t)}$ denotes the rate of total potential environmental impacts generated or consumed by chemical reactions within the chemical process system.

At steady state, the left-hand side of equation (3.1) becomes zero and therefore:

$$\dot{I}_{in}^{(t)} - \dot{I}_{out}^{(t)} + \dot{I}_{gen}^{(t)} = 0 \tag{3.2}$$

The total potential environmental impact consists of both product and non-product streams. $\dot{I}_{in}^{(t)}$ and $\dot{I}_{out}^{(t)}$ can be found by the following equations:

$$\dot{I}_{in}^{(t)} = \sum_j \dot{I}_{j,in}^{(t)} = \sum_j^{Streams} \dot{M}_{j,in} \sum_k^{Comps} x_{kj} \psi_k \tag{3.3}$$

And similarly:

$$\dot{I}_{out}^{(t)} = \sum_j \dot{I}_{j,out}^{(t)} = \sum_j^{Streams} \dot{M}_{j,out} \sum_k^{Comps} x_{kj} \psi_k \tag{3.4}$$

where $\dot{I}_{j,in}^{(t)}$ and $\dot{I}_{j,out}^{(t)}$ are the rate of PEI for the stream j for input and output streams, respectively. $\dot{M}_{j,in}$ and $\dot{M}_{j,out}$ are the mass flow rates of input and output stream j, respectively. x_{kj} is the mass fraction of component k in the stream j. And ψ_k is the overall PEI of component k. Equation (3.2) is a definition for $\dot{I}_{gen}^{(t)}$.

3.3.2 The potential environmental impact indices for pollutants

As defined earlier in this thesis, the non-product streams are considered as wastes. Since one of the objectives of this research is to reduce the wastes using WAR algorithm, there is no need to evaluate the total potential environmental impacts. Instead, the PEIs of non-product streams will be calculated only. Thus, we replace the superscript (t ≡ total) with (NP ≡ non-product) in all above equations.

$$\dot{I}_{in}^{(NP)} - \dot{I}_{out}^{(NP)} + \dot{I}_{gen}^{(NP)} = 0 \tag{3.5}$$

$$\dot{I}_{in}^{(NP)} = \sum_j \dot{I}_{j,in}^{(NP)} = \sum_j^{Streams} \dot{M}_{j,in} \sum_k^{Comps} x_{kj}^{NP} \psi_k \tag{3.6}$$

$$\dot{I}_{out}^{(NP)} = \sum_j \dot{I}_{j,out}^{(NP)} = \sum_j^{Streams} \dot{M}_{j,out} \sum_k^{Comps} x_{kj}^{NP} \psi_k \tag{3.7}$$

Two impact categories are used to identify the friendliness of a manufacturing process:

- The generation of PEI within the process, and
- The emissions of PEI by the process.

There are three indices for each impact categories, totally six indices. Four indices are driven from first two indices $\dot{I}_{gen}^{(NP)}$ and $\dot{I}_{out}^{(NP)}$ as follows:

$\dot{I}_{gen}^{(NP)}$ is the rate of total potential environmental impacts generated or consumed by chemical reactions within the chemical process system. And $\dot{I}_{out}^{(NP)}$ is the rate of total potential environmental impact existing in the output streams from the chemical process system. The unit of both $\dot{I}_{gen}^{(NP)}$ and $\dot{I}_{out}^{(NP)}$ is the potential environmental impact per unit time; e.g. hr, min etc.

The unit of $\dot{I}_{gen}^{(NP)}$ and $\dot{I}_{out}^{(NP)}$ can be expressed as the potential environmental impact per kg products. To do so, they are divided by the plant production rate:

$$\hat{I}_{gen}^{(NP)} = \frac{i_{gen}^{(NP)}}{\sum_p \dot{P}} = \frac{i_{out}^{(NP)} - i_{in}^{(NP)}}{\sum_p \dot{P}} = \frac{\sum_j \dot{M}_{j,out} \sum_k x_{kj}^{NP} - \sum_j \dot{M}_{j,in} \sum_k x_{kj}^{NP}}{\sum_p \dot{P}} \qquad (3.8)$$

$$\hat{I}_{out}^{(NP)} = \frac{i_{out}^{(NP)}}{\sum_p \dot{P}} = \frac{\sum_j \dot{M}_{j,out} \sum_k x_{kj}^{NP}}{\sum_p \dot{P}} \qquad (3.9)$$

Now, there are four indices in order to calculate the environmental impacts.

$i_{gen}^{(NP)}$ and $\hat{I}_{gen}^{(NP)}$ indicate the pollution generation potential of a chemical process. They are useful tools to address internal environmental friendliness of a process in terms of generation of significant desirable products and minimum undesirable environmental impacts. This means we still need pollution control equipment but at a minimum cost.

Apparently, judgment will be made after comparing the indices for all process alternatives. The smaller the indices values are, the more environmental effective process is.

The first index, $i_{gen}^{(NP)}$, can be used for comparison of different design alternatives on absolute basis while the next index, $\hat{I}_{gen}^{(NP)}$, is used to compare the alternatives independently from the plant size.

$i_{out}^{(NP)}$ and $\hat{I}_{out}^{(NP)}$ are also two indices of the second impact category, which indicate the pollution emission potential of a chemical process. They are also useful tools to address external environmental friendliness of a process in terms of emission of significant desirable products and minimum undesirable environmental impacts. Again, the smaller the indices values are, the more environmental effective process is. The first index, $i_{out}^{(NP)}$, can be used for deciding which

site is compatible with the rate of total non-product streams while the next indices, $\hat{I}_{out}^{(NP)}$, is used to compare design alternatives independent to the plant size.

3.3.3 The methodology of finding the effects of the emission to eight PEI categories

So far ψ_k was introduced in equations (3.3), (3.4), (3.6) and (3.7). ψ_k is the overall PEI of chemical k. Therefore, it must be determined for different chemicals over a wide range of different environmental impacts, which is not an easy task since the impacts are measured on relatively different scales and need to be normalized for summation. ψ_k is calculated from the following equation:

$$\psi_k = \sum_i^{EnvCat} \alpha_i \, \psi_{ki}^S \tag{3.10}$$

where summation is taken over the potential environmental impacts categories. The waste reduction (WAR) algorithm employs eight environmental impact categories for the assessment of PEI indices: HTPI, HTPE, TTP, ATP, GWP, ODP, PCOP and AP. These categories are mentioned in Section 3.2 and details have been provided in APPENDIX B.

Weighting factor, α_i, represents the site effects on the environmental pollution and has the unit of PEI per mass. When the process location is not known, like the current research, the weighting factor would have equivalent value of unity ($\alpha_i = 1$) for all categories (Cabezas et al., 1997). It enables the designer to add up all PEI categories into a single amount called PEI index. The designer will decide whether or not it should be considered in calculations. For instance, an off-shore well has zero weighting factors for terrestrial toxicity potential (TTP) while similar on-shore well has unity weighting factor for TTP.

ψ_{ki}^S is the specific PEI of chemical k for an impact category i and can be calculated from the following equation:

$$\psi_{ki}^{S} = \frac{(\text{Score})_{k,i}}{\langle(\text{Score})_{k}\rangle_{i} + 2\,\sigma_{i}} \qquad\qquad (3.11)$$

where $(\text{Score})_{k,i}$ is the relative score of chemical k (arbitrary scale) for an impact category i, $\langle(\text{Score})_{k}\rangle_{i}$ is the arithmetic average of the score of all components k for the impact category i, and σ_i is the standard deviation of all chemical scores in impact category i.

The chemical environmental impact categories and the values for the $(\text{Score})_{k,i}$ are taken on from the researches of Heijung et al. (1992) and normalization are made by using the equation (3.10) to find the values of ψ_{ki}^{S} for the chemical k within the impact category i. There are eight environmental impact categories for the assessment of PEI indices (Section 2.4): HTPI, HTPE, TTP, ATP, GWP, ODP, PCOP and AP. This equation solves all environmental impact categories (i's) for each chemical k.

3.4 SOFTWARE REQUIREMENT FOR PEI CALCULATIONS

Calculation of PEI categories is time consuming so; there is a high demand to software to calculate the PEIs and to integrate the PEI into process design. Therefore, HYSYS and ChemCAD process simulators are used in this work. Cabezas et. al. (2009) developed WAR algorithm as one of CHEMCAD modules. Chemstation Inc. has added a module called WAR Algorithm into CHEMCAD 6.2.0.3348 with the help of Cabezas et al. (1998-2009) for the calculation of the pollution indices of different streams in a process (Figure 3.2).

This module calculates all of the PEIs associated with each category for a wide range of chemicals. The simulator then adds up total index of all chemical components in a stream.

There is also standalone software developed by the same experts in EPA called WAR GUI (2008). WAR GUI estimates the impact of wastes material and energy in terms of fossil fuel combustion and CO_2 emission rate to environment based on WAR algorithm methodology.
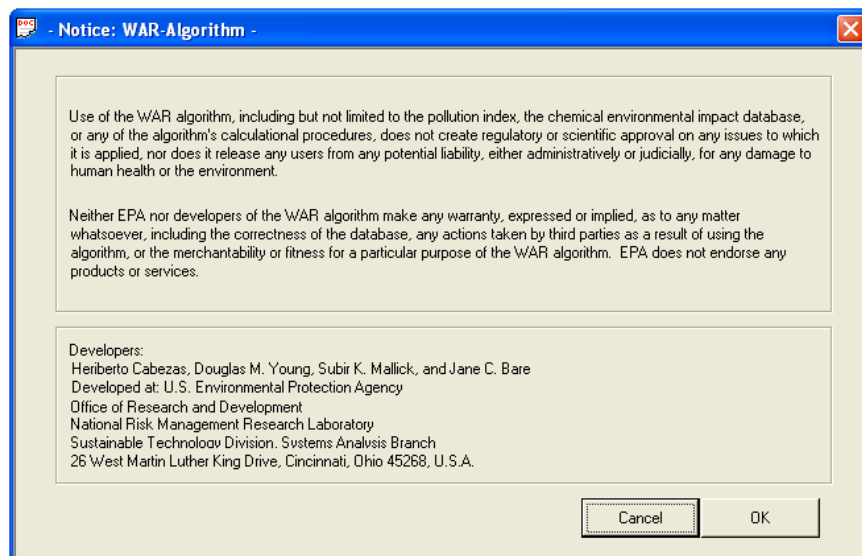
Figure 3.2 A notification from EPA as developer of WAR algorithm as a module of CHEMCAD software (Cabezas et al., 1998-2009).

Chapter 4

METHODOLOGY FOR POTENTIAL ENVIRONMENTAL IMPACTS ASSESSMENT: ENERGY

A new methodology is presented for relating the generation and/or the consumption of heat and electrical energy to the rate of CO_2, NO_2, and SO_2 emissions to the environment. Two indices have been introduced in this chapter for the precise determination of emissions of these gases to the atmosphere and are of help in the analysis and comparison of the quality and efficiency of energy options. The indices have proved that there is no linear relationship between energy consumptions and the emission of above environmental gas pollutants (unlike EIA and EPA methodologies) and can be applied to any industry in which heat or electricity is used. The new methodology requires minimal data, such as fossil fuel characteristics and heat flow through heaters and electrical energy consumption by fans, pumps, and compressors. Two case studies are provided to illustrate how the new methodology quantifies such emissions and how the technique can be employed in screening alternative technologies or designs.

The new energy indices presented in this chapter has foremost advantages as follows:

1. Simple.
2. Quantification of emission rates.

3. Accurate: It precisely calculates the gas emission rates: i.e. CO_2, SO_2 and NO_2 per hour. Hence, it provides another angle of view to see insight of the processes in terms of environmentally friendliness of a chemical process.

4. Establishes a perfect relationship between energy consumption in a chemical industry and above-mentioned emissions.

5. Needs min. data; e.g. fossil fuel characteristics, energy consumption by e-motors from nameplates.

6. No need to fossil fuel flow rates in power plants.

7. It proves that an economic design is coined to sustainability.

8. And finally, this index is an effective screening tool for decision-makers to evaluate and select the most energy efficient and environmentally friendliest process design among other design array.

4.1 METHODOLOGY FOR ENERGY IMPACT ASSESSMENT

This research offers a new methodology to establish a direct relationship between the energy produced from fossil fuels in the form of heat or electrical power to the polluting gas emissions, e.g. CO_2, NO_2 and SO_2. This relationship can be accurately established using the stoichiometry of the combustion of carbon, nitrogen and sulfur atoms using: (a) the chemical composition of the fuel, (b) the enthalpy of combustion of fossil fuels, and (c) the heat content of the fuel. The advantages of this new methodology are as follows:

- The calculation can be made using minimal available data.

- The methodology can be used at an early stage of process design, despite lack of detailed process data. It can also be used in an operating plant for the estimation of emission rates based on energy consumption by pumps, compressors, etc.

- Unlike the EPA and EIA methods, there is no need to determine the flow rate of fuel.

- The method can be extended to non-process applications in which heat or electricity is generated or consumed by or from fossil fuels.

- It provides detailed information about process units, chemical or petrochemical complexes, and fossil-fueled power plants in terms of environmental acceptability.

4.2 THE DEPENDENCY OF POLLUTING GAS EMISSIONS ON ENERGY GENERATION

When the objective is the estimation of CO_2 emission rate from the combustion of a fuel, assuming the combustion is complete due to reasonably high amount of Air/Fuel ratio, the following equation applies:

$$\dot{I}_e = \frac{(\dot{Q} \times x_c \times MW_{CO_2})}{(\Delta H_{Comb.} \times MW_C)} \tag{4.1}$$

where $\dot{Q}$ is the heat flow (kCal/h), x_c is the mass fraction of carbon component in the fuel, MW_{CO2} and MW_C are the molecular weights of carbon dioxide (kg CO_2/kgmole) and carbon atom (kg C/kgmole), respectively and ΔH_{Comb} is the enthalpy of fuel combustion (kCal/ kg fuel). $\dot{I}_e$ is the emissions rate of carbon dioxide to the atmosphere in kgCO_2/h.

In practical applications in which a hydrocarbon fuel is burned, ΔH_{Comb} is replaced by HV (Annamalai and Puri, 2002), the heating value of a fuel:

$$HV = - \Delta H_{Comb} \tag{4.2}$$

In the course of the fuel combustion water is generated. Depending on the state of the produced water, the heat value is defined as lower heat value (LHV) for gaseous water phase and higher (or gross) heat value (HHV) for liquid aqueous phase:

$$\text{LHV} = \Delta H_{\text{React.}} - \Delta H_{\text{Prod., H2O (g)}} \tag{4.3a}$$

$$\text{HHV} = \Delta H_{\text{React.}} - \Delta H_{\text{Prod., H2O (l)}} \tag{4.3b}$$

Thus, replacing ΔH_{Comb} by the heat value (HV), followed by rearrangement of equation (4.1) for a general equation gives:

$$\dot{I}_{J,k} = x_i \times \left(\frac{\dot{Q}_{i,k}}{\eta_k \times HV}\right) \times \left(\frac{MW_j}{MW_i}\right) \tag{4.4}$$

$$\dot{I}_J = \sum_k \dot{I}_{J,k} = \sum_k x_i \times \left(\frac{\dot{Q}_{i,k}}{\eta_k \times HV}\right) \times \left(\frac{MW_j}{MW_i}\right) \tag{4.5}$$

$$\dot{I}_e = \sum_j \dot{I}_J \tag{4.6}$$

In the above equations, η is the efficiency; k is process unit (e.g. fired heater, heater, and electromotor). For instance, when the estimation of the emission due to electricity consumption by a compressor is of interest, in this case k is an electromotor η_k is the total efficiency, given by the multiplication product of conversion efficiencies of boiler and steam turbine. $\dot{Q}_{i,k}$ is the fraction of the heat flow and/or the energy consumption related to component i (kcal/h), where i = C, S and N, in process unit k. HV is the fuel heat value (kCal/kg fuel), x_i is the mass fraction of component i, and MW is its molecular weight (kg/kgmole). The subscripts i denotes the atom content of the fuel (i = C, S or N) and j denotes the gas emitted to the atmosphere (j = CO_2, SO_2, NO_2). $\dot{I}_{J,k}$ is the gas emission rate to the atmosphere in the form of component j due to either heat or electricity consumption in the process unit k in kg CO_2 (or SO_2 or NO_2) per hour.

In the equation (4.5), it is assumed that each atom contributes to the heat flow or the energy generation based on its content in the fossil fuel. This assumption is valid, since the heat flow

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is a size-dependent property, which means that the fuel heat flow depends on the flow rate of individual components in the fuel. In other words, the heat flow is the sum of the heat released by combustion of each component of the fuel, and doubling the flow rate of each component of the fuel doubles the corresponding heat flow.

Depending on the nitrogen to oxygen ratio, oxidation of nitrogen gives two distinct products; a 7:8 ratio gives nitric oxide (NO) and a 7:16 ratio gives nitrogen dioxide (NO_2) (McMurray and Fay, 2003). Similarly, the burning of fossil fuels containing sulfur releases SO_2 into the atmosphere. While SO_2 is slowly oxidized to SO_3 by oxygen in the atmosphere, on the large scale this reaction can be catalyzed by V_2O_5 and in the presence of heat and water produces sulfuric acid. Both SO_2 and SO_3 are known to give rise to acid rain, a major environmental issue (McMurray and Fay, 2003). Hence, in the present paper it is assumed that the combustion reactions conducted in the presence of excess air and that the nitrogen and sulfur content in a fossil fuel is each converted to the most stable form (NO_2 and SO_2, respectively).

Since hydrogen and water are not regarded as pollutants, neither of these is of interest in terms of gaseous emissions.

It is very important to know that in a chemical process plant, the gas emissions related to energy consumptions such as electric motors do not necessarily take place in the plant location itself, but may occur in power plants or co-generation plants in which fossil fuels are burned to generate heat or electricity.

Steam turbine plants using fossil fuels account for the greatest proportion (more than 42%) of industrial applications. Among other fossil fuels gas provides the best energy source, since it generates fewest pollutants, at the same time requiring few handling facilities such as piping

or storage tanks (EPA, 1997). A study has shown that the emission of CO_2 from fossil fuels gave the highest figures (EPA, 1997) among other pollutants.

Combining the equations (4.5) and (4.6) gives:

$$\dot{I}_e = \sum_k \sum_j \sum_i x_i \times \left(\frac{\dot{Q}_{i,k}}{\eta_k \times HV}\right) \times \left(\frac{MW_j}{MW_i}\right) \qquad (4.7)$$

In order to assist process design, it is helpful to have an index independent of process size. This can be achieved by dividing both sides of equation (4.7) by the total production rate, which gives:

$$E = \frac{\dot{I}_e}{\sum_n \dot{P}_n} = \frac{\sum_k \sum_j \sum_i x_i \times \left(\frac{\dot{Q}_{i,k}}{\eta_k \times HV}\right) \times \left(\frac{MW_j}{MW_i}\right)}{\sum_n \dot{P}_n} \qquad (4.8)$$

where $n = 1,2,3,\dots$ represents the product streams in the process.

To illustrate the use of the proposed energy index given by Equations (4.5) and (4.7), it may be helpful for us to consider two case studies. In both cases, the production rates are the almost the same and therefore, the Equation (4.8) gives no preference to any alternatives because as stated earlier it is useful for comparing of the processes with different capacities.

Case study 1: Chlorination of methane

The production of chloromethane is an important reaction in the petrochemical industry due to their widespread application as solvents. One mole of methane reacts with four moles of chlorine to give carbon tetrachloride. The chlorination is a heterogeneous catalytic reaction, taking place in four steps as represented in equations (4.9) through (4.12) and the overall equation (4.13):

CH$_4$	+	Cl$_2$	→	CH$_3$Cl + HCl	(4.9)
CH$_3$Cl	+	Cl$_2$	→	CH$_2$Cl$_2$ + HCl	(4.10)
CH$_2$Cl$_2$	+	Cl$_2$	→	CHCl$_3$ + HCl	(4.11)
CHCl$_3$	+	Cl$_2$	→	CCl$_4$ + HCl	(4.12)

In summary:

$$CH_4 \quad + \quad 4\,Cl_2 \quad \rightarrow \quad CCl_4 \quad + 4\,HCl \qquad (4.13)$$

The rate constant of chlorination reactions ranges from very low, such as the chlorination of benzene (Levenspeil, 1999):

$$C_6H_6 + Cl_2 \rightarrow C_6H_5Cl + HCl \qquad\qquad k = 0.412 \text{ (liter/kmol.hr)} \qquad (4.14)$$

to very high; e.g. the chlorination of hydrogen molecules in presence of light to produce hydrogen chloride. Other chlorination reactions fall in between this range; e.g. the chlorination of C-H bond of cyclopentane at 40 ^{o}C in gas phase (Denisov, 1974):

$$C_5H_{10} + Cl_2 \rightarrow C_5H_9Cl + HCl \qquad\qquad \log k = 10.08 \qquad (4.15)$$

And also the formation of the following compounds at 25 ^{o}C (Denisov, 1974):

$$Cl_2C = CH_2 \qquad\qquad\qquad \log k = 9.46 \qquad (4.16)$$

$$Cl_2C = CHCl \qquad\qquad\qquad \log k = 9.25 \qquad (4.17)$$

$$Cl_2C = CCl_2 \qquad\qquad\qquad \log k = 8.89 \qquad (4.18)$$

The chlorination of methane involves a complex network of series and parallel reactions. The reactions (4.9) to (4.12) represent a series of reactions with respect to chlorinated species and parallel reactions with respect to Cl$_2$ (Missen et al., 1999).

Several factors affecting the kinetics of the chlorination of methane have been studied by researchers such as gas flow regime and gas-phase thermal reaction (Rozanov and Treger, 2010), CH_4/Cl_2 ratio and catalysts (Bucsi and Olah, 1992), effects of N_2 gas as an inert diluents on the photo-chlorination of methane and its selectivity (Cabrera et al., 1990), reaction temperature and pressure for industrial applications (Rozanov and Treger, 2010; Wiberg and Motell, 1963; Goldfinger et al., 1958).

The present case study made by HYSYS process simulator is close to the technology developed in Germany (Rozanov and Treger, 2010) and the thermodynamic and kinetic data are collected from Goharrokhi et al. (2009). The reactants are well mixed in a CH_4/Cl_2 molar ratio of 0.5 at 25 ºC and 1000 kPa. The chlorination reaction takes place in the gaseous phase at around 430 ºC.

In this case study, the objectives follow:

1) To design simplified processes for the chlorination of methane,

2) To estimate the emission of CO_2, SO_2 and NO_2 gases to the atmosphere as pollutants due to energy (steam and/or electric power) consumption in heater in corresponding designs.

3) To compare emission rates in all designs in "kg/hour" and finally to make conclusion.

In Figure 4.1a, the methane and chlorine feeds are heated up to 427 ^{o}C and then, sent to a PFR reactor.

(a)
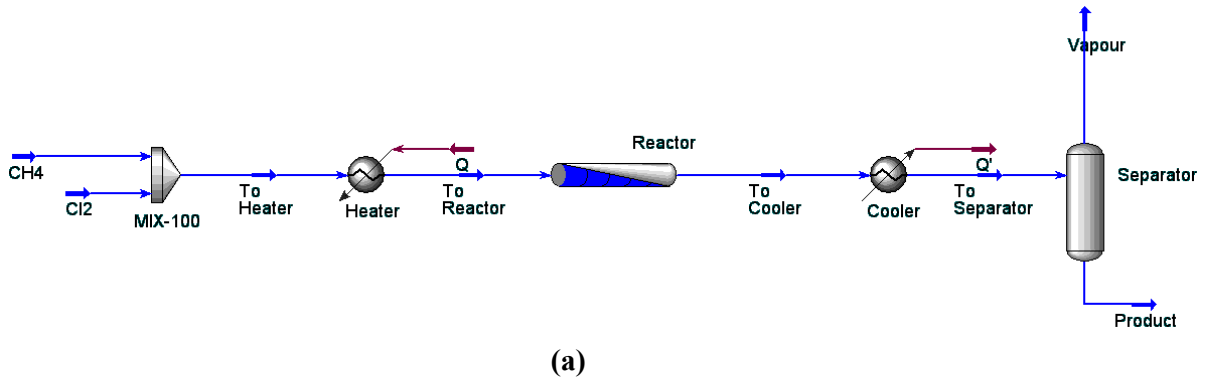
The reaction product (called "To Cooler") is the PFR outlet stream, which is cooled down to 10 °C before sending to the separator. The two phase flow stream entering to separator is separated into liquid stream (Product) and the vapour stream (Vapour). The liquid stream is not regarded as finished product and undergoes separate treatment in a downstream plant (not shown). The vapour stream; however, is considered as non-product, which is subject to waste treatment in downstream plant or control station.

In the alternative design (Figure 4.1b), a heat exchanger is simply added to the process in order to utilize the heat released from the chlorination reactions for the heating of feed stream to the PFR reactor and in turn, it decreases the temperature of the outlet stream from the PFR (marked "To Cooler"). This allows us to study the environmental effect of this well-known heat recovery system.

An alternative to this design involves the recycling of the vapor stream to the beginning of the process (Figure 4.1c).

The "Product" flow rates of the original and the alternative designs are 3931 and 3911 kg/h, respectively, about 0.5% difference. The fuel for the boilers is heavy fuel oil (HFO). Based on the compositions and characteristics of the HFO, attributed to each chemical component in the fuel, $\dot{Q}_i$, was calculated, and data of interest are listed in Table 4.1.
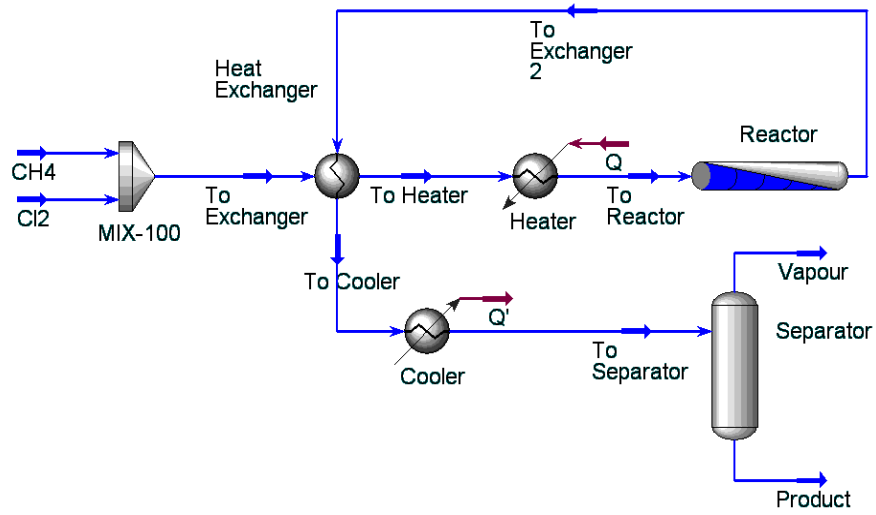
(b)
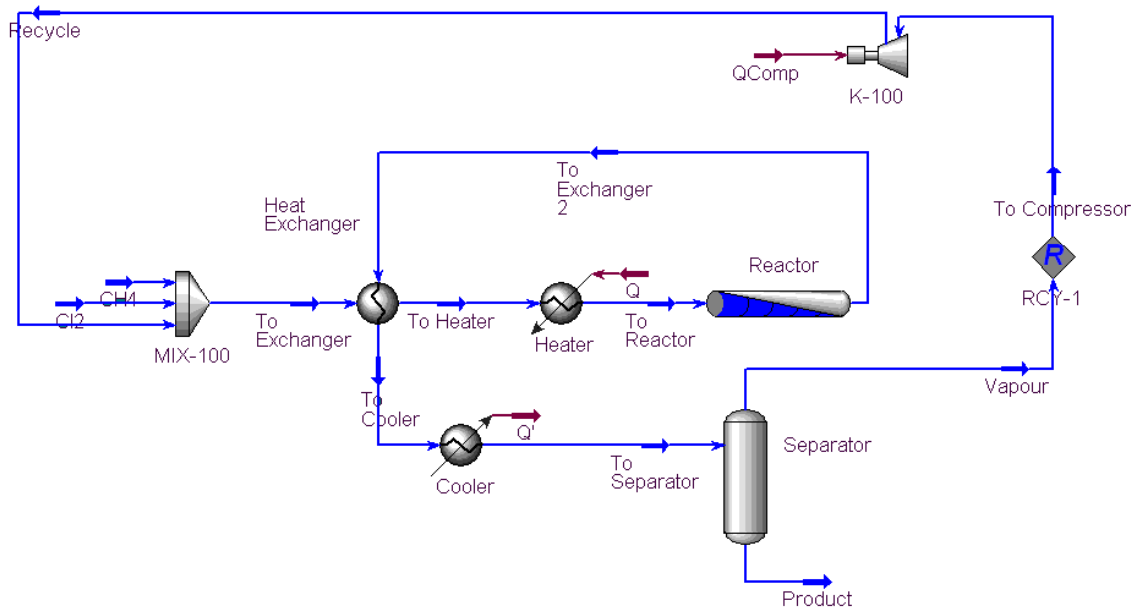
(c)

Figure 4.1. Chlorination of methane. (a) The chlorination design without heat exchanger. (b) The chlorination design with heat exchanger. (c) The chlorination design with heat exchanger and recycling.

Table 4.1: The characteristics of heavy fuel oil and the breakdown of heat flow and energy consumption in three designs.

Characteristics of Heavy Fuel Oil	Value	Heat Flow, $\dot{Q}_{i,k}$, in kJ/h (Design without Exchanger) [i]	Heat Flow, $\dot{Q}_{i,k}$, in kJ/h (Design with Exchanger) [ii]	Heat Flow, $\dot{Q}_{i,k}$, in kJ/h (Design with Exchanger & Recycling) [iii]	
				Heat	Power
Sp. Gr.	0.941				
HV of Fuel	18,200 Btu/Lb **(42,293 kJ/h)**				
S	2.7 wt%	113,836.5	3059.1	194,994	107,784
C	84.8 wt%	3,575,308.8	96,078.4	6,124,256	3,385,216
N	0.5 wt%	21,080.8	566.5	36,110	19,960
H	11.93 wt%	502,988.6	13,516.7	861,585	476,245

i   Calculation of this column is based on the 1ˢᵗ column of Table 4.2 for energy flows. For instance, in the original design, the heat flow is 4.2×10^6 kJ/h. Hence, the contribution of C in heat flow is 4.2×10^6 kJ/h $\times$ $0.848 = 3.58 \times 10^6$ kJ/h.

ii Similar to item i above, in the design with exchanger, the heat flow is 1.1×10^5 kJ/h. Hence, the contribution of C in heat flow is 1.1×10^5 kJ/h $\times 0.848 = 9.6 \times 10^4$ kJ/h.

iii Similar to item i above, in the design with exchanger & recycling, the heat flow is 7.2×10^6 kJ/h. Hence, the contribution of C in heat flow is 7.2×10^6 kJ/h $\times 0.848 = 6.1 \times 10^6$ kJ/h. As such, the contribution of C in power consumption is 3.99×10^6 kJ/h $\times 0.848 = 3.38 \times 10^6$ kJ/h.

Important Note: The values of heat flow and power consumption are calculated by mass and energy balance from HYSYS process simulator.

Taking 75% as the conversion efficiency of the boiler (Coulson and Richardson, 2001), it is now possible to calculate the emission rates of all three gases and to compare the three process designs using (4.5) with the proviso that $k = 1$ for "with" and "without" heat exchanger designs (Figures 4.1a,b) and k = 2 for heater and compressor (Figure 4.1c).

A. Without exchanger design: In the original design (Figure 4.1a), the amount of heat flow by steam in the heater is 4.2×10^6 kJ/h (Table 4.2). The emission rates of pollutants to the environment can be calculated using equation (4.5):

$$\dot{I}_{CO2} = \frac{3{,}575{,}308.8 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44 \left(\frac{kgCO_2}{kgmole}\right)}{0.75 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 12 \left(\frac{kgC}{kgmole}\right)} = 350.3 \; \frac{kgCO_2}{h}$$

Similarly, the gas emission rates for SO_2 and NO_x are 0.19 kg SO_2/h and 0.01 kg NO_2/h:

$$\dot{I}_{SO2} = \frac{113{,}836.5 \left(\frac{kJ}{h}\right) \times 0.027 \left(\frac{kgS}{kgFuel}\right) \times 64 \left(\frac{kgSO_2}{kgmole}\right)}{0.75 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 32 \left(\frac{kgS}{kgmole}\right)} = 0.19 \; \frac{kgSO_2}{h}$$

$$\dot{I}_{NO2} = \frac{21{,}080.8 \left(\frac{kJ}{h}\right) \times 0.005 \left(\frac{kgN}{kgFuel}\right) \times 46 \left(\frac{kgNO_2}{kgmole}\right)}{0.75 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 14 \left(\frac{kgN}{kgmole}\right)} = 0.01 \; \frac{kgNO_2}{h}$$

B. With exchanger design: In the design with exchanger (Figure 4.1b), the amount of heat flow by steam in the heater is 1.133×10^5 kJ/h (Table 4.2). So, the rate of CO_2 emission to the environment can be estimated using equation (4.5):

$$\dot{I}_{CO2} = \frac{96{,}078.4 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44.01 \left(\frac{kgCO_2}{kgmole}\right)}{0.75 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 12.01 \left(\frac{kgC}{kgmole}\right)} = 9.4 \; \frac{kgCO_2}{h}$$

Similarly, the gas emission rates of SO_2 and NO_2 are 5 g SO_2/h and 0.3 g NO_2/h, respectively.

C. With exchanger and recycling design: In this design (Figure 4.1c) we can calculate the gas emissions for both heater and compressor. Total heat flow is 1.121×10^7 kJ/h (Table 4.2). So, the rate of CO_2 emission to the environment can be estimated using equation (4.5):

$$\dot{I}_{CO2} = \frac{6{,}124{,}256 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44.01 \left(\frac{kgCO_2}{kgmole}\right)}{(0.75) \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 12.01 \left(\frac{kgC}{kgmole}\right)}$$

$$+ \frac{3{,}385{,}216 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44.01 \left(\frac{kgCO_2}{kgmole}\right)}{(0.75 \times 0.35) \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 12.01 \left(\frac{kgC}{kgmole}\right)} = 1.547 \; \frac{tons\; CO_2}{h}$$

Similarly, the gas emission rates of SO_2 and NO_2 are 856 g SO_2/h and 49 g NO_2/h, respectively.

4.3 RESULTS FROM CHLORINATION PROCESS DESIGN

Table 4.2 summarizes the result for the above calculated emission rates and heat flows, and also production rates for all three designs. The addition of an exchanger results in a significant reduction in the size of both cooler and heater in alternative design including a heat exchanger compared to the original design. Surprisingly, it also reveals that the recycling of vapor to the beginning of the process, as in the alternative design (Figure 1c), causes a huge increase in energy consumption, particularly by the compressor.

As mentioned earlier, due to a lack of information regarding the contribution of fossil fuel types to CO_2 emissions, the EIA conversion factor (Equation 2.2) is based on the average emission for all three types of fossil fuels, and this gives an approximate value. As it can be seen in Table 4.2, the difference between the EIA index and the proposed alternative varies

from 25% in the original design to 55% in the alternative containing heat exchanger and recycling. The reason for this significant variation is that the conversion efficiency of the compressor and boiler are allowed for the new index.

Unlike EIA's and EPA's methodologies, in new energy impacts index there is no linear relationship between energy consumption and gas emission (Table 4.2) due to ignorance of efficiency factors of boiler and turbine in both methodologies. For instance, the energy consumption ratio in the alternative design with heat exchanger and recycling process to the alternative design with heat exchanger (without recycling) process is 100, while the corresponding emission ratio is 165.

Similarly, the design with heat exchanger and without recycling process emits least polluting gases to the atmosphere by a factor of about 40 and 165 compared to both alternatives. This means the design with heat exchanger and without recycling process is not only economic, but also it helps to preserve fossil fuel resources and clean air (the concept of sustainability). Hence, Figure 1b is the best design among other alternatives.

Due to equal production rate, the denominator of the emission *"E"* in the equation (4.8) is almost the same for all designs; therefore, we did not proceed to calculate *"E"*. The present values of emission rates clearly prove that the alternative design is desirable process.

Table 4.2: Comparison of new emission index with the existing methods in three designs of the chlorination of methane.

	Energy Consumption[i] (kJ/h)	Product Stream (kg/h)	New Emission Index (kg CO_2/h)	New Emission Index (kg SO_2/h)	New Emission Index (kg NO_2/h)	Changes with Respect to the Original Design (New Index)	EIA's[ii] Method (kg CO_2/h)	EPA's[iii] Method (PEI/h)	Changes with Respect to the Original Design (EIA & EPA)
Original Design	4.2 x 10⁶	3,931	**350.3**	0.19	0.01	-	264.6	18.06	-
Alternative Design with Heat Exchanger	1.1 x 10⁵	3,910.4	**9.4**	0.005	0.0003	**-97.3%**	6.93	0.473	**-97.3%**
Alternative Design with Heat Exchanger & Recycling	1.1 x 10⁷	3,903.6	**1547**	0.856	0.049	**341.6%**	693	47.3	**161.9%**

(i)   From mass and energy balance made by HYSYS process simulator.

(ii) EIA method from equation (2.2).

(iii) EPA method from WAR GUI software (WAR GUI, 2008).

Important Note 1: The calculation of emissions due to heat flow or power consumptions for all three process designs are given in pages 71-72.

Case Study 2: Hydrogenation of unsaturated hydrocarbon

Hydrogenation is widely applied in refineries as an effective way to protect the process equipment from corrosion and the environment from emissions. For instance, monomers (particularly) containing divinyl group may cause branching of monomers to produce macromolecules with large molecular weights under certain conditions similar to gel or gum formation (Rudin, 1999). Gums are harmful for gasoline end users and for environment, which can be eliminated by hydrogenation reaction.

For a specific hydrogenation process different alternatives may be designed, one of which is environmentally friendlier and inherently safer among other alternatives array. So, how can a process designer or a decision maker screen out other alternatives and pick the best design with this regard? In this case study, the new composite indices will answer to this question.

The unsaturated hydrocarbons in product stream are undesirable and regarded as non-products or wastes to be separated in downstream. Hydrogenation is a heterogeneous equilibrium catalytic reaction upon which the value of final products is significantly raised by eliminating the unsaturated hydrocarbons.

From the Le Chatelier's principle: "In an equilibrium reaction, any changes in concentration, temperature, volume or partial pressure in either side of the reaction equation, moves the equilibrium to the direction to counteract the change", it can be concluded:

1   When exothermic reaction is concerned, the reactor temperature has to be decreased.

2   When the number of the moles decreases in the course of the reaction, the pressure will drop in gas phase reaction. So, the reactor pressure should be increased.

3   In hydrogenation case, the hydrogen is consumed. Thus, the hydrogen pressure at the inlet to the PFR should be increased.

4.4 REACTION MODELING

In this case study, the hydrogenation of unsaturated hydrocarbon was modeled by Aspen HYSYS 2006. Studies show that Pd is the best catalyst for industrial hydrogenation applications due to its significant conversion factor and high selectivity effect (Krupka et al., 2006). The commercial form of industrial scale palladium catalyst is palladium oxide39 on γ-alumina as base metal. Therefore, it is crucial to pay attention to this matter that in initial start-up the catalyst should undergo the reduction reaction by the injection of hydrogen rich gas into the reactor bed in order for the oxygen atoms of the palladium oxide to react with catalyst. Otherwise, the catalyst would be inactive and any free oxygen would be harmful in terms of reactor safety and reaction by-product.

Pd/α-Al$_2$O$_3$ is highly selective with no significant deactivation (Seth et al., 2007). The effects of internal diffusion on the rate of hydrogenation reaction of styrene by applying different Pd particle sizes revealed that the small particle size accounts for kinetics phenomena (Zhou et al., 2007).

In order to model the hydrogenation reaction, the reaction rate and order, the values for activation energy, frequency factor, and referenced temperature at which these values have been investigated must be known. The hydrogenation reactions rate has been presented by Seth et al. (2007):

$$-r_A = k \, C_A C_{H_2}^{1/2} \tag{4.19}$$

Given E and K_{ref} at T_{ref}, the k value is calculated by Arrhenius' equation:

$$k = k_{ref} \, exp \left[-\frac{E}{R} \left(\frac{1}{T} - \frac{1}{T_{ref}} \right) \right] \tag{4.20}$$

where k_{ref} is the frequency factor at a reference temperature T_{ref}, E is the activation energy, and R is the general gas constant. The above model calculates k at any arbitrary temperature. The reference values of k_{ref} and T_{ref}, and E for the hydrogenation of some olefins are given in Table 4.3 (Sarkar et al., 2006; Seth et al., 2007; Zhou et al., 2007).

There is still a need to other data for modeling the hydrogenation process such as the chemical composition and the condition of feed stream(s) at battery limit (B.L.). Tables 4.4 and 4.5 show the condition and the composition of the feed stream, respectively.

Table 4.3: The kinetics data of hydrogenation reactions of some olefins.

Reactants	k_{ref} $[mol/(s)(kg.cat)] \times (m^3/mol)^{3/2}$	T_{ref} °C	E J / mol	Reference
1-Butene	1.482×10^{-5}	50	34,900	Seth et al., 2007
Iso-butene	2.0958×10^{-6}	50	39,100	Seth et al., 2007
Iso-octene	1.23×10^{-4}	110	10,506	Sarkar et al., 2006
Styrene	0.0415	50	26,030	Zhou et al., 2007

Now, it is possible to design a hydrogenation of unsaturated hydrocarbons. There are four unsaturated hydrocarbons containing C=C bonds in Table 4.5, which are undesirable and therefore, subject to hydrogenation reaction.

Ordouei et al. (2011) have used the above reaction model to design a hydrogenation plant.

Figures 2a,b and Figures 3a,b show two hydrogenation designs.

Table 4.4: The conditions of the feed streams.

No.	Parameter	Plant Feed	H$_2$ Feed	H$_2$ Make-Up
1	Pressure (bar)	29	29	27
2	Temperature (^{o}C)	100	100	25
3	Mass Flow Rate (Kg/h)	12,500	500	100

Table 4.5: The compositions of the feed streams at Battery Limit in wt%.

No.	Components	Hydrocarbon Feed Stream (wt %)	H$_2$ Feed Stream (wt %)	H$_2$ Make-Up Stream (wt %)
1	Iso-Butane	1.02	0	0
2	n-Butane	0.79	0	0
3	Iso-Pentane	0.96	0	0
4	n-Pentane	0.17	0	0
5	Iso-Butene	0.91	0	0
6	Iso-octene	10.92	0	0
7	Iso-octane	0	0	0
8	1-Butene	0.54	0	0
9	Styrene	15.53	0	0
10	Ethyl-Benzene	2.31	0	0
11	Benzene	48.01	0	0
12	Toluene	18.84	0	0
13	Hydrogen	0	100	100
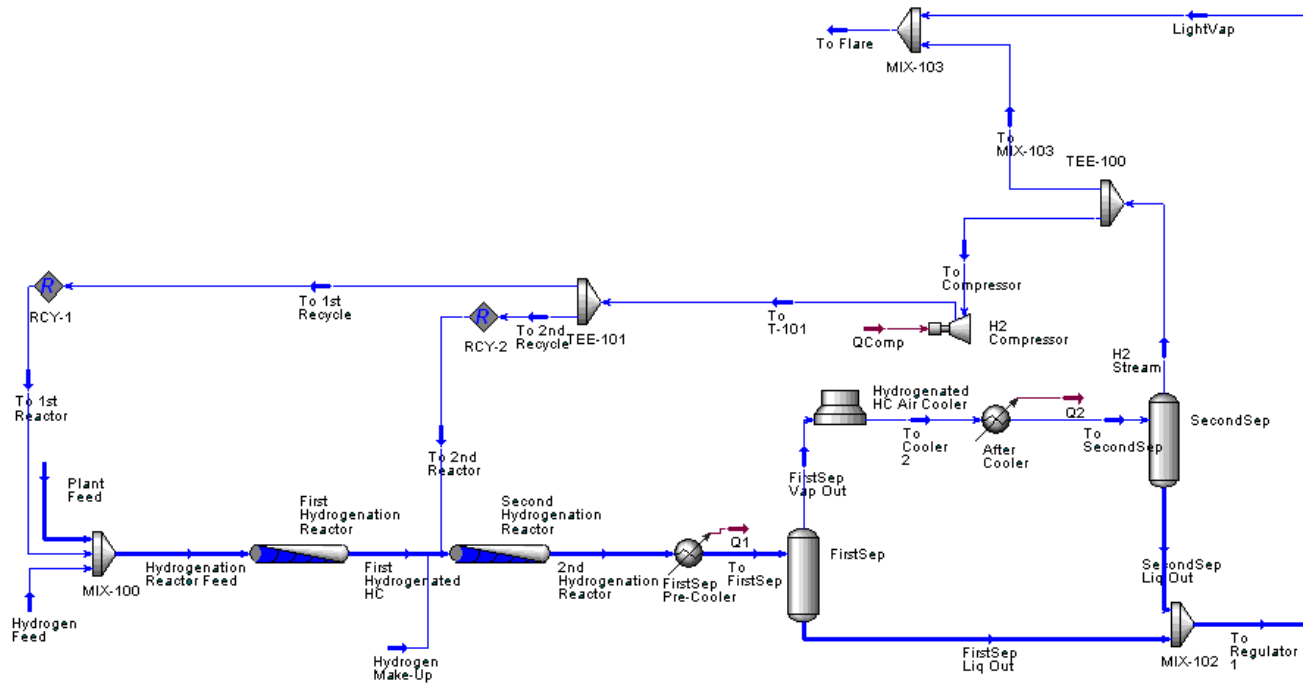
Figure 4.2a Hydrogenation Process; Original design: reaction and phase separation.
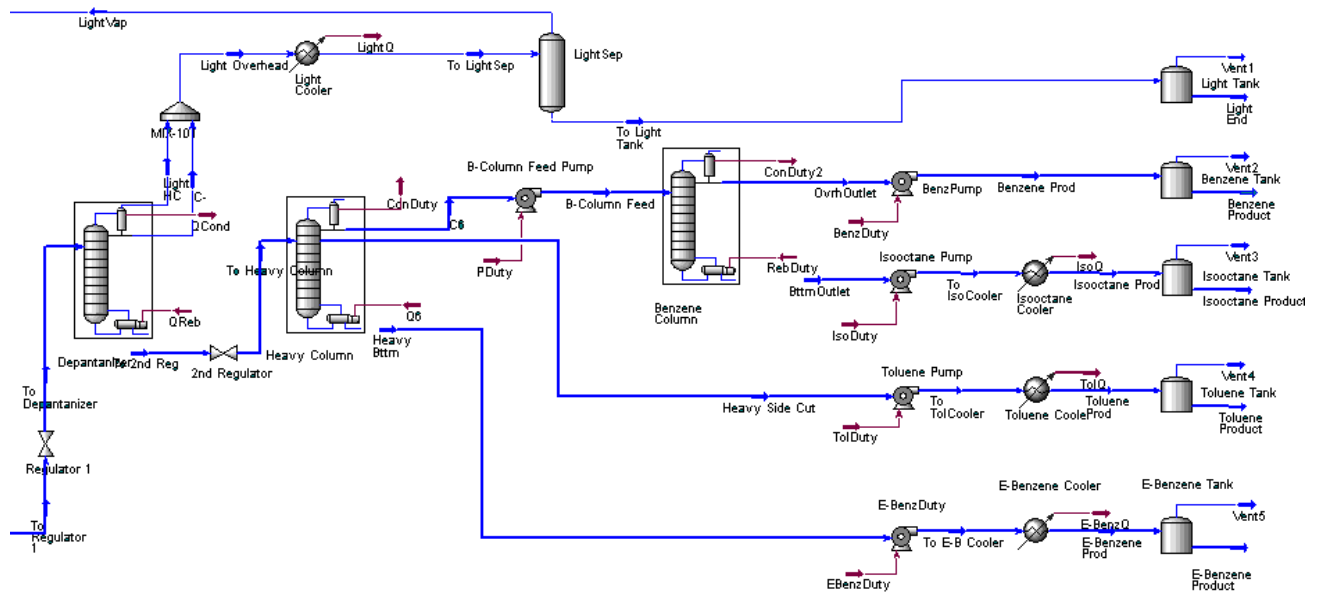
Figure 4.2b Hydrogenation Process; Original design: purification section.
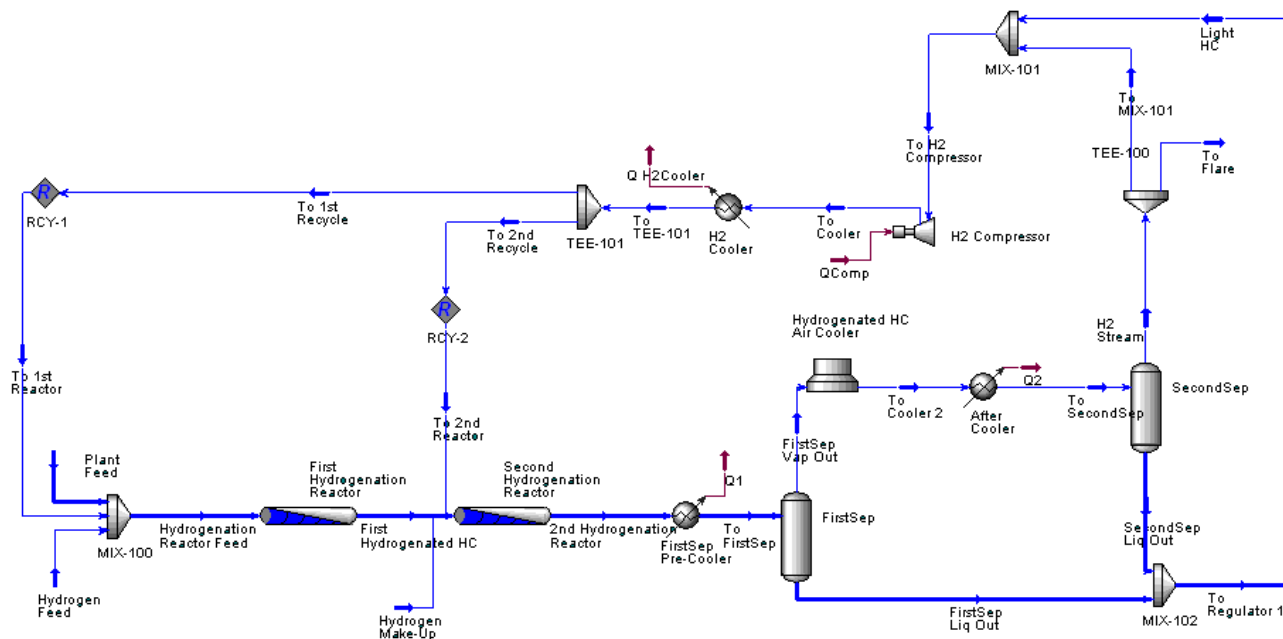
Figure 4.3a Hydrogenation Process: Alternative design; reaction and phase separation.
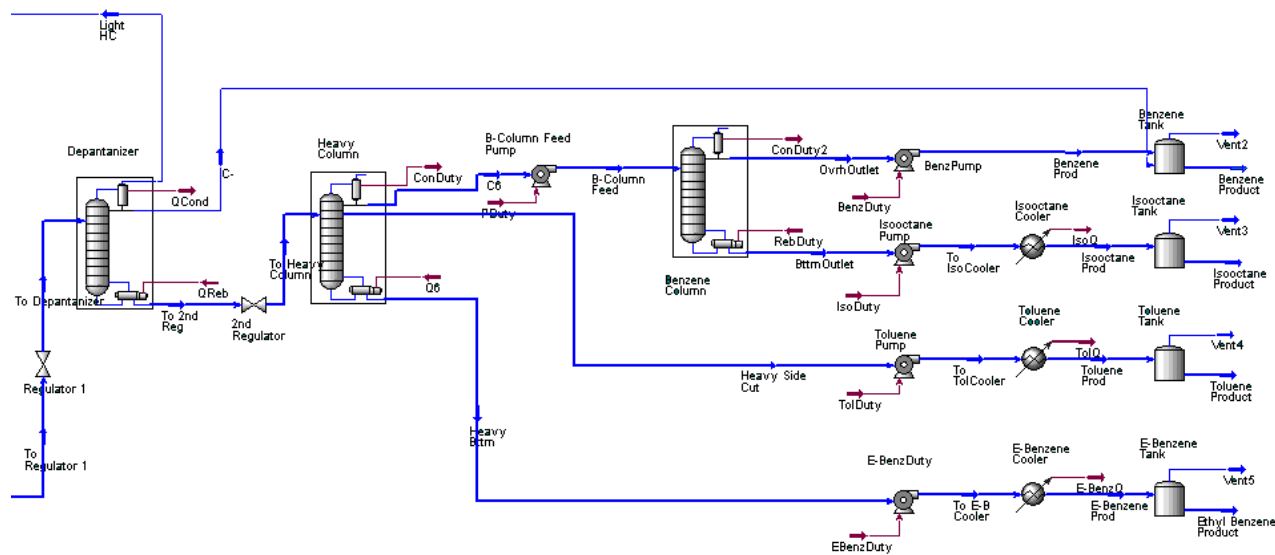
Figure 4.3b Hydrogenation Process: Alternative design; purification section.

4.5 PROCESS DESIGN AND DESCRIPTION

The Plant Feed stream enters the plant battery limit and goes directly to the tubular reactor. The fresh H_2 stream is mixed with the Plant Feed stream in the mixer MIX-100 in order to achieve a maximum mixedness of feed streams prior to the PFR reactor. Both PFR reactors may be regarded as just one double bed PFR and H_2 make-up and recycled streams are used in the middle of the reactor for the following purposes:

(1)   As a quench line for internally controlling the reaction temperature and

(2)   To satisfy the criteria of the Le Chatelier's principle in order to achieve the higher production rate through an increase in reaction efficiency.

A mixture of saturated and four unsaturated hydrocarbons; i.e. 1-Butene, Iso-Butene, Iso-octene and Styrene, and hydrogen gas are then introduced to the 1st PFR reactor. The outlet product stream from the 2nd reactor is a two phase flow stream at about 150 ^{o}C, which is subject to cooling followed by phase separation. The cooling operation causes of a decrease in the vapor volume. Hence, the product stream from the second PFR is sent to Pre-Cooler in order to recover the vapour phase partially followed by phase separation in a flash drum.

The most portion of the vapor from the second flash drum is pressurized in a compressor and returned to the beginning of process and to second PFR entrance. The remaining portion of the vapor is mixed up with vapor phase of the flash drum located on Depentanizer overhead in order to burn in a flare system; however, due to heat content of the stream it may be used either in boiler for fuel atomization and/or heat generation. So, one may consider it as a by-product stream.

The outlet gas from the drum bears further cooling operation through an Air-Cooler followed by a shell and tube After-Cooler in order to condense and separate further liquid in second flash drum. The two phase flow from the After-Cooler is then sent to the Second (Flash) Drum in order to remove the gas flow from the liquid stream. The liquid outlet streams from

the 1st and the 2nd flash drums are then mixed-up in a static mixer prior to depressurizing the stream by Regulator 1 and delivering to Depantanizer in purification section.

The light hydrocarbon from Depentanizer overhead in the first design is subject to cooling and phase separation. The liquid outlet from the drum is "Light End" and delivered to Light Tank, while the vapor phase is used for heat generation (boilers, incinerators, etc.) or sent to "Flare". In the alternative design; however, the liquid phase from Depentanizer condenser is directly sent to Benzene Tank, while the vapour phase from the condenser pressurized in H$_2$ compressor and returned to the beginning of the process and to the second PFR inlet pipe.

The bottom product of Depentanizer in both designs are first depressurized in "2nd Regulator" and then introduced to Heavy Column, where ethyl benzene is separated from the bottom of the column and sent to the corresponding storage tank after being cooled down in shell and tube cooler. A side cut separates toluene from the stream and sends it to a cooler and then to a storage tank.

The overhead of this column contains Benzene and Iso-octane. Therefore, it is sent to Benzene Column for further purification. The feed stream is split into Benzene from overhead and Iso-octane from the bottom outlet followed by cooling down each product and sending them to corresponding storage tanks.

Unlike the original design, in the alternative design (Figures 4.3a,b), both of liquid and vapour phases of Depentanizer overhead are sent to the beginning of the process after being pressurized in H$_2$ compressor. In the original design, the pyrolysis gasoline is converted and separated into five distinctive products, while in the alternative design there are four products.

Similar to Table 4.2, following table represents the heavy fuel oil characteristics and heat flow:

Table 4.6: The characteristics of heavy fuel oil and the breakdown of HV and heat flow for both designs.

Characteristics of Heavy Fuel Oil	Value	Heat Flow, $\dot{Q}_{i,k}$, in kJ/h (Original Design)[i]		Heat Flow, $\dot{Q}_{i,k}$, in kJ/h (Alternative Design)[i]	
		Heat	Power	Heat	Power
Sp. Gr.	0.941				
HV of Fuel	18,200 Btu/Lb **(42,293 kJ/h)**				
S	2.7 wt%	848,693	4,207	889,500	27,898
C	84.8 wt%	26,655,234	132,125	27,936,877	876,193
N	0.5 wt%	157,165	779	164,722	5,166
H	11.93 wt%	3,749,964	18,588	3,930,271	123,266

i   For calculation method please refer to the footnotes of Table 4.1

4.6 RESULT FROM HYDROGENATION PROCESS DESIGN

The energy impacts have been calculated for entire processes. The result is summarized in Table 4.7. The energy impacts on the environment from heat and power consumption are lower in the original design compared to the alternative design.

Table 4.7: Comparison of new emission index with existing ones in both designs of Hydrogenation process.

	Total Energy Consumption[i] (kJ/h)	Product Stream (kg/h)	New Emission Index[ii] (kg CO_2/h)	New Emission Index (kg SO_2/h)	New Emission Index (kg NO_2/h)	EIA's Method[iii] (kg CO_2/h)	EPA's Method[iii] (PEI/h)
Original Design	31.59×10^6	12,427	**2,650**	1.46	0.08	**1,990**	135.82
Alternative Design	33.98×10^6	12,482	**2,984**	1.65	0.09	**2,141**	146.09

i   From mass and energy balance made by HYSYS process simulator.
ii   The CO_2 emission rate [equation (2.2)] in alternative design has increased by 12.6%.
iii   The CO_2 emission rate (or PEI/h; WAR GUI, 2008) in alternative design has increased by 7.5%.

4.7 CONCLUSIONS

This research presents a screening index for the quantification and selection of an optimal process in terms of energy consumption and economic design, leading to the conservation of fossil fuel resources and preservation of clean air. The index has been applied to two different case studies.

The energy impact of the design alternatives have been assessed using the new proposed index and also by the EIA and EPA methods. The newly proposed index offers greater detail about the various emissions of the processes and gives a more accurate assessment.

Hence, the new methodology has a number of other advantages:

(a) It is a simple and user-friendly tool for the quantification and measurement of emission rates.

(b) It is accurate and calculates precisely the emission rates of CO_2, SO_2 and NO_2.

(c) It requires relatively readily available data, such as fossil fuel composition and heat value, heat flow through a heat exchanger, or electric power consumption of the electromotors of pump compressors, fans, blowers, etc.

(d) It is applicable to both the early stages of process design where there is a lack of process data, as well as to the estimation of emission rates in operating plant due to energy consumption by process equipment such as pumps, compressors, etc.

(e) It is not limited to chemical processes and can be extended to the generation of heat or electricity from fossil fuels.

(f) There is no need to measure fuel flow rate.

(g) It provides detailed information in terms of pollutant gases emissions from fossil fuel combustion due to heat and power consumptions within process alternatives, which reveals the environmentally friendliness of processes.

(h) Unlike the EPA and EIA methods, the new index provides no linear relationship between energy consumption and gas emissions.

(i) The new index demonstrates that an economic design can be linked to sustainability.

The new proposed energy index ranks process alternatives in terms of sustainable energy and environmental impact. It provides an effective tool for decision makers to identify the most sustainable process design. The index can be used for both existing processes and to identify potential new designs, and it presents a vital tool for minimizing adverse environmental effects in order to combat climate change and maintain good air quality. The index is also useful for energy efficiency in terms of improving energy intensity and environmental effects. The new indices also ascertain that the concept of sustainability is coined with economic.

Hence, the new indices are effective tools for decision-makers to screen out the most sustainable process design among other design array.

Chapter 5

NEW METHODOLOGY FOR EVALUATION OF RISKS TO PROCESS SAFETY

In chapter 2 the methodologies for risk assessment and inherent safety design were discussed. The substitution of hazardous chemicals with benign materials is not the only way to design an inherently safer process. For instance, raw materials used in petrochemical and refinery plants predominantly contain flammable and toxic hydrocarbons and almost impossible to be replaced by other chemicals. Hence, the inherent safety in this case is accomplished by minimizing the mass fraction of hazards in product as well as waste streams (source reduction) resulting in "safety improvements" and "environmental protection".

The equation (2.12), introduced by Al-Sharrah et al. (2007) is a fairly simple methodology. The index evaluates the safety risks of a process design and the alternatives in terms of frequency of accidents, size of the process, inventory and chemical toxicity to human life and it includes previous history and adverse effects of risk to human. However, due to very important constraints in Al-Sharrah's methodology, an index improvement will help researchers and designers to get information on the insight of chemical processes.

The new risk indices presented in this chapter is a strong screening tool with the prominent advantages among existing methodologies, including:

- Quantitative

- Simple, user friend and accurate

- Applicable at early design phase when detailed process data is lacking

- Reliable (e.g. cannot be rejected by new methodologies)

- Based on previous accidents' history

- Scientific and regulatory based (to be based on EPA's databases, which are world widely accepted by scientists and regulators).

- Mainly focused on the mass fraction of hazardous chemicals in process streams while maintaining the importance of the following metrics: "frequency of accidents", "severity of the accident" and "chemical inventory"

- Builds a linear relationship between the risk index and the mass fraction of hazardous materials in streams; the concept of inherent safety.

- Publicity: Licensing and manufacturing companies convince regulators and also potential clients that they are committed to inherently safer design.

- Requires minimum available process data, convenient at conceptual design phase

- Reduced capital costs since the most convenient step for economically source (hazard) reduction is the conceptual design phase (Tchobanoglous, 2009).

5.1 THE LIMITATIONS OF AL-SHARRAH'S METHODOLOGY

From section 2.5, we learned that the existing risk assessment methodologies are comprehensive, time consuming and require detailed process data and therefore, they are not suitable for conceptual design. Hence, there is still a demand to new simple indices for use in the conceptual design phase for evaluation of different proposals when new or retrofitting processes are concerned. Supposing the situations like tendering a chemical process project

where a number of proposals are sent to a client asserting to design the safest process; each proposal provides minimum process data such as general process description, simple block diagram, chemical compositions, mass fraction of hazardous materials in product and waste streams, such new indices shall only employ the above data in addition to chemical toxicity, process inventory, and the history of previous accidents in corresponding processes for risk estimation and the screening purpose of all proposals.

Although the recently improved risk index given by equation (2.12) is applicable in the majority of such situations, it gives unfavorable results in the following instances:

- The above index adds up all streams within entire process (instead of products and waste streams). Then, it multiplies the result by one month production of the process as maximum inventory, which results in an unrealistic increase in the risks associated with the process.

- In case of comparing two processes with the same flow rate of fresh feed; i.e. one with waste recycling and the other without it, the number of streams within the recycling process will be more and consequently, the associated risks will vividly increase resulting in rejection of the all types of recycling designs. This is an unacceptable result since the waste recycling, source reduction and prevention of waste generation are all remedies to minimize pollution and hazards within manufacturing plants (Pankratz, 2001).

- In equation (2.12), the term "*Size*" of a plant most probably equals to three as stated earlier. Although most reactants and products go through these three sections, tripling the estimated risks of the process may be misleading. For instance, in reaction section the reactants transform to products in the course of reaction and will not exist in other sections and therefore, tripling the corresponding hazard leads to a misleading or even the wrong result. Furthermore, it is possible to isolate any risks in each section or equipment by

control valves or block valves and so on. Hence, the term "*Size*" in such cases should equal to unity (one process).

- When two process designs with the same risks are concerned, equation (2.12) gives no result except when the both designs handle single component streams. For multi-component streams the purity of the product streams is so vital in choosing the inherently safer design. In the latter case, both severity and mass fractions of hazardous chemicals (impurities) are important.

5.2 THE NEW RISK INDEX FOR USE IN CONCEPTUAL DESIGN

The new risk indices proposed in this paper resolve the above deficiencies by evaluation of the risks associated with the mass flow rate of hazardous chemical components in both product and waste streams within a process instead of risk assessment associated with the whole process.

Based on the fundamental equation (2.11), the new indices are also function of either of accident frequency and hazard effects of chemical components.

A chemical process plant may have multiple product streams; therefore, the risk for all streams can be estimated as follows:

$$(R.I)^P = \sum_i \sum_j M_j \times f_i \times H_i \times x_{i,j} \tag{5.1}$$

Similarly, the risk for more than one waste streams can be calculated by following equation:

$$(R.I)^W = \sum_i \sum_j M_j \times f_i \times H_i \times x_{i,j} \tag{5.2}$$

where *R.I* is an abbreviation for Risk Index, superscripts *P* and *W* denote product and waste streams, respectively. So, $(R.I)^P$ and $(R.I)^W$ express the impacts of the calculated risks in "number of affected people per year", which is the maximum potential risks attributed to the total product streams and the total waste streams, respectively. Subscripts *i* and *j* designate the

"chemicals within the streams" and the "streams within the process", respectively. M_j stands for the mass in tons chemical released to the environment and is defined as maximum one month production of the process plant or one month inventory (Couper et al., 1990), which can be calculated from design basis. f_i represents the frequency of accident for chemical component i in "number of accidents per year" (Belke, 2000).

H_i denotes the hazard effects of chemical i, in "number of people affected per ton of chemical released" to the environment (ARIP, 1999). $x_{i, j}$ is the mass fraction of component i in stream j $(i, j = 1, 2, …)$. Table 5.1 presents the data of "H" and "f" for some chemicals.

$(R.I)^P$ is an acceptable risk since it is associated with the product streams, which corresponds to company's profits. However, the process design with the least $(R.I)^P$ is desirable when other design factors such as design cost favour that design. In case of the possibility of substitution of a hazardous material in a process with a benign substance at the same production rate, the $(R.I)^P$ will be less for the same process so; the process will be inherently safer.

Conventionally, chemical process designers considered a storage tank at the plant battery limit (B.L.) of maximum capacity of one month production (Couper et al., 1990) as inventory aiming to prevent downstream plants from shut-down in case of failing the upstream process, because the tank at B.L. would give enough time to operation or maintenance staffs for troubleshooting while supplying feed to downstream plants.

The author's observations and experience show that recently, the inventory at B.L. has been superseded in most processes especially in refineries and petrochemical complexes. Therefore, in this paper one month production of product and waste streams is considered as maximum inventory.

Table 5.1: Data for the severity and the likelihood of accidents for some chemicals. Adapted from Al-Sharrah et al. (2007).

No.	Chemical	H People affected per tonne chemical released	f [a] Number of accident.year^{-1}
1	Acetaldehyde	0.1202	0.008
2	Acetic Acid	0.0229	0.038
3	Acrolein	0.5763	0.064
4	Acrylic Acid	0.0561	0.038
5	Acrylonitrile	0.4224	0.042
6	Ammonia	0.1357	0.016
7	Benzene	0.1465	0.008
8	Butadiene	0.1233	0.013
9	Carbon Tetrachloride	0.1827	0.056
10	Chlorine	0.8105	0.022
11	Cumene	0.0742	0.008
12	Ethane	0.1526	0.014
13	Ethyl Benzene	0.0451	0.008
14	Formaldehyde	1.8414	0.009
15	Hydrogen Chloride	0.4273	0.06
16	Hydrogen Cyanide	5.9972	0.064
17	Hydrogen Fluoride	0.0116	0.064
18	Nitric Acid	0.2298	0.038
19	Pentane	0.1515	0.013
20	Phenol	0.0002	0.008
21	Phosphoric Acid	0.0133	0.038
22	Styrene	0.4484	0.008
23	Sulphuric Acid	0.0149	0.038
24	Toluene	0.0747	0.008
25	Vinyl Acetate	0.1866	0.042
26	Vinyl Chloride	0.0337	0.042
27	Xylene	0.2348	0.008
28	CH_4	N/A	0.03

[a] Considering the number of processes to be equal to unity (i.e. one process), frequency of accidents (Belke, 2000) can be modified as reported in column four in number of accidents per year.

Table 5.1 (Cont'd): Data for the severity and the likelihood of accidents for some chemicals. Adapted from Al-Sharrah et al. (2007).

No.	Chemical	H People affected per tonne chemical released	f^a Number of accident.year^{-1}
29	CH_2Cl_2	0.21	0.04
30	Chloroform	0.02	0.04
31	CCl_4	0.1827	0.056
32	Cl_2	0.8105	0.022
33	HCl	0.4273	0.06
34	CH_3Cl	0.07	0.04
35	Iso-Butane	0.0832	0.013
36	n-Butane	0.3296	0.013
37	Iso-Pentane	0.1761	0.013
38	n-Pentane	0.249042	0.013
39	Iso-Butene	0	0.013
40	Iso-Octene	0.3199	0.013
41	Iso-Octane	0.3535	0.013
42	1-Butene	0.1996	0.013
43	Styrene	0.4484	0.008
44	Ethyl-Benzene	0.0451	0.008
45	Benzene	0.1465	0.008
46	Toluene	0.0747	0.008
47	Hydrogen	0	0.013

[a] Considering the number of processes to be equal to unity (i.e. one process), frequency of accidents (Belke, 2000) can be modified as reported in column four in number of accidents per year.

In some of traditional risk assessment methodologies, the metrics such as population densities and the types of land were used as the basis for risk management in construction step of an industry (Henselwood et al., 2006). This approach has only been used in construction phase and cannot be used in conceptual design stage, since the population distribution becomes important when the plant location is concerned but neither plant location nor population density is the scope of conceptual design.

Furthermore, in case of an accident in a process, the population living around the plant area is a key point to estimate the maximum number of affected people; however, the population density has no influence on total risk associated with a process safety itself, since the risk is a function of frequency and consequences (or likelihood and severity).

Above all, in some incidents leading to release of toxic materials, zero people have been affected since nobody was in the proximity of the accident when it happened (Al-Sharrah et al., 2007). This divulges that zero affected people means that the process involved neither is inherently safe nor is it influenced by population density.

The total risk, $(R.I)^T$, is the summation of the risks associated with products and wastes:

$$(R.I)^T = (R.I)^P + (R.I)^W$$

(5.3)

Dividing both sides of equation (5.3) by annual production capacity of the process plant in tonne per year, results in a new risk index as follows:

$$\frac{(R.I)^T}{\sum_j P_j} = \frac{(R.I)^P}{\sum_j P_j} + \frac{(R.I)^W}{\sum_j P_j}$$

(5.4)

where subscript j denotes the stream no. of products. The left hand side of equation (5.4) represents the total risks per tonne products. The first term of the right hand side of equation

(5.4) represents the risks associated with product streams per tonne products and the second term represents the risks associated with waste streams per tonne products.

The normalized index, equation (5.4), is independent from the process size and enables a process engineer to compare two processes with different production capacities. Equations (5.1), (5.2) and (5.4) are all of great importance in ranking of process designs from safety point of view.

When other circumstances in two or more designs are the same, the term $\frac{(R.I)^P}{\sum_j P_j}$ would merely be eminent for the ranking of the process designs.

Case Study 1: Chlorination of methane

The theory of this case study was discussed in Chapter 4 and therefore, it is not replicated here. The original design is shown in Figure 4.1a.
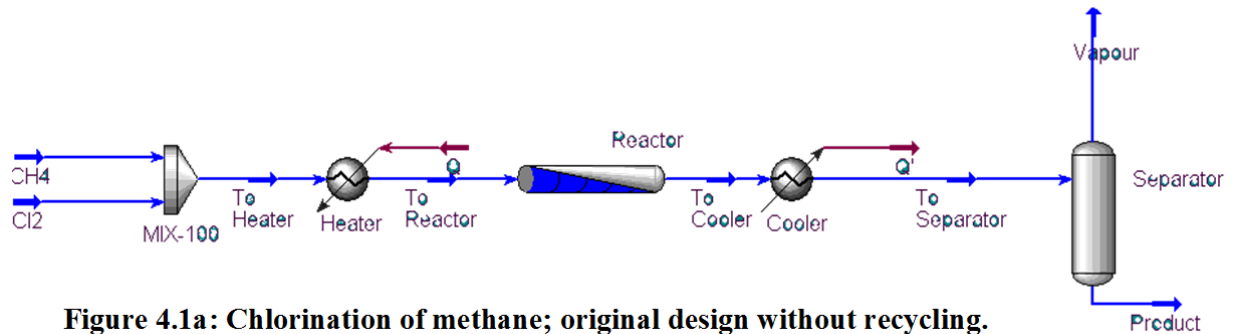
Figure 4.1a: Chlorination of methane; original design without recycling.

Table 5.2 shows the compositions, the component flow rates in each stream and the total flow rate of streams in Figure 4.1a.

Table 5.2: Detailed information about the compositions and the flow rate of each stream in the design without recycling.

Composition Name	CH_4	Cl_2	To Heater	To Reactor	To Separator	Vapour	Product	To Cooler
				Streams Flow Rates (kg/h)				
CH_4	802	0	802	802	203	188	15	203
CH_2Cl_2	0	0	0	0	300	2	298	300
$CHCl_3$	0	0	0	0	280	1	279	280
CCl_4	0	0	0	0	280	3	2787	2790
Cl_2	0	7091	7091	7091	0	0	0	0
HCl	0	0	0	0	3646	1674	1972	3646
CH_3Cl	0	0	0	0	674	52	622	674
TOTAL Flow Rate (kg/h)	802	7,091	7,893	7,893	7,893	1,920	5,973	7,893

The estimated safety risks associated with each stream and based on the data of Table 5.1 is presented in Table 5.3.

Table 5.3: The estimated K (Al-Sharrah's method) in Affected People per Year for each stream in design without recycling

CH4	Cl2	To Heater	To Reactor	To Separator	Vapour	Product	To Cooler
				Affected People/Year			
0	91.03	91.03	91.03	91.32	31.04	60.28	91.32

Equation (2.12) estimates the total risk to the process based on Al-Sharrah et al. index (2007). In this method, all streams are involved in calculation by summation of risk associated with each chemical followed by multiplication of the result by three. For instance, H and f of chlorine stream is given in Table 5.1 (item 32) and its flow rate in Table 5.2. Thus:

$$K_{Cl2} = H_{Cl2} \times f_{Cl2} \times M_{Cl2} \times Size = 0.8105 \times 0.022 \times 7{,}091 \times 3 = 379.3 \text{ Affected People/Year.}$$

This calculation will be continued for all streams within the process and then the K's of all streams will be summed up. The result is given below.

K = 1,641 Affected People/Year

While equation (5.3) calculates the total risk to the process based on the new proposed index, which is:

$$(R.I)^T = 91.32 \text{ Affected People/Year}$$

An alternative design to the chlorination process plant is to recycle the non-product (or waste) stream to the beginning of the process. Recycling is known as an effective and an economic way to increase the production rate and to minimize the wastes. In the present recycling design, the vapour stream from separator is pressurized by a compressor and then recycled to the plug flow reactor. Figure 5.1 is a simplification of the chlorination process in order to illustrate the safety indices introduced earlier in this chapter.
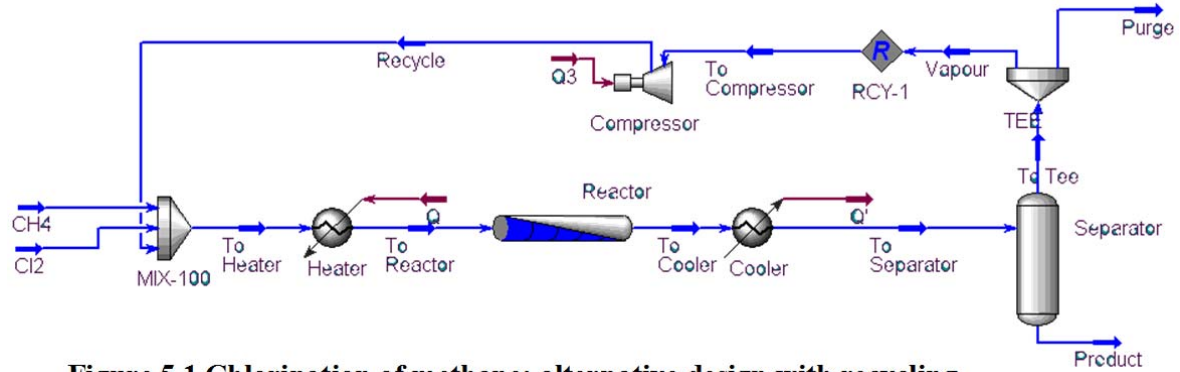
Figure 5.1 Chlorination of methane; alternative design with recycling.

Table 5.4 provides data for the compositions and the flow rates of each stream in the alternative design (Figure 5.1).

Table 5.4: Detailed information about the compositions and the flow rate of each stream in the design with recycling.

Composition Name	CH_4	Cl_2	To Heater	To Reactor	To Separator	Vapour	Product	To Cooler	Recycle	To Compressor	To Tee	Purge
						Streams Flow Rates (kg/h)						
CH_4	802	0	5084	5084	4314	4300	14	4314	4282	4282	4300	0
CH_2Cl_2	0	0	97	97	870	99	771	870	97	97	99	0
$CHCl_3$	0	0	63	63	1399	63	1336	1399	63	63	63	0
CCl_4	0	0	31	31	1083	30	1053	1083	31	31	30	0
Cl_2	0	7091	7091	7091	0	0	0	0	0	0	0	0
HCl	0	0	60064	60064	63710	60606	3104	63710	60064	60064	60606	0
CH_3Cl	0	0	1916	1916	2970	1946	1023	2970	1916	1916	1946	0
TOTAL Flow Rate (kg/h)	802	7,091	74,345	74,345	74,345	67,045	7,300	74,345	66,452	66,452	67,045	0

98

The ratio of recycling stream to fresh feed streams is around 9 in this design. The non-product stream is connected to the compressor suction line resulting in putting the system under pressure. In case the compressor malfunctions, the pressure in the suction line might fluctuate. This is harmful to the process equipment and to the plant; in order to prevent any accident in the process a vacuum breaker is designed, which is called "purge" in this design.

So, the purge is used for equipment safety reasons and therefore, its flow rate in the steady state design is assumed to be zero. The product stream is subject to washing and purification in downstream process, which is not shown in Figure 5.1. Table 5.5 represents the estimated risks associated with each stream.

Table 5.5: The estimated K in Affected People per Year for each stream in design without recycling.

Affected People/Year											
CH_4	Cl_2	To Heater	To Reactor	To Separator	Vapour	Product	To Cooler	Recycle	To Compressor	To Tee	Purge
0	91	1204.6	1204.6	1196.5	1123.7	72.8	1196.5	1113.6	1113.6	1123.7	0

Equation (2.12) estimates the total risk to the process based on Al-Sharrah's index, 9,441 affected people/year multiplied by 3 the max. number of processes, which gives:

K = 28,322 Affected People/Year

While equation (5.3) calculates the total risk to the process based on new index, which is:

$(R.I)^T$ = 1,196 Affected People/Year

In both designs, it is assumed that the chlorine is dry and that the product (carbon tetrachloride) will be separated in downstream perfectly. A comparison is provided in Table 5.6:

Table 5.6: Comparison of the safety indices of the designs of with and without recycling.

Risk Indices (Affected People/Year)	Without Recycling	With Recycling
K	1,641	28,322
$(R.I)^T$	91	1,196

The objective of this process is to produce more carbon tetrachloride; therefore, by comparing the composition of the product stream in each design we can see which design meets this objective. For the same fresh feed rate to the PFR reactor (7,893 kg/h), the original design produces more carbon tetrachloride (2,787 kg/h) than the alternative design with recycle (1,053 kg/h) as shown in Table 5.7.

Table 5.7: Comparison between two designs for the CCl4 product rate based on the same fresh feed rate to the reactor.

Composition	Product in Original Design (kg/h)	Product in Recycling Design (kg/h)
CH_4	15	14
CH_2Cl_2	298	771
$CHCl_3$	279	1,336
CCl_4	**2,787**	**1,053**
Cl_2	0	0
HCl	1,972	3,104
CH_3Cl	622	1,023
TOTAL (kg/h)	**5,973**	**7,300**

Below is a list of remarks to explain why in spite of our anticipation, the original design is much safer than the alternative design:

a) The size of the PFR reactor is the same for both designs.

b) The fresh feed is the same for both designs.

c) The recycling operation leads to mixing effects of the chemicals in PFR reactor and consequently, the PFR characteristics has changed to CSTR.

d) The CSTR has usually lower conversion factor than PFR at the same volume due to the reasons mentioned in item c. That is why CCl_4 has lower production rate in recycling design (Table 5.7).

5.3 RESULT (CHLORINATION PROCESS)
As indicated in Table 5.6, both K and $(R.I)^T$ indices estimate much higher risks for recycling case compared to non-recycling process. Therefore, considering the production rate of each process, the original design is preferred since the recycling of non-products has adverse effects on process safety as well as the production rate.

This case study shows that equation (2.12) always gives higher risks than equation (5.3) and therefore, it is misleading due to reasons mentioned in section 5.1.

There are several explanations for such negative impacts of recycling on the process performance such as the selection of a wrong point for recycling, need for more cooling of product stream and so forth. This study showed that for this particular design, the recycling point was not a good option and therefore, it was rejected.

It has to be noted that total safety is different from the inherent safety of a process. Total safety is the summation of inherent safety and external safety of the process. In other words, all chemical processes are safe, since they have to be, but some processes are inherently safer

than others (Heikkilä et al., 1996). It is possible to use simple cheap ways to design inherently safer processes (Kletz, 2001).

Case Study 2: Hydrogenation of unsaturated hydrocarbon

The theory of this case has also been studied in Chapter 4; therefore, it is not repeated here. Figures 4.2a, b and 4.3a, b show two hydrogenation designs. The kinetic data are provided in Table 4.3. The purity, flow rate, number of products and wastes, and the risks assessment of all products and waste streams in two process designs are summarized in Table 5.8.

Table 5.8: The summary of risk analysis of hydrogenation original design and alternative

Products	Original Design				Alternative Design			
	Products Conditions		Risk Index		Products Conditions		Risk Index	
	Flow rate, kg/h	Purity, %	#Affected People/ Year	#Affected People/ tonne Prod x 10^-6	Flow rate, kg/h	Purity, %	#Affected People/ Year	#Affected People/ tonne Prod x10^-6
Light End	246.6	N/A	0.32	2.9	0		0	0
Benzene	6242	93	25.86	237.6	6111	87	24.46	223.7
Isooctane	760	57	2.76	25.4	648	18	2.62	23.9
Toluene	2325	71	5.96	54.8	2379	51	6.73	61.6
E-Benzene	2853	70	6.18	56.8	3344	63	7.34	67.1
Total Products	12427		41.08	377.5	12482		41.15	376.3
Total Wastes	273.4		0.18	1.6	221.7		0.11	1.0

The products and waste stream are listed in the first column. The table is divided into two sections; "Original design" and "Alternative Design". Each part is divided into two sub-sections; "Product Conditions" (divided into "Purity" and "Flow Rate") and "Risk Index" (divided into "Affected People per Year" and "Affected People per Tonne Products".

Now, it is possible to analyze both processes in terms of inherent safer design based on the new developed indices. Attention should be paid that Figure 4.2a and Figure 4.3a are very similar.

Table 5.9 represents the flow rates of the chemical species in all products and waste streams for both the original and the alternative designs. This data has obtained from HYSYS process simulator software.

5.4 RESULT (HYDROGENATION PROCESS)

Table 5.9 shows that the total flow rate and therefore, annual capacity of alternative design is higher than that of original design; however, the purity of all products in the original design is higher compared to the alternative design, which is absolutely a strong positive point due to producing more valuable products while using almost the same equipment and operation. Besides, there is one more product in the original design.

Therefore, equation (4.7) have been used to assess inherent safer design, but in case of comparing two or more processes with significant differences in production rates, the equation (4.8) should be used for cross checking purposes. This fact shows the importance of the equation (4.8) when process size (total annual capacity) is concerned.

Table 5.9: The flow rates of chemical compositions in all waste/product streams within both processes (original and alternative designs) from HYSYS process simulator.

Composition	Original Design Products, Flow Rates (kg/h)						Alternative Design, Products Flow Rates (kg/h)				
	Light Ends	Benzene	Isooctane	Toluene	E-Benzene	Wastes (H2 Stream)	Benzene	Isooctane	Toluene	E-Benzene	Wastes (H2 Stream)
Iso-Butane	79.4	1.0	0.0	0.0	0.0	48.2	91.0	0.0	0.0	0.0	38.4
n-Butane	62.2	25.7	0.0	0.0	0.0	26.5	99.0	0.0	0.0	0.0	8.1
Iso-Pentane	0.0	117.9	0.0	0.0	0.0	2.0	117.2	0.0	0.0	0.0	2.9
n-Pentane	0.0	20.8	0.0	0.0	0.0	0.3	20.7	0.0	0.0	0.0	0.4
Iso-Butene	71.6	3.8	0.0	0.0	0.0	37.0	97.5	0.0	0.0	0.0	16.2
Iso-octene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Iso-octane	0.0	335.3	498.9	554.0	0.9	0.7	261.4	154.8	966.2	6.4	1.0
1-Butene	33.4	2.4	0.0	0.0	0.0	16.7	52.8	0.0	0.0	0.0	7.4
Styrene	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0	0.0
Ethyl-Benzene	0.0	0.0	0.0	199.8	2067.7	0.0	0.0	0.0	169.1	2098.5	0.1
Benzene	0.0	5735.0	259.9	2.3	0.0	4.5	5371.9	493.9	128.6	0.1	7.7
Toluene	0.0	0.0	1.2	1569.3	784.3	0.3	0.0	0.0	1115.3	1239.2	0.5
Hydrogen	0.0	0.0	0.0	0.0	0.0	137.3	0.0	0.0	0.0	0.0	139.2
TOTAL	246.6	6241.9	760.0	2325.3	2853.0	273.4	6111.5	648.7	2379.2	3344.2	221.7

In the above case study, the equation (4.7) suffices to conclude that the original design is inherently safer due to similar production rates. However, equation (4.8) has been applied to the case study to probe the validity of above suggestion as the difference in normalized risk index is insignificant (~ 0.3%). And for such difference it is not wise to give-up the process with more products and higher purity.

In other words, one more product and less risk index of product streams, $(R.I)^P$, in the original design (41.08 max. affected people per year) compared to the alternative design (41.15 max. affected people per year) means that the original design is inherently safer. The difference between normalized risk indices in maximum affected people per tonne products (377.5×10^{-6} for the original design and 376.3×10^{-6} for alternative design) is about 0.3% and negligible.

The risk index for individual product streams in one design may be more or less compared to another design, but the overall risk index for whole product streams within the process does matter. For instance, from Table 5.8, the annual capacity of benzene production and its purity in the original design are higher than those in the alternative design by 1,100 tonnes/year and 6%, respectively. Therefore, the associated risk indices are higher.

Also, there is no linear dependency between the flow rates of two distinctive streams and the associated risk indices within the same process; for example, the flow rate of benzene stream is 2.5 times as much as toluene stream and about twice compared to ethyl-benzene in the original design; however, the risk indices of benzene stream are more than four times as much as both toluene and ethyl-benzene product streams.

The equation (4.7) divulges that the risk associated with a process design is highly dependent on the mass fraction of hazardous impurities in the product streams. The state of the art of inherently safer design is to reduce the hazardous chemicals in the product streams. And the

most convenient step for economically source (hazard) reduction is the conceptual design (Tchobanoglous, 2009).

For the waste stream, even though the risk indices of waste stream in the original design are higher compared to the alternative design, they are about 0.4% of the total risks in corresponding design [equations (4.7) and (4.8)] and again it is negligible.

Moreover, the so-called waste stream in our case study has heat content and can be used for heat generation, as stated before. So, it may be considered as a byproduct stream.

To recap, the total risks based on the equation (4.7) are 41.26 for both designs and based on the equation (4.8) are 379.1×10^{-6} for the original design and 377.3×10^{-6} for the alternative design.

Thus, the original design is more desirable due to diversity of products, higher purity of products and inherently safer design.

5.5 DISCUSSION AND CONCLUSIONS

This research offers new simple and quantitative inherent safety indices, which requires minimum available process data and can be employed during conceptual design phase to eliminate or minimize the hazardous chemicals in the process involved. The new indices follow:

a) $R.I$ (the number of affected people per year) and

b) $R.I / \Sigma P_j$ (the number of affected people per tonne products).

The latter is independent from the process size (production capacity). Two case studies were provided to examine the application of these indices. The result reveals that the risk of a process design highly depends on the hazardous materials (as impurities) within the product streams. Then, the risk can be minimized at the conceptual design stage by reducing the mass

fraction, $x_{i,j}$, of hazardous materials in product and waste streams, which is the spirit of inherently safer design (ISD). The new indices have a great contribution on ISD including the following advantages compared to the existing methodologies (Table 2.3):

1. Simple and user friend

2. Quantitative and mathematical model for risk evaluation

3. Safe results and based on the reliable database of undesirable events or accidents

4. Predicts the risks of a process in terms of human fatalities

5. The metrics "frequency of accidents" based on previous history of accidents in similar processes, "severity of accident" and "chemical inventory" have great influences on the risks associated with a process. The new indices probe that the mass fraction of hazardous chemicals in process streams has also substantial contribution to hazardousness of a process.

6. A linear relationship between the risk index and the mass fraction of hazardous materials has been established in this paper.

7. They can be used as a strong screening tool for design engineers, decision makers and regulators.

8. They can be used as commercial tool for publicity to convince the regulators and potential clients for their commitment to safe design.

9. Since the most convenient step for source/hazards reduction is the conceptual design, the new indices help to reduce capital costs by a decrease in hazards generation leading to design smaller waste treatment facilities and control stations. Hence, the core of the presented new indices in this paper is economically and inherently safer process design.

Chapter 6

APPLICATIONS: CASE STUDY 1; PRODUCT DESIGN: CANADIAN GASOLINE BLENDS

The industrial sector is always willing to improve its profits without compromising product quality, and gasoline blending is an example. Usually, there are different choices of gasoline blends in a gas station - regular, premium, mid-grade, super, with ethanol at various percentages, and so on. The blends with higher octane numbers are more expensive compared to regular gasoline by 12-13% (Minnesota Department of Commerce, 2004).

In this case study, using a tool to estimate the octane number, the primary energy intensity (PEI), safety risk and profitability of gasoline blended with different chemicals such as methanol, ethanol and isooctane are analyzed. In fact, it turns out to be difficult to establish a clear trade-off between these metrics and economic return, so a methodology called Analytical Hierarchy Process (AHP) was employed to estimate *Key Performance Indicators (KPI).* Cost-KPI analysis was then carried out to rank the blends, and the result shows that methanol blended gasoline has the highest KPI and the lowest price among the product array.

6.1 ANALYTICAL HIERARCHICAL PROCESS (AHP) METHODOLOGY

Analytical Hierarchical Process is a multi-criteria method used for decision making, which was developed by Thomas L. Saaty (2008). The AHP method is a driving ratio scales from pairwise comparisons, in which a decision is broken down into several steps. The comparisons are scored in the range from 1 to 9 where 1 is assigned for equivalent importance and 9 for outright superiority. All other odd and even numbers fall in between.

The inputs can be either of actual measurement; e.g. price, weight, and subjective opinion; e.g. preference. The outputs; however, may be ratio scales from Eigenvector method and/or consistency index from Eigenvalue method.

There are several applications of AHP including "evaluation of product features", "selection from strategic planning alternatives", "screening a set of Key Process Indices", "making integrated decisions with multiple outputs from different shareholders".

The AHP methodology is based on mathematical concepts.

1. The objective or problem definition; e.g. production of sustainable gasoline blends.

2. Configuration of a hierarchy from objective; e.g. gasoline blends, then metrics (criteria); e.g. safety risk, environmental impact and energy impact, followed by sub-criteria; e.g. the values of each metric. For this reason, let $\{A_1, A_2, ..., A_n\}$ and $\{w_1, w_2, ..., w_n\}$ be metrics and current weights, respectively, where n denotes the number of metrics. The matrix W represents the ratios of all weights (Alonso, 2006):

$$W = [w_i/w_j] = \begin{pmatrix} w_1/w_1 & w_1/w_2 & \cdots & w_1/w_n \\ w_2/w_1 & w_2/w_2 & \cdots & w_2/w_n \\ \vdots & \vdots & & \vdots \\ w_n/w_1 & w_n/w_2 & \cdots & w_n/w_n \end{pmatrix}$$

3. Pairwise comparison of elements in each criteria and building matrix: The matrix A=[a$_{ij}$] exhibits the referee's (expert's) preference within pairwise comparison of criteria and sub-criteria (a_i vs. a_j for all $i,j = 1,2,...,n$) where a$_{ij}$ is positive and reciprocal (i.e. $a_{ij} > 0$ and $a_{ij} = 1/a_{ji}$).

$$A = [a_{ij}] = \begin{pmatrix} 1 & a_{12} & \cdots & a_{1j} & \cdots & a_{1n} \\ 1/a_{12} & 1 & \cdots & a_{2j} & \cdots & a_{2n} \\ \vdots & & & & & \\ 1/a_{1j} & 1/a_{2j} & \cdots & a_{ij} & \cdots & a_{in} \\ \vdots & & & & & \\ 1/a_{1n} & 1/a_{2n} & \cdots & 1/a_{in} & \cdots & 1 \end{pmatrix}$$

The a_{ij} elements are the referee's estimates of the ratios w_i/w_j (i.e. $a_{ij} = w_i/w_j$) for $i,j = 1,2,...,n$. So, the vector w is the vector of existing weights of metrics and therefore, it is our objective to find it by eigenvector method.

The comparisons are scored in the range from 1/9 (for least importance) to 9 (for outright superiority). All other odd and even numbers (1/8, 1/7, …, 7, 8) fall in between.

4. Calculation of the sum of each column (S_{Ci}).

5. Normalization of the matrix in item 3 above and then calculation of the sum of each row (x_i).

6. Calculation of weight of each metric followed by the ranking of the metrics.

7. Calculate the Eigenvector of a matrix and normalize principal Eigenvector and Eigenvalue. Find the sum of each row in the normalized matrix and name it matrix A.

8. Determine Eigenvalue, λ_{max}:

$$\lambda_{max} = \Sigma S_{Ci} \times x_i = S_{C1} \times x_1 + S_{C2} \times x_2 + \dots \qquad (6.1)$$

where S_{Ci} is the summation product of column i of original matrix (item 4) and x_i is summation product of row i of matrix A (item 5).

9. Consistency analysis: Both matrices A and W are equal when matrix A is absolutely consistent then, λ_{max} = n (item 8) and $Aw = \lambda_{max} w$. However, the referees' (experts') judgments are not perfect in almost all cases. In other words, $\lambda_{max} > n$ when matrix A is not absolutely consistent so, the consistency index (CI) and the level of inconsistency (CR or Consistency Ratio) have to be measured.

10. Calculate the consistency index (CI) using below equation:

$$CI = \frac{\lambda - n}{n - 1} \qquad (6.2)$$

The term (λ − n) is called the consistency condition, which is used in calculating the consistency index. *CI* is similar to standard deviation of error estimation and mean deviation.

11. Verify the consistency ratio through the following equation and

$$CR = \frac{CI}{RI} \begin{cases} < 0.1 \text{ for all matrices A with n>3 and} \\ \\ \\ < 0.08 \text{ for n} = 3 \text{ to yield satisfactory results} \end{cases} \qquad (6.3)$$

Random index (RI) is the mean deviation of selected comparison values by chance from true ones (Table 6.1):

Table 6.1: Random Index (RI) used in Analytical Hierarchy Process (AHP).

N	1 - 2	3	4	5	6	7	8	9	10
RI	0.0	0.58	0.9	1.12	1.24	1.32	1.41	1.45	1.49

12. Continuation of items 3 to 9 for sub-criteria.

13. Cost-benefit analysis and conclusion.

6.2 WHAT IS THE OCTANE NUMBER (ON)?

Compressed gasoline-air mixtures in an internal combustion engine should burn smoothly, but tend to ignite prematurely during compression, creating engine knock - rattling or pinging sounds in one or more cylinders - which can eventually damage the engine. Octane number (ON) is a metric of the antiknock quality of a gasoline. In the past, tetraethyl lead, $Pb(C_2H_5)_4$, was added at about 2.5 grams per gallon of gasoline to increase ON; however, due to the shift away from leaded gasoline, more expensive compounds, such as aromatics and highly branched alkanes, were added to maintain high ON values.

ON is a metric indicating the resistance of a motor fuel to pre-ignition knock (csgnetwork, 2012). It ranges from 100 for isooctane (a highly branched alkane with minimal knock) to zero for heptane (a straight hydrocarbon chain with bad knock). The ON of a straight-run gasoline is 70 (Speight, 2007). Other octane facts (Minnesota Department of Commerce, 2004) include:

- A gasoline with relatively high ON burns slowly, resulting in prevention of engine knock.

- The engine knock is not necessarily due to the wrong gasoline formulation, there might be problems with electronic control systems, ignition timing, exhaust gas recirculation, and so on.

- In general, branched isomers are less susceptible to premature ignition because of the molecular structure; therefore these molecules serve as anti-knock agents.

The following typical cracking reaction may take place in a refinery:

$C_{13}H_{28}$ (alkane, l) $\rightarrow$ C_8H_{18} (alkane, l) + C_2H_4 (alkene, gas) + C_3H_6 (alkene, gas).
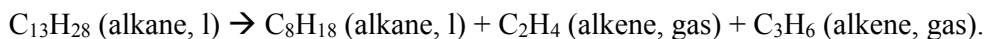
During this process, isomerization reactions can be favored in order to generate more branched isomers, which resist pre-ignition in gasoline engines, therefore they serve as anti-knock additives to the gasoline.

ON is an arithmetic average of the research octane number and the motor octane number, which are determined by ASTM D2699 and ASTM D2700 standards, respectively. In addition, different methods for predicting ON of a fuel and fuel-additive mixtures have been introduced based on the chemical properties of the mixture components. For instance, Albahri (2002) introduced a structural group based method for calculation of the ON by tabulating the functional groups into paraffins, olefins, cyclics, and aromatics, giving 33 different groups,

and assigning an ON value to each group. Then, the following equation was used to calculate a research ON.

$$RON = \left[104.8 - 5.395\left(\sum_i ON_i\right) + 6.532\left(\sum_i ON_i\right)^2 - 5.165\left(\sum_i ON_i\right)^3 + 0.6189\left(\sum_i ON_i\right)^4\right] \quad (6.1)$$

Rao (2007) asserted that the ON's of hydrocarbon mixtures are not additive, and therefore they cannot be calculated by summation of the ON of individual hydrocarbons. He reported that the ON of a hydrocarbon is influenced by other properties of the hydrocarbon such as boiling point, density, molecular structure, the number of branches in an isomer, and molecular weight.

Alexandrovna and Tuyen (2010) introduced the following model based on different naphtha process streams (reformates, isomerates, straight-runs and alkylates):

$$ON_{mix} = \sum_i ON_i \times C_i \pm \sum_i C_i \times B_i \qquad (6.2)$$

where

$$B_i = \alpha . D_i^n \qquad (6.3)$$

C_i is the concentration of hydrocarbons and oxygenates in the mixture, α and n are the empirically determined kinetic coefficients for the intensity of intermolecular interactions from the dipole moment D.

Aspen HYSYS (Aspen Technology Inc., 2006) has a proprietary method for the calculation of ON, which is widely accepted. This software was used for this study.

6.3 THE IMPACTS OF BLENDING ETHANOL AND GASOLINE ON MILEAGE AND RETAIL GASOLINE PRICE

Organically-sourced ethanol produced from plants, typically sugar cane or corn, but perhaps in the future more suitable sources such as corn stover, grasses and wood chips, is called bio-ethanol. With no taxes, royalties, and perhaps even with subsidies, it is considered economic and suitable for blending with gasoline. Blending of ethanol and gasoline in the US was studied by NREL (National Renewable Energy Library, 2008) and the following results were published:

1. Over 70% of gasoline at the pump in the US contains ethanol.

2. The standard E10 blend contains 10% ethanol and 90% gasoline and is sold as "regular gasoline".

3. Renewable Fuel Standards legislation passed as an amendment to the Energy Independence and Security Act (EISA) demands E10 as the minimum ethanol grade gasoline in the US until 2022.

4. Up to 20% of ethanol blended (E20) into gasoline apparently presents no problems for the current vehicle fleet or fuel dispensing devices.

5. Substitution (blending of ethanol and gasoline) has adverse effects on mileage because of the lower energy content of ethanol, approximately 67% the energy of gasoline. E10, E15, and E20 blends have mileage reductions of 3.9%, 5.0% and 7.7%, compared with E0. However, ethanol addition decreases the retail gasoline price in the US by almost 17% compared with E0.

6. The US energy policy encourages using blended gasoline through mandates and subsidies, whereas fossil fuels have additional taxes, different in each state.

6.4 THE EFFECTS OF ETHANOL, METHANOL AND ISOOCTANE BLENDS ON THE OCTANE NUMBER

The addition of ethanol to gasoline is economically beneficial for oil companies and reduces the consumption of fossil fuel. In this section, a typical gasoline composition is adapted from Lin and Chou (1995), and the ON's for E10, E15 and E20 were calculated by Aspen HYSYS software to be 73.8, 73 and 72, respectively. The ON of the reference molecule isooctane is defined as equal to 100; therefore the addition of ethanol to gasoline causes a decrease in the octane number. (However, a more precise ON for isooctane is apparently about 98 – EIA, 2002).

For this study, ethanol (EtOH), methanol (MeOH) and isooctane were used as substitutions at the fuel consumption flow rate of 5 kg/h and the flow rate of the pure fossil gasoline changed from 85 to 95 kg/h for blending purposes in order to calculate octane numbers (Figure 6.1).
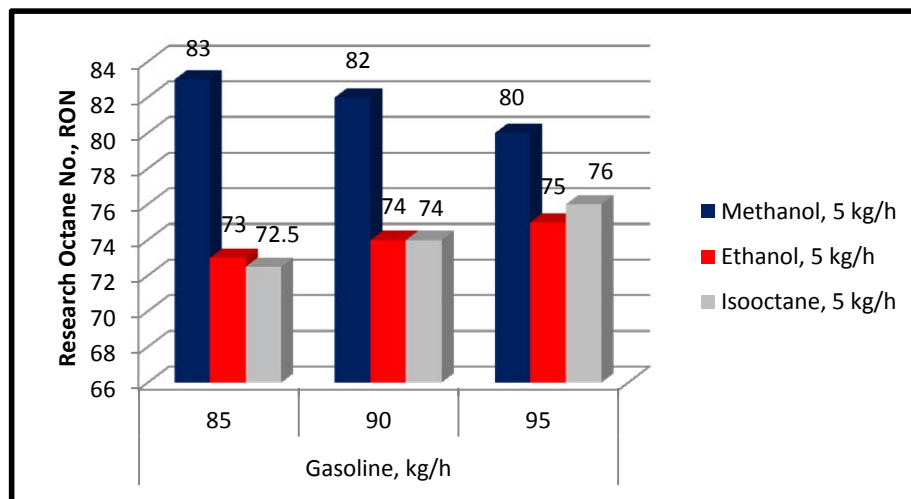
Figure 6.1. Comparing the octane no. of gasoline with MeOH, EtOH, and isooctane blends.

EtOH and isooctane blends have almost the same ON values compared to MeOH blend, which has a higher ON even at 5 wt% (or M5). MeOH is clearly a better option than EtOH

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and isooctane in terms of octane number. (Of course, there may be other reasons for using or not using MeOH; for example, MeOH is made almost exclusively from natural gas, a fossil fuel). The reason for using M5 is that in U.S. and Canada, bio-ethanol and gasoline are blended by law, but unlike the US, which uses E10, in Canada E5 is used, meaning 5% EtOH blended with 95% fossil fuel (Financial Post, 2012). Therefore, the MeOH blend (M5) was simulated to study its characteristics as an alternative to E5.

6.5 IMPACTS OF ETHANOL, METHANOL AND GASOLINE BLENDS ON HEAT VALUE, MILEAGE AND PRICE

Comparisons of mileage loss of EtOH, MeOH and isooctane blends with pure fossil gasoline were made based on their heat values. Table 6.2 lists the mass heat value of each chemical, blend, and mileage loss corresponding to each blend. From Table 6.2, we can see that MeOH blend has the least heat value and the highest mileage loss.

Table 6.2: Comparison of the mass heat values and the mileage loss of chemicals.

No	Chemical	Heat Value of Chemical kJ/kg	Heat Value of Blend kJ/kg	Mileage Loss %
1	Isooctane	4.47×10^4	4.23×10^4	0.28
2	Ethanol	2.68×10^4	4.14×10^4	-1.83
3	Methanol	1.99×10^4	4.11×10^4	-2.65
4	Pure Gasoline	Reference, E0	4.22×10^4	0

For a volume of pure fossil gasoline that would achieve 100 km distance, E5 and M5 would achieve 98.2 km and 97.4 km, respectively. The economic evaluation is presented in Table 6.3, where the chemical prices are compared.

Table 6.3: Price comparisons of pure gasoline and other chemicals used in this case study.

No	Chemical	Price, US$/gal	Reference
1	Gasoline	3.67	(EIA, 2014)
2	Isooctane	6.91	(Business Analytic Center, 2014)
3	Ethanol	2.30-2.93	(ICIS, 2014)
4	Methanol	1.51-2.53	(ICIS, 2014)

The costs of gasoline blends are calculated by a simple summation:

$$Blend\ Cost = \sum_i (Price)_i \times x_i \qquad (6.4)$$

where subscript i denotes the blend component and x_i represents the mass fraction of the component i. Thus, the cost of isooctane (I5), EtOH (E5) and MeOH (M5) blends in US$/gal are 3.87, 3.62, and 3.59, respectively (Table 6.4).

Table 6.4: Comparison of the prices of blends used in this case study.

No	Gasoline Blend	Price, U$/gal
1	Isooctane (I5)	3.87
2	Ethanol (E5)	3.62
3	Methanol (M5)	3.59

In this study, the price averages of EtOH and MeOH have been used for calculations. The comparison between the prices of gasoline blends is made in Figure 6.2; M5 blend has the lowest price. At this point, one might suggest that M5 is the best among the blends for its higher octane number and lower price, but other factors arise.
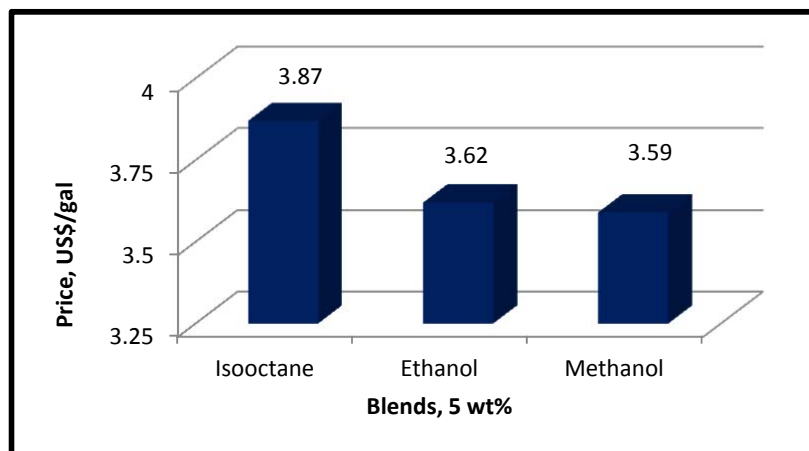
Figure 6.2. Comparison of prices among gasoline blends.

6.6 IMPACTS OF ETHANOL, METHANOL AND GASOLINE BLENDS ON ENVIRONMENT IN POTENTIAL ENVIRONMENTAL IMPACTS (PEIS)

Perhaps most important, an energy impact index and safety risk index, as well as the material impact index from the WAR algorithm (Cabezas et al., 1997 and 1999; Young and Cabezas, 1999; Young et al., 2000), were applied to the blends in order to estimate total energy and material impacts on the environment and to assess safety risks of blends.

In this study, the impact of power consumption or heat generation due to using a static mixer for the model (Figure 6.3) means that the differences in the energy impacts of the blends on the environment are equal to zero:

$$I_e = 0 \tag{6.5}$$
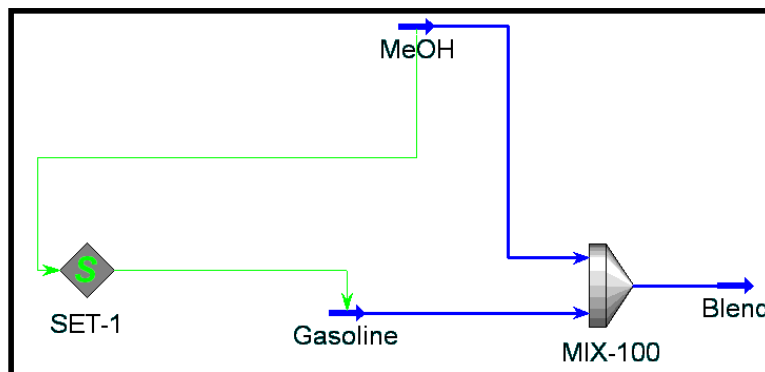
Figure 6.3. Modeling of gasoline and methanol blends with HYSYS 2006.

The material impacts of blends on the environment are calculated in PEI/h and shown in Figure 6.4; M5 has the lowest impacts on the environment.

The small differences between all three blends in PEI/h are due to using 5% chemicals for each. This means 95% fossil gasoline for each blend wouldn't make significant variations in the result at almost 95% confidence level.
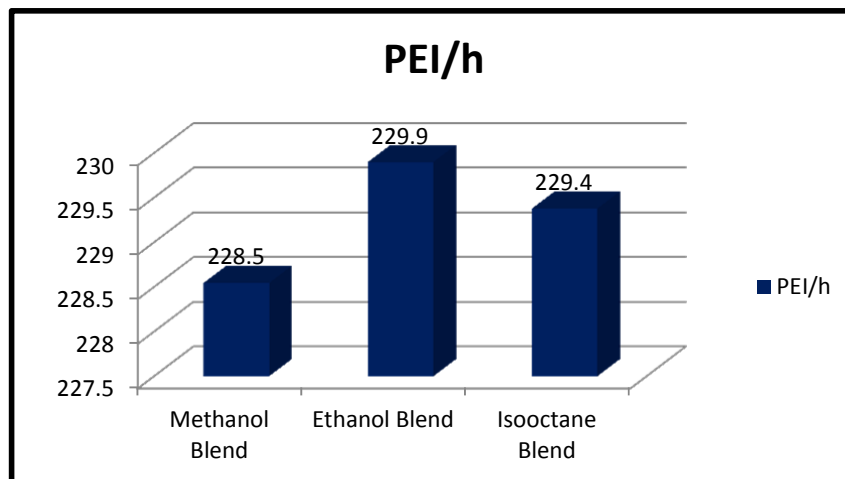
Figure 6.4. The comparison of impacts of blends on the environment.

6.7 THE IMPACTS OF ETHANOL, METHANOL AND GASOLINE BLENDS ON SAFETY RISK

The safety risks associated with each blend were estimated as "Number of Affected People per Year" based on the methodology originally presented by Al-Sharrah et al. (2007) and Ordouei et al. (2014a). Results are shown on Figure 6.5. The higher risk index for MeOH and isooctane blends was predictable, since LD_{50} (in rat mg/kg) for MeOH, isooctane and EtOH are 5600, 5000 and 9000, respectively, meaning that the lower the LD_{50}, the higher risk the chemical has. Other factors such as gasoline composition remain unchanged.
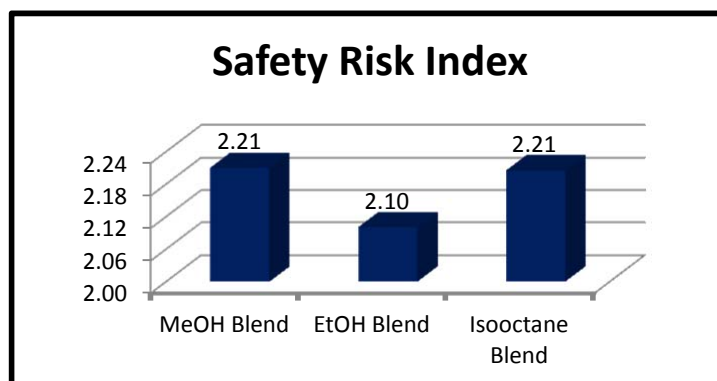
Figure 6.5. Safety risk index for methanol, ethanol and isooctane blends.

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6.8 BLENDS METRICS

The results from previous sections are summarized in Table 6.5. Clearly, isooctane is not the best substitution for increasing ON only.

Price, environmental impact and safety must be accounted for quantitatively. Thus, isooctane can be replaced by better alternatives.

Table 6.5: The summary of the blends metrics.

Characteristics	Blends, 5%		
	Isooctane	EtOH	MeOH
Octane No.	76	75	80
Mileage Loss, %	0.28	-1.83	-2.65
Price, US$/gal	3.87	3.62	3.59
Environmental Impacts, PEI/h	229.4	229.9	228.5
Safety Risk Index, No. of Affected People/Year	2.21	2.10	2.21
Energy Impacts, kg gases/h	N/A	N/A	N/A

Other studies confirm that this result is known and is affecting blending approaches (EIA 2012).
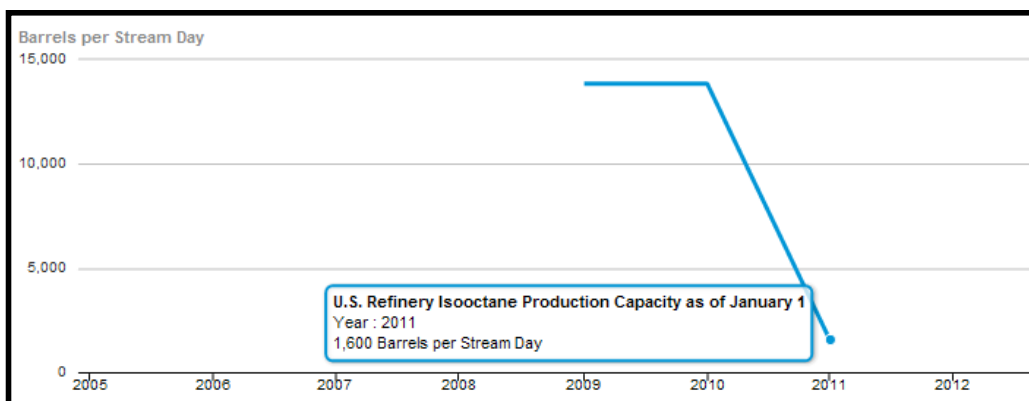
Figure 6.6. US Refinery isooctane production capacity (EIA, 2012).

Up to 2010, the isooctane production rate in the USA was about 13,900 barrels per stream day, but it has dropped dramatically down to 1600 barrels per stream day (Figure 6.6) in the space of two years.

6.9 ANALYTICAL HIERARCHY PROCESS (AHP) METHODOLOGY

In preceding sections, the most important factors affecting the I5, E5 and M5blends were estimated. Table 6.4 contains factors which have positive or negative influences on the blends qualities; for instance, a higher ON is considered a positive factor affecting car engine life, whereas a higher PEI value has adverse environmental consequences. Moreover, PEI values are much higher than the value of other factors so that a method of including all of the impact factors in an appropriate manner is needed. Thus, the objective of this section is to rank the factors in Table 6.4 in an appropriate way, using the Analytical Hierarchy Process (AHP) methodology for weighting and ranking of the factors (Saaty, 2008); the results are summarized in Table 6.6.

Table 6.6: The result of weighting and ranking of factors.

Analytical Hierarchy Process	Weight	Rank
Octane No.	12%	3
Mileage Loss	8%	4
Environmental Impacts	55%	1
Safety Risk Index	25%	2

As it can be seen from the table, the highest priority belongs to environmental impacts, then to safety risk index, followed by octane number, followed by mileage loss. Also, the price is not considered in the analysis at this stage because the ranking of economic factors is contentious (some always place it first, some always place it last). To make an unbiased analysis, economic issues are addressed in a cost-KPI analysis.

6.10 RESULT

The weights and the ranks of the three major factors are shown in Table 6.5, yet it is still difficult to compare the blends based on this table because the contribution to the values of each factor in Table 6.4 is unknown. To make a better judgment about the positive and negative effects of factors, including correcting for the different magnitude of the PEI effects, the factors of each blend were compared with the corresponding factors of other blends using AHP methodology to develop Table 6.7.

Table 6.7: The contribution of each Sub-criterion in metrics: (a) Octane number. (b) Mileage loss. (c) Environmental impacts. (d) Safety risks.

(a)		(b)		(c)		(d)	
Octane No., 12%		Mileage Loss, 8%		Environmental Impact, 55%		Safety Risk, 25%	
75	2%	-2.56	1%	228.5	39.8%	2.1	16.6%
76	2%	-1.83	2%	229.4	10.6%	2.21	4.2%
80	8%	0.28	5%	229.9	4.6%	2.21	4.2%

The breakdown of the weight of each factor has been clarified and it is now possible to compare the blends in terms of the Key Performance Indicator (here one may take KPI as a proxy for net benefits or utility) based on the data of Table 6.6. For instance, isooctane blend (I5) has the following characteristics:

ON=76, Mileage loss=0.28, Price = 3.87, PEI/h = 229.4 and safety risk index = 2.21

Hence,

KPI = 2% + 5% + 10.6% + 4.2% = 21.8%   (6.6)

Similarly, KPIs for E5 and M5 are 25.2% and 53%, respectively.

The final step is to perform cost-KPI (similar to cost-benefit) analysis using the information about blend prices in Table 6.3 as the input cost and the KPIs (as expressions of the utility or benefit) are shown in Figure 6.7.

This figure shows that the cost-KPI for each blend is a useful screening tool for decision makers to pick the best blend among several alternatives. In this case, MeOH (35.9, 53) is the best overall, followed by EtOH (36.2, 25.2), and finally isooctane (38.7, 21.8).
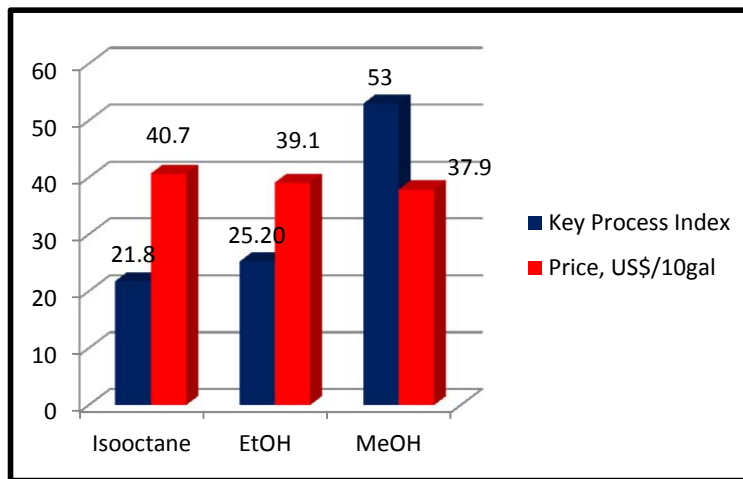
Figure 6.7. Cost-KPI analysis including safety risk index for three blends.

6.11   DISCUSSION

A unique set of metrics has been provided in this research called "Sustainability Indices", which have wide variety of applications. In this chapter the above indices were successfully applied for product design. In this section, two more special cases are discussed:

A. What-if one or both new proposed methodologies conflict the existing one?

It is imperative to pay attention to both safety and environmental issues during the preliminary design stage. In this chapter that dealt with product design, if one considers only the existing methodologies for the estimation of the impacts of materials on the environment (e.g. WAR algorithm) and ignores the new safety risk index, the ranking shown in Figure 6.7 will change as follows (Figure 6.8):

MeOH (35.9, 64.5) then, isooctane (38.7, 23.8) and finally EtOH (36.2, 11.7) since the KPI of isooctane blend increases by 100% compared with that of EtOH blend, which means higher ON, higher mileage, and lower PEI, while its price increases by 7%.

Although only a limited case has been analyzed – M5, E5 and I5 – it is clear that an appropriate methodology is needed to choose the best blend with the metrics that are available through analysis and cost data. It is also necessary to apply care in the choice of metrics, as adding or dropping a metric will lead to different results.
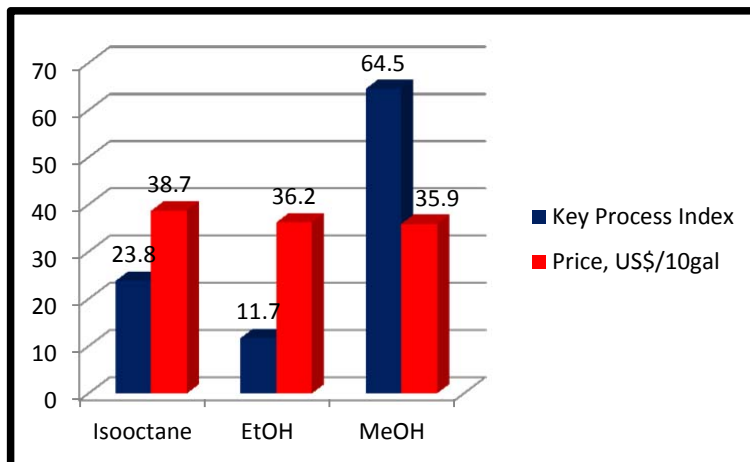
Figure 6.8. Cost-KPI analysis excluding safety risk index for three blends.

B. The estimation of the blends metrics at the same mileage

Estimation of the metrics (similar to Table 6.5) at the same mileage namely, using the certain amount of different blends to drive a car at the same mileage may be possible; however, it is beyond the scope of the present research.

In order to estimate the metrics table at the same mileage for the new blends, there is a high demand to find the relationships between (a) the mileage and the "**fuel consumption**" of the designed blends (i.e. I5, E5 and M5) by a car to calculate the blend costs, and (b) the mileage and the "**heat values**" of the designed blends (section 6.5 of the present thesis; National Renewable Energy Library, 2008). Otherwise, the estimation of the metrics for a fixed mileage by the existing data is misleading, not to mention that the cost-benefit analysis is not possible in such case.

Such investigations can only be done by auto industries since the objective here is to examine the quality of their car engine to prove their combustion efficiency.

The present research is concerned with sustainable product design, which means to estimate the afore-mentioned impacts of the new products (or a chemical process) on the environment and process safety at certain production rate.

In other words, although both trends deal with product quality control, the former approach is engine oriented in auto industries while the latter is blends focused in product design.

6.12   CONCLUSIONS

The blends of fossil fuel (gasoline molecules) and three chemicals (methanol, ethanol and isooctane) were modeled by Aspen HYSYS and the factors affecting the quality of 5% blends were studied for the specific M5-E5-I5 set. The most important metrics are octane number, mileage loss, the impacts of the energy and material on the environment, safety risk and economic factors (costs). The process was modeled in such a way that the energy consumption was zero for all blends. All factors except cost were weighted according to the Analytical Hierarchy Process methodology in order to rank the blends in terms of Key Performance Indicators (KPI), followed by a cost-KPI analysis.

The cost-KPI analysis indicated that methanol blend (M5) was the best substitution for pure gasoline. It is even more economical and environmentally friendlier than the equivalent ethanol blend – E5. Further study on the application of risk index metrics showed that M5 is also inherently safest blend. The risk index has a significant consequence in ranking the blends. Another equally important conclusion is that in this particular case study the higher value of KPI, the cheaper the blend is.

Chapter 7

The impacts of material and energy as well as the evaluation of the risks to process safety have been explained in details in Chapters 3, 4, and 5 respectively, followed by case studies in order to illustrate how the methodologies apply to individual process design.

In chapter 6 gasoline blends as new product design were investigated and a variety of metrics have been analyzed; e.g. Octane Number, Mileage Loss, Environmental Impacts, and Risk Index. Since some metrics favor to one blend and the others don't, it is almost impossible to select the best designed product. Therefore, a multi criteria decision-making tool called Analytical Hierarchical Process (AHP) was employed, which gives a value as one Key Performance Indicators (KPI) to each product. Then, Cost-KPI (analogous to cost-benefit) analysis was applied to rank the products.

The main feature of the present research is to introduce three major indices as "Composite Indices" as a competent tool for the ranking of chemical processes at early design stage when detailed process data is lacking. The indices follow:

1. The impacts of "material" streams within a process on the environmental

2. The impacts of "energy" streams within a process on the environmental and

3. The "risks" of the design to process safety

Other metrics may apply depending on the process under study as in gasoline blends case study.

In this chapter, two case studies are presented: Cradle-to-Cradle thinner recovery design and the hydrogenation of unsaturated hydrocarbons followed by cost estimation; however, the latter is accomplished through a conventional profitability analysis.

Case study 1: Sustainable Development (Thinner Recovery Process)

Sustainable development makes it possible to preserve resources and maintain ecological balance, while utilizing natural reserves. Researchers have made many attempts in different ways to provide distinctive methodologies in order to achieve sustainability in chemical process design; e.g. Life Cycle Assessment (LCA), WAR algorithm, etc.

The LCA methodology is widely used for the estimation of impacts of chemicals, processes and services on the environment. This methodology evaluates the impacts from raw materials to disposal including land filling so; it is sometimes referred to as Cradle-to-Grave Analysis (see section 2.2.5).

Although it is emphasized that the WAR algorithm is applicable merely in the manufacturing step of the life cycle of a chemical (Young and Cabezas, 1999), in very limited cases such as combined processes and under certain conditions; e.g. present case study, it can be employed as a Cradle-to-Cradle analysis tool within Cradle-to-Grave (LCA) methodology.

7.1 CRADLE-TO-CRADLE DESIGN:
In this case study, the Cradle-to-Cradle assessment is applied to the painting unit of automotive industries. In such factories there are several steps for manufacturing of a car, including painting where the paint is mixed with thinner as a solvent. Painting is an important

process in automotive industries, since customers spend for favorite colours while purchasing automobile. In addition, thinner solvent is also used in large amounts to flush the painting facility such as paint storage tanks, pumps, pipes, pistols etc. Therefore, the painting unit generates a large quantity of wastes as pollution, which is mainly associated to thinner and disposed.

The painting unit is also important due to the potential environmental impacts (PEIs) as well as the safety risks associated with thinner as it is composed from several hydrocarbons and therefore, it is a flammable and toxic solvent.

Hence, it turns out that the integration of a chemical process into an automotive factory will increase the company's profitability while protecting the environment from pollutants by the isolation of thinner (a valuable solvent) from the waste by means of separation techniques. Figure 7.1 represents such combined processes.
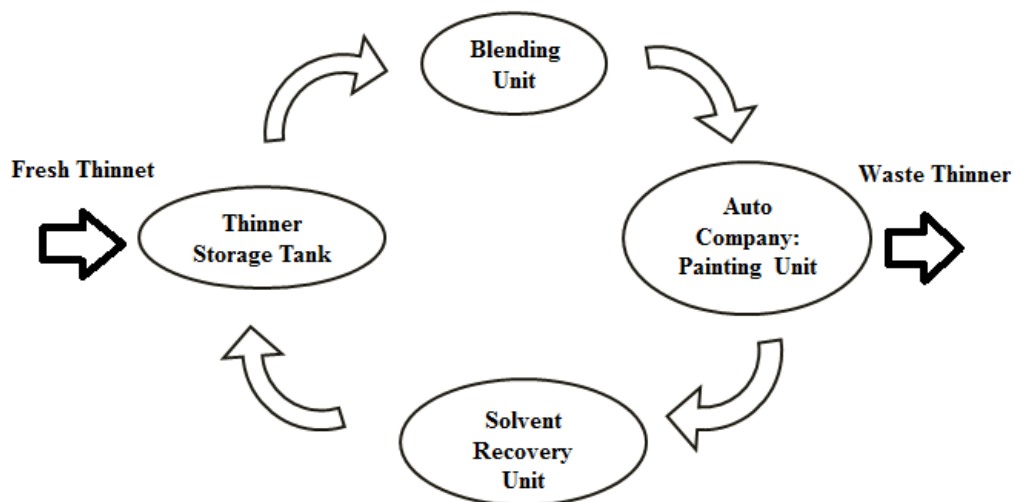
Figure 7.1. Cradle-to-Cradle integrated process.

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In this flow chart thinner is delivered from storage tanks to the Blending Unit of automotive plant to be mixed up with paint. The product will be sent to "Painting Unit" to paint the cars where significant amounts of wastes are generated. This process is used in conventional automotive design.

In sustainable design using new composite indices a few chemical process units (equipment) are installed in the automotive factory to add a separation facility called "Solvent Recovery Unit" whose function is to separate the thinner from the wastes and then to return it to "Thinner Storage Tank". The residual has heat content which can be recovered in an incinerator. The fresh thinner should be always supplied to the storage tank as make-up.

7.1.1 Standalone process:

Figure 7.2 illustrates standalone facility used for handling of thinner solvent in an auto manufacturing plants used by the majority of auto industries in the world; including North America.
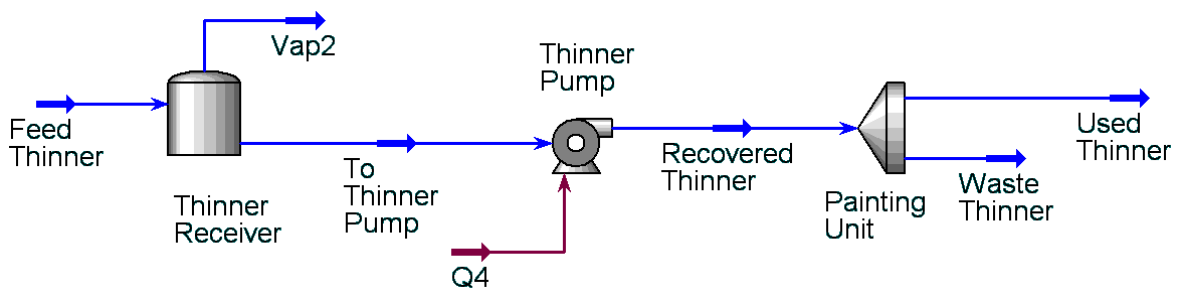
Figure 7.2. A standalone facility for the handling of thinner.

Generally, in auto industries, fresh thinner is supplied to the factory (to storage tanks), mixed up with paint in a mixing tank and then, pumped to painting unit into pistols through the pipes in order to coat the cars. When it comes to changing the colour of the next batch of cars, all painting facilities such as pumps, mixing and storage tanks, pipes and pistols will be

flushed out with thinner. The majority portion of thinner is coated on the cars manufactured, while a significant amount of thinner is accounted as waste due to flushing of the painting facilities.

The resulted effluent (waste) needs cost-effective waste treatment facilities, since the government penalizes pollution generating industries based on the waste volume and concentration.

In this design, the "Used Thinner" stream has the flow rate of 7,905 lb/h and represents the product stream, which is used for coating the cars. The "Waste Thinner" with the flow rate of 5,270 lb/h represents the effluent thinner, which is used for the cleaning and flushing.

7.1.2 Combined process:

The waste thinner in preceding section can be reduced by employing combined processes; a combination of the Thinner Recovery Unit and automotive factories (Figure 7.3).

In both designs, the "Used Thinner" stream represents the amount of the thinner used for coating the cars. The flow rate of the "Used Thinner" for both standalone and combined designs are almost the same; i.e. 7,926 lb/h and 7,906 lb/h, respectively. The flow rate of "Sludge" and "To Incinerator" streams in the combined process is totally about 152 lb/h. It is crucial to note that the "Waste Thinner" stream in the combined process (5,284 lb/h) is recycled to the beginning of the process and therefore, it is not considered as a waste stream anymore. The flow rate of the "Waste Thinner" in the standalone design is 5,270 lb/h. The streams "Vent1", "Vent2" and "ATM" have nil flow rates at steady state operation and have no contribution in waste generation.

7.1.3   Process description

The waste thinner from the existing and from similar automotive factories contains 10 wt% sludge at most. Therefore, the objective of this chemical plant is to remove the sludge and other impurities such as remaining paints from the thinner by separation techniques. The waste thinner is received as Crude Thinner in W/T Separator, a three phase separator, through which sludge is removed.

The thinner on the upper phase of the W/T Separator is pumped to the fourth tray of a distillation tower called "Thinner Tower", which is equipped with totally six trays, after passing through a heat exchanger to increase the waste thinner's temperature up to 150 $^{\circ}$F. In order to decrease utility consumption, the heat transfer is carried out by the Recovered Thinner stream at 230 $^{\circ}$F as heating medium. The Recovered Thinner is then discharged to Thinner Control Tank for the quality and the quantity control. Fresh thinner would be fed in to the tank through Make-Up Thinner stream when needed.

When everything is approved by quality control department, the thinner is pumped to Painting Unit by Thinner Pump. The thinner temperature is controlled by a cooler, which may be used intermittently. The waste thinner from the Painting Unit is recycled to the beginning of the combined plant; i.e. the W/T Separator.

The vent from condenser is negligible and therefore, discharged to atmosphere (ATM). The bottom outlet from the Thinner Tower contains hydrocarbons as well as remaining paint and has a flow rate of about 53 lb/h and a heat value of about 1.74×10^{6} Btu/lbmole. Therefore, using the heat content in a boiler or an incinerator would save energy consumption.
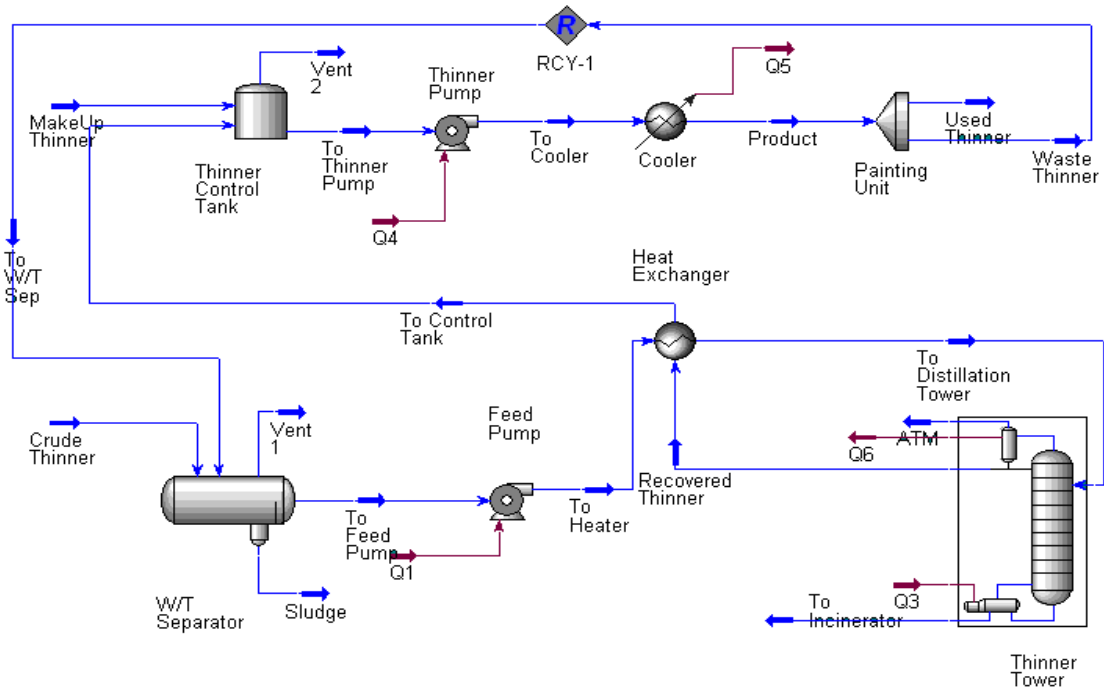
Figure 7.3. Thinner recovery in a combined process plant: A separation unit and a painting unit.

7.2 COMPOSITE METRICS EVALUATION

Metrics of material and energy impacts on the environment as well as the risk to process safety are used for the assessment of two processes mentioned above.

7.2.1   The impacts of material on the environment (WAR algorithm):

The estimation of the material impacts on the environment is based on the index from WAR (WAste Reduction) algorithm (Cabezas et al., 1997 and 1999; Young and Cabezas, 1999; Young et al., 2000). The values of the index are calculated using the WAR GUI (2008) software developed by EPA, and are reported in Potential Environmental Impacts per hour (PEIs/hr.).

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Material Impacts on the Environment:

Standalone design: $M_{Imp.}$ = 2,710 PEI/h

Combined design: $M_{Imp.}$ = 58.8 PEI/h

7.2.2 The impacts of energy on the environment (new energy index):

The estimation of the energy impacts on the environment is based on the indices introduced by Ordouei et al. (2014b) for the calculation of CO_2, SO_2 and NO_2 emission rates to the environment. The emission rates can be calculated by the following equations (Section 4.2):

$$\dot{I}_e = \sum_j \dot{I}_j = \sum_j \sum_k \dot{I}_{J,k} = \sum_j \sum_k x_i \times \left(\frac{\dot{Q}_{i,k}}{\eta_k \times HV}\right) \times \left(\frac{MW_j}{MW_i}\right) \qquad (4.7)$$

Where $\dot{I}_e$ is the total gas emission rate to the atmosphere from the process; η_k is the conversion efficiency of heat generator k; e.g. boiler, incinerator and steam turbine. As an example, the efficiency of a typical fossil fueled steam turbine generator is:

η_k = 75% x 35% = 26.25 %

since the conversion efficiencies are 75% for boiler itself (Coulson and Richardson, 2001) and 35% for steam turbine (EPA, 1997a).

$\dot{Q}_{i,k}$ is the fraction of the heat flow or the energy consumption (kCal/h) related to component i in heat generator k, where i represents carbon (C), sulfur (S) and nitrogen (N) HV is the fuel heat value (kCal/ kg fuel), x_i is the mass fraction of component i, MW_j is molecular weights (kg/kgmole) where j denotes gas emitted to the atmosphere ($j = CO_2$, SO_2, NO_2). $\dot{I}_{J,k}$ is the gas

emission rate to the atmosphere in the form of component j from heat generator k in kg CO_2 (or SO_2 or NO_2)/h.

Based on the above information and also the available data pertaining to the compositions and characteristics of fossil fuel (Heavy Fuel Oil or HFO in this case study), the HHV of each component and heat flow, $\dot{Q}$, were broken down and attributed to their chemical components as shown in Table 7.1.

Table 7.1: The characteristics of heavy fuel oil and the breakdown of heat flow and power consumption in both designs.

No.	Characteristics of Heavy Fuel Oil	Value	Heat Flow, $\dot{Q}_i$, in kJ/h (Standalone)	Heat/Power Flow, $\dot{Q}_i$, in kJ/h (Combined)	
1	Sp. Gr.	0.941		**Heat**	**Power**
2	HV of the Heavy Fuel Oil	42,293 kJ/h			
3	S	2.7 wt%	23.8	75,006.0	70.0
4	C	84.8 wt%	746.5	2,355,744.0	2,198.2
5	N	0.5 wt%	4.4	13,890.0	13.0
6	H	11.93 wt%	105.0	331,415.4	309.3

Important Note: The values of heat flow and power consumption are calculated by mass and energy balance from HYSYS process simulator.

In a combined process similar to Figure 7.2, more energy is used compared to a standalone plant (Figure 7.1). Hence, it is predictable that the corresponding energy impacts on the environment ($E_{Imp.}$) be higher than that in standalone plant.

Below is the detailed calculation method for the estimation of the energy impacts on the environment (Ordouei et al., 2014b).

Estimation of the energy impacts of the *"Standalone"* process on the environment

$$\dot{I}_{SO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{23.8 \left(\frac{kJ}{h}\right) \times 0.027 \left(\frac{kgS}{kgFuel}\right) \times 64 \left(\frac{kgSO_2}{kgmole}\right)}{0.2625 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 32 \left(\frac{kgS}{kgmole}\right)} = 1.14 \times 10^{-4} \frac{kgSO_2}{h}$$

$$\dot{I}_{CO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{746.5 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44 \left(\frac{kgCO_2}{kgmole}\right)}{0.2625 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 12 \left(\frac{kgC}{kgmole}\right)} = 0.2 \frac{kgCO_2}{h}$$

$$\dot{I}_{NO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{4.4 \left(\frac{kJ}{h}\right) \times 0.005 \left(\frac{kgN}{kgFuel}\right) \times 46 \left(\frac{kgNO_2}{kgmole}\right)}{0.2625 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 14 \left(\frac{kgN}{kgmole}\right)} = 6.6 \times 10^{-6} \frac{kgNO_2}{h}$$

Estimation of the energy impacts of *"Combined"* process on the environment (Power)

$$\dot{I}_{SO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{70.0 \left(\frac{kJ}{h}\right) \times 0.027 \left(\frac{kgS}{kgFuel}\right) \times 64 \left(\frac{kgSO_2}{kgmole}\right)}{0.2625 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 32 \left(\frac{kgS}{kgmole}\right)} = 1.2 \times 10^{-4} \frac{kgSO_2}{h}$$

$$\dot{I}_{CO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{2{,}198.2 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44 \left(\frac{kgCO_2}{kgmole}\right)}{0.2625 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 12 \left(\frac{kgC}{kgmole}\right)} = 0.62 \frac{kgCO_2}{h}$$

$$\dot{I}_{NO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{13 \left(\frac{kJ}{h}\right) \times 0.005 \left(\frac{kgN}{kgFuel}\right) \times 46 \left(\frac{kgNO_2}{kgmole}\right)}{0.2625 \times 42{,}293 \left(\frac{kJ}{kgFuel}\right) \times 14 \left(\frac{kgN}{kgmole}\right)} = 1.9 \times 10^{-4} \frac{kgNO_2}{h}$$

Estimation of the energy impacts of *"Combined"* process on the environment (Heat)

$$I_{SO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{75{,}006\left(\frac{kJ}{h}\right) \times 0.027\left(\frac{kgS}{kgFuel}\right) \times 64\left(\frac{kgSO_2}{kgmole}\right)}{0.75 \times 42{,}293\left(\frac{kJ}{kgFuel}\right) \times 32\left(\frac{kgS}{kgmole}\right)} = 0.13\ \frac{kgSO_2}{h}$$

$$I_{CO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{2{,}355{,}744\left(\frac{kJ}{h}\right) \times 0.848\left(\frac{kgC}{kgFuel}\right) \times 44\left(\frac{kgCO_2}{kgmole}\right)}{0.75 \times 42{,}293\left(\frac{kJ}{kgFuel}\right) \times 12\left(\frac{kgC}{kgmole}\right)} = 230.9\ \frac{kgCO_2}{h}$$

$$I_{NO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{13{,}890\left(\frac{kJ}{h}\right) \times 0.005\left(\frac{kgN}{kgFuel}\right) \times 46\left(\frac{kgNO_2}{kgmole}\right)}{0.75 \times 42{,}293\left(\frac{kJ}{kgFuel}\right) \times 14\left(\frac{kgN}{kgmole}\right)} = 7.2 \times 10^{-3}\ \frac{kgNO_2}{h}$$

From the existing information, the emission rates of CO_2, SO_2, and NO_2 in both process designs are calculated and summarized in Table 7.2.

The result reveals that all above emissions in standalone design are negligible compared to the combined design. As such, the emission rates of NO_2 and SO_2 in both designs are negligible compared to the emission rate of CO_2. On the other hand, the flow rate of waste stream in standalone design is much higher than that of combined design.

So, the impacts of energy consumptions to the environment:

$I_e = 0.2$ (kg gases/h)

$I_e = 231.6$ (kg gases/h)

Table 7.2: Comparison of total energy and total emissions in both designs at the same production rate (7,906 lb/h) using new energy/emission index.

	Steam to Reboiler[i] (kJ/h)	Power[i] (kJ/h)	Waste Streams (Lb/h)	New Emission Index (kg CO$_2$/h)	New Emission Index (kgSO$_2$/h)	New Emission Index (kg NO$_2$/h)	Total New Emission Index (kg gas/h)	EIA's[ii] Method (kgCO$_2$/h)	EPA's[iii] Method (PEI/h)
Standalone Design	-	880.3	**5,270**	0.2	1.14×10^{-4}	6.6×10^{-6}	**0.2**	**0.06**	**1.87×10^{-4}**
Combined Design	2,778,000	2,592.2	**152**	231.5	0.1	0.007	**231.6**	**175.2**	**0.23**

i. From mass and energy balance made by HYSYS process simulator.

ii. EIA method from equation (2.2).

iii. EPA method from WAR GUI software (WAR GUI, 2008).

Important Note 1: The calculation of emissions due to heat flow or power consumptions for all three process designs are given in pages 137-138.

7.2.3 The assessment of risk on process safety

The risk to the process safety was estimated in "Number of Affected People per Year" based on the methodology originated by Al-Sharrah et al. (2007) and then developed by Ordouei et al. (2014a). The method of calculations and the results follows:

$$(R.I)^W = \sum \sum M_j \times F_i \times H_i \times x_{i,j} \tag{5.2}$$

Risk assessment to the process:

Standalone design: $(R.I)^W$ = 26.97 (Number of affected people/year)

Combined design: $(R.I)^W$ = 0.47 (Number of affected people/year)

7.3 THE PRICE OF FRESH THINNER

The Feed Thinner in Figure 7.2 and the Make-Up Thinner in Figure 7.3 represent the fresh thinner feed in respective processes. The flow rates of Feed Thinner and Make-Up Thinner streams are 5,976 kg/h and 764.3 kg/h, respectively. The price of the fresh thinner is C$ 825 per tonne on average; therefore, the price of thinner consumed in each design is C$/h 4,930 and C$/h 630, respectively.

7.4 COST ESTIMATION

In Appendix A the capital cost estimation is discussed briefly. In this section, equations (A.2) and (A.3) have been used:

$$C_e = a + b\, S^n \tag{A.2}$$

$$C = F\, (\Sigma\, C_e) \tag{A.3}$$

Table 7.3: The result of the estimation of FCI, WCI and TCI

No.	Description	Factor	Standalone	Combined
**Estimation of Fixed Capital Investment (FCI)			
	Major equipment, total purchase cost**	C_e	207,829	291,067
1	Equipment Erection (f_{er})	0.3	62,349	87,320
2	Piping (f_p)	0.8	166,263	232,854
3	Instrumentation & Control (f_i)	0.3	62,349	87,320
4	Electrical (f_{el})	0.2	41,566	58,213
5	Civil (f_c)	0.3	62,349	87,320
6	Structures & Buildings (f_s)	0.2	41,566	58,213
7	Lagging & Paint (f_l)	0.1	20,783	29,107
	**ISBL Cost: C=ΣCe x**	3.3		
8	Offsites (OS)	0.3	62,349	87,320
9	Design & Engineering (D&E)	0.3	62,349	87,320
10	Contingency (X)	0.1	20,783	29,107
**Total Fixed Capital Cost:** $C_{fc} = C (1+OS)(1+DE+X)$			
	$C_{fc} = C$ x	1.82		
	$C_{fc} = ΣC_e$ x	**6.0**		
	**Total Fixed Capital Investment (FCI); USD**		1,248,221	1,748,150
**Estimation of Total Capital Investment (TCI)			
	Description**	**Factor**	**Standalone**	**Combined**
	In our case study: WCI=0.1TCI since it is a recycling process and has the majority of raw material recycled.	FCI/0.9	**1,386,912**	**1,942,389**
**Estimation of Working Capital Investment (WCI)			
	Description**	**Factor**	**Standalone**	**Combined**
	In our case study: WCI=0.1TCI since it is a recycling process and has the majority of raw material recycled.	10% of TCI	**138,691**	**194,239**

The parameters a, b, n, and F can be found from reference books. From Table A.2 (Estimation of FCI by typical factors) the Working Capital Investment (WCI) is about 10-20% of Total Capital Investment (TCI).

In this case study, since the recovery unit is likely to be located in an existing automotive plant, the WCI value is therefore estimated as 10% of TCI. Table 7.3 summarizes the result of Fixed Cost Investment (FCI), Working Capital Investment (WCI) and Total Cost Investment (TCI).

7.5 RESULT: ANALYSIS OF THE COMPOSITE INDICES

The cost estimation (in U$) of two designs is summarized in Table 7.4. As shown in this table, the standalone process design requires lower capital investment since recycling processes always encompass more equipment, higher energy consumption and consequently more investment; however, the more investment accounts for the lower potential impacts of materials on the environment and lower penalty due to waste minimization.

Table 7.4: The summary of the metrics of both designs.

Metrics	Standalone	Combined	Change, %
Waste Generation (Lb/Hr)	5,270	152	-3,367
Environmental Impacts, PEI/Hr	2,710	58.8	-2,651
Energy Impacts, kg gases (CO_2+SO_2+NO_2) /Hr	0.2	231.6	115,700
Safety Risk Index, No. of Affected People/Year	26.97	0.47	-5,638
Total Capital Investment, US$	1,386,912	1,942,389	40 [i]
Fresh Thinner Cost, U$ / Year	43,200,000	5,500,000	-685

i   This change is made only within the first year of operation of combined process. In fact, the capital expenses is onetime payment and will not apply to the rest of the plant operation.

The combined process design in this paper reimburses the capital cost within the first year after starting up the process (Table 7.4). It needs about U$ 560,000 more capital investments while saving about U$ 38,000,000 a year for using the recovered thinner compared to standalone process.

From Table 7.4 we can also see that combined processes has minimized waste generation and made a significant reduction in revolving costs for fresh thinner. It has also decreased both environmental impacts of materials as well as the potential risk dramatically.

For cross checking of the energy impacts in both designs in PEI/h (Section 2.4.1.1), the WAR GUI software (EPA, 2008) and the emission rates from Table 7.2 are used to compare with the environmental impacts (Table 7.4). It can be seen that energy impact of combined processes in PEI/h is much less than that of the standalone design.

Although the combined process comprises more capital cost and more energy impacts on the environment due to using more process units, consuming more energy in the form of electricity and heat compared to standalone process, other metrics especially lower cost for purchasing the fresh thinner favour for the combined design. Therefore, we can conclude that a combined process is an economically feasible process that is environmentally friendly.

Case Study 2: Hydrogenation heterogeneous catalytic equilibrium reaction

7.6 HYDROGENATION OF UNSATURATED HYDROCARBON: DESIGN APPROACH

The theory of this case has also been studied in Chapter 4; therefore, it is not repeated here. Figures 4.2a,b and 4.3a,b show two hydrogenation designs. The kinetic data and fresh feed compositions and condition are provided in Tables 4.3, 4.4 and 4.5, respectively.
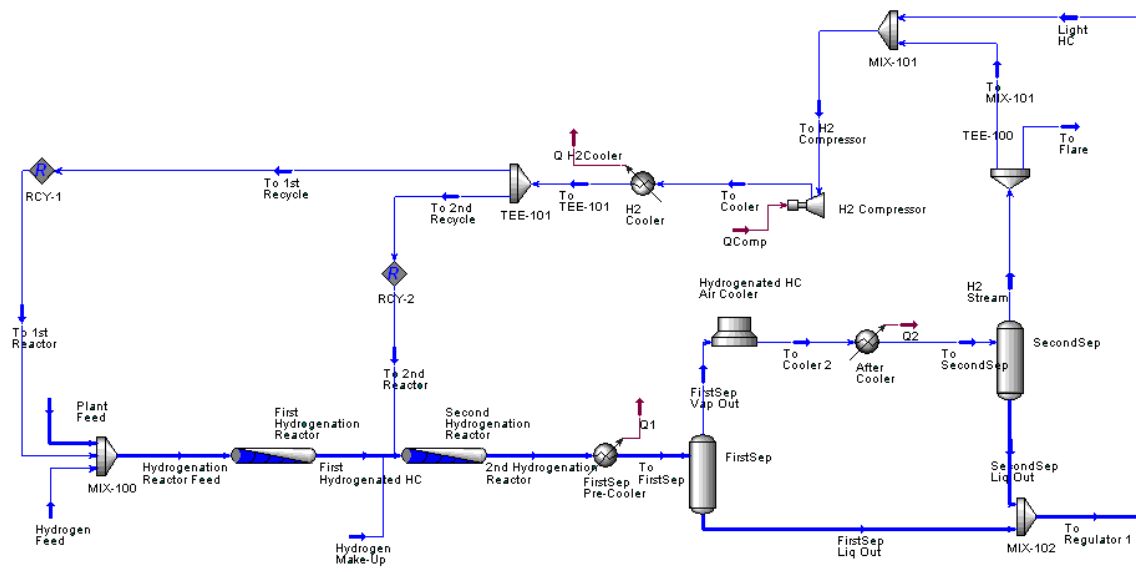
Figure 4.2a Hydrogenation Process: Original design; reaction and phase separation.

Figure 4.2b Hydrogenation Process: Original design; purification section.

Figure 4.3a Hydrogenation Process: Alternative design; reaction and phase separation.
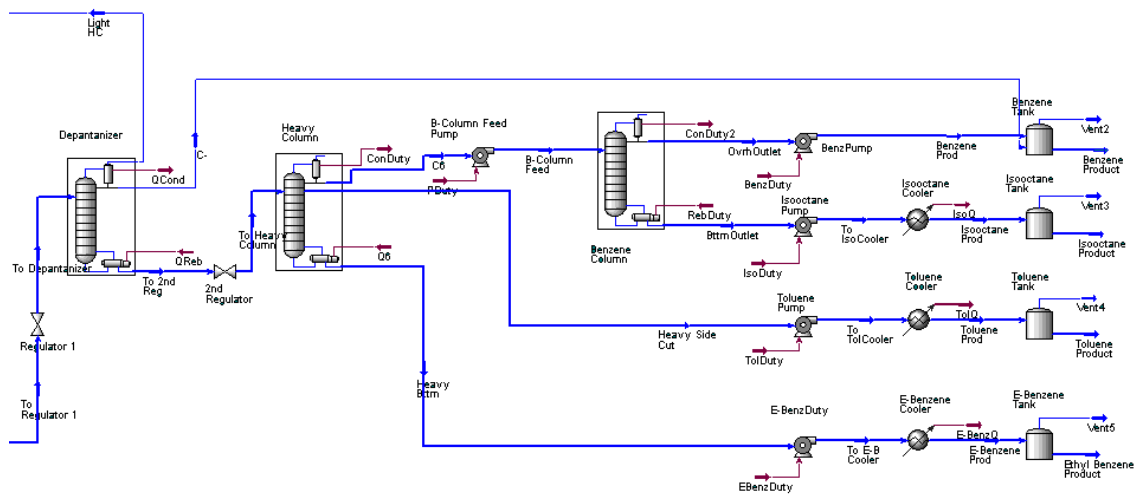
Figure 4.3b Hydrogenation Process: Alternative design; purification section.

The flow rate, number of products and wastes, Potential Environmental Impacts and the risks assessment of each stream in two process designs are summarized in Table 7.5 based on the available data from HYSYS process simulator.

Table 7.5: The material and energy impacts of the process on the environment and the risks to the process designs.

	Hydrogenation of Unsaturated Hydrocarbons									
	Original Design					Alternative Design				
Products	Flow rate, kg/h	Material Impacts Index		Safety Risk Index		Flow rate, kg/h	Material Impacts Index		Safety Risk Index	
		PEI/h	PEI/ kg Prod	#Affected People/ Year	#Affected People/ ton Prod x 10^-6		PEI/h	PEI/ kg Prod	#Affected People/ Year	#Affected People/ton Prod x10^-6
Light End	246.6	414.6	0.03	0.32	2.9	N/A	N/A	N/A	N/A	N/A
Benzene	6242	3062.3	0.49	25.86	237.6	6111	3392.9	0.27	24.46	223.7
Isooctane	760	362.5	0.03	2.76	25.4	648	308.5	0.02	2.62	23.9
Toluene	2325	2752.0	0.22	5.96	54.8	2379	2320.8	0.19	6.73	61.6
E-Benzene	2853	3585.8	0.29	6.18	56.8	3344	4277.2	0.34	7.34	67.1
Wastes	273.4	226.9	0.02	0.18	1.6	221.7	132.2	0.01	0.11	1.0
Total	12427	10177	1.06	41.08	377.5	12482	10299	0.83	41.15	376.3

7.7 ESTIMATION OF THE IMPACTS OF MATERIAL ON THE ENVIRONMENT AND RISK ON PROCESS SAFETY

At the first glance, one may select the alternative design whose product flow rate is higher and that of waste stream is lower, compared to the original design. In addition, the risk indices as well as the PEIs of streams in original design are higher than those in alternative design. However, a profound analysis of data available in Tables 7.5 and 7.6 reveals that the diversity of products and corresponding purities favour for the original design. It turns out that the purification section in the original design is more efficient compared to the alternative design.

Table 7.6: The flow rates of products in original and alternative designs of purification section.

No.	Product Name	Original Design		Alternative Design	
		Flow Rate, kg/h	Annual Capacity, Tonnes	Flow Rate, kg/h	Annual Capacity, Tonnes
1	Light End	246.6	1,980	0	0
2	Benzene	6,242	49,940	6,111	48,888
3	Isooctane	760	6,080	648	5,180
4	Toluene	2,325	18,600	2,379	19,030
5	E-Benzene	2,853	22,820	3,344	26,750
	TOTAL	12,427	99,420	12,482	99,848
Heat & Power Consumption		Heat (kJ/h)	Power (kJ/h)	Heat (kJ/h)	Power (kJ/h)
		31,411,056	155,699	32,032,759	1,032,523

7.8 ESTIMATION OF THE IMPACTS OF ENERGY ON THE ENVIRONMENT (NEW INDEX)

Now, we turn our attention to energy impacts on the environment. Based on the atom content and the characteristics of heavy oil, the heat value (HV) of the fuel is broken down and attributed to their components (Table 7.7).

The energy impacts have to be calculated for both processes entirely. The energy is used in two different ways:

a) Steam for heating of process medium in re-boilers, heaters etc.

b) Electric power for driving pumps, fans and compressors.

By employing the last row of Table 7.6 (Heat & Power Consumption), collected from HYSYS process simulator, and the Table 7.7, we can calculate the contribution of fuel components to the heat and power consumption by process units within the plant (Table 7.8).

Table 7.7: The characteristics of heavy fuel oil and the breakdown of HV and heat flow.

Characteristics of Heavy Fuel Oil	Value
Sp. Gr.	0.941
HV of Heavy Oil	18,200 Btu/Lb **(42,293 kJ/h)**
S	2.7 wt%
C	84.8 wt%
N	0.5 wt%
H	11.93 wt%

Table 7.8: The contribution of chemical elements in energy consumption in Hydrogenation designs.

Fuel Main Chemical Components	Heat Flow, $\dot{Q}_i$, in kJ/h (1st Alternative)[i]		Power, $\dot{Q}_i$, in kJ/h (2nd Alternative)[i]	
	Heat	Power	Heat	Power
S	848,693	4,207	889,500	27,898
C	26,655,234	132,125	27,936,877	876,193
N	157,165	779	164,722	5,166

i   The calculation method can be found in footnotes of Table 4.1

The impacts of energy are calculated in accordance with the energy index methodologies (equation 4.5) presented by Ordouei et al. (2014b), the result for the original design follows:

$$I_{SO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{848,693 \left(\frac{kJ}{h}\right) \times 0.027 \left(\frac{kgS}{kgFuel}\right) \times 64 \left(\frac{kgSO_2}{kgmole}\right)}{0.75 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 32 \left(\frac{kgS}{kgmole}\right)} = 1.44 \frac{kgSO_2}{h}$$

$$I_{CO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{26,655,234 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44 \left(\frac{kgCO_2}{kgmole}\right)}{0.75 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 12 \left(\frac{kgC}{kgmole}\right)} = 2,613 \frac{kgCO_2}{h}$$

$$I_{NO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{157,165 \left(\frac{kJ}{h}\right) \times 0.005 \left(\frac{kgN}{kgFuel}\right) \times 46 \left(\frac{kgNO_2}{kgmole}\right)}{0.75 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 14 \left(\frac{kgN}{kgmole}\right)} = 0.08 \frac{kgNO_2}{h}$$

And for the contribution of the power in gas emissions to the environment:

$$I_{SO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{4,207 \left(\frac{kJ}{h}\right) \times 0.027 \left(\frac{kgS}{kgFuel}\right) \times 64 \left(\frac{kgSO_2}{kgmole}\right)}{0.2625 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 32 \left(\frac{kgS}{kgmole}\right)} = 0.02 \frac{kgSO_2}{h}$$

$$I_{CO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{132,125 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44 \left(\frac{kgCO_2}{kgmole}\right)}{0.2625 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 12 \left(\frac{kgC}{kgmole}\right)} = 3.40 \frac{kgCO_2}{h}$$

$$I_{NO2} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{779 \left(\frac{kJ}{h}\right) \times 0.005 \left(\frac{kgN}{kgFuel}\right) \times 46 \left(\frac{kgNO_2}{kgmole}\right)}{0.2625 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 14 \left(\frac{kgN}{kgmole}\right)} = 1.2 \times 10^{-3} \frac{kgNO_2}{h}$$

Similarly, the impacts of heat flow and power consumption of the alternative design can be calculated as follows:

$$I_{SO2}^{\cdot} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{889,500 \left(\frac{kJ}{h}\right) \times 0.027 \left(\frac{kgS}{kgFuel}\right) \times 64 \left(\frac{kgSO_2}{kgmole}\right)}{0.75 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 32 \left(\frac{kgS}{kgmole}\right)} = 1.51 \frac{kgSO_2}{h}$$

$$I_{CO2}^{\cdot} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{27,936,877 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44 \left(\frac{kgCO_2}{kgmole}\right)}{0.75 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 12 \left(\frac{kgC}{kgmole}\right)} = 2,739 \frac{kgCO_2}{h}$$

$$I_{NO2}^{\cdot} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{164,722 \left(\frac{kJ}{h}\right) \times 0.005 \left(\frac{kgN}{kgFuel}\right) \times 46 \left(\frac{kgNO_2}{kgmole}\right)}{0.75 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 14 \left(\frac{kgN}{kgmole}\right)} = 0.085 \frac{kgNO_2}{h}$$

And for the contribution of the power in gas emissions to the environment in the alternative design:

$$I_{SO2}^{\cdot} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{27,898 \left(\frac{kJ}{h}\right) \times 0.027 \left(\frac{kgS}{kgFuel}\right) \times 64 \left(\frac{kgSO_2}{kgmole}\right)}{0.2625 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 32 \left(\frac{kgS}{kgmole}\right)} = 0.14 \frac{kgSO_2}{h}$$

$$I_{CO2}^{\cdot} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{876,193 \left(\frac{kJ}{h}\right) \times 0.848 \left(\frac{kgC}{kgFuel}\right) \times 44 \left(\frac{kgCO_2}{kgmole}\right)}{0.2625 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 12 \left(\frac{kgC}{kgmole}\right)} = 245.4 \frac{kgCO_2}{h}$$

$$I_{NO2}^{\cdot} = \frac{\dot{Q}_i \times x_i \times MW_j}{\eta \times HV \times MW_i} = \frac{5,166 \left(\frac{kJ}{h}\right) \times 0.005 \left(\frac{kgN}{kgFuel}\right) \times 46 \left(\frac{kgNO_2}{kgmole}\right)}{0.2625 \times 42,293 \left(\frac{kJ}{kgFuel}\right) \times 14 \left(\frac{kgN}{kgmole}\right)} = 7.7 \times 10^{-3} \frac{kgNO_2}{h}$$

Table 7.9 summarizes both types of heating and power consumptions in the first column, the flow rate of product streams in the second column and total emission of gas pollutants to the atmosphere in third to fifth columns for CO_2, SO_2 and NO_2, respectively. The last two columns exhibit the energy impacts using EIA's and EPA's methods, respectively. The energy impacts from the original design on the environment are lower compared to the alternative design.

The indices introduced in this research only apply to heating and electrical forms of energy excluding cooling water, which is used for removing the heat from process hot streams. The rationale underlying this fact follows:

a) It is imperative to know that this simplified process is a part of a huge refinery complex including cooling tower.

b) In cooling tower systems, there is huge cooling water circulation pumps to which above energy indices can be applied.

c) This means that in large scale the total heat and electric power consumption has to be calculated first and then, the equation (3) should be applied for the estimation of pollutant emissions to the atmosphere.

Table 7.9: Comparison of emission impacts in both designs of hydrogenation process.

	Total energy consumption (kJ/h)	Product stream (kg/h)	Total emissions (kg CO_2/h)	Total emissions (kg SO_2/h)	Total emissions (kg NO_2/h)	EIA's Total emissions[i] (kg CO_2/h)	EPA's Total impacts[ii] (PEI/h)
Original design	31.59×10^6	12,427	**2,616**	1.46	0.08	2,000	136
Alternative design	33.98×10^6	12,482	**2,984**	1.65	0.09	2,080	142

i   From Equation (2.2)
ii   Section 2.4.1 and Software WAR GUI (2008).

Important Note 1: The calculation of emissions due to heat flow or power consumptions for all three process designs are given in pages 149-150.

7.9 DISCUSSING THE CALCULATED METRICS

Table 7.10 represents the value of the major metrics of the new composite indices for both hydrogenation process design alternatives; i.e. risk index, the PEIs of waste streams as well as the impacts of energy on the environment.

Table 7.10: The values of each metrics for the original and alternative designs.

Metrics	Original Design	Alternative Design	Change, %
Total Safety Risks (#Affected People/Year)[*]	41.26	41.26	0
Energy Impacts: Heating and Power (kg CO_2 /h)	2,650	2,984	12.6
The Impacts of Waste Streams (PEI/h)	226.9	132.2	-
Total Impacts of Product & Waste Streams (PEI/h)[*]	10,404	10,431	0.26

* Total Risks/Impacts is the summation of the risks impacts of both products and wastes streams

Judgment can now be made based on the metrics above. From above table, the total risk is the same for both designs, while the energy impact is lower in the original design.

The PEIs are tricky in this case study. The PEI of so-called waste stream (To Flare) in the original design is almost twice as much as that in the alternative design. As stated earlier, the stream "To Flare" can be either sent to hydrogen recovery unit for further purification or used in heat generation unit; e.g. incinerator, boiler, fired heater etc. since it has heat value.

The stream "To Flare" in the original design contains hydrogen and butanes by about half wt%.

A chemical stream must have at least one of the following criteria to be regarded as a fuel in a power plant (EPA, 1997a):

a) 70% methane,

b) 60% propane, or

c) 25% hydrogen.

In this case, the total PEIs of the products and "To Flare" streams in original and alternative designs are 10,177 PEI/h and 10,299 PEI/h, respectively. Therefore, this result favours for the original design.

In other words, the original design is inherently safer and environmentally friendlier and better in terms of purity of products compared to the alternative design.

7.10 COST ESTIMATION

Cost estimation and profitability analysis will be carried out using the following equation Turton et al. (2012):

$$log\ C_P{}^0 = K_1 + K_2\ log\ (A) + K_3\ [log\ (A)]^2 \tag{7.3}$$

where C_P is the equipment cost (U\$). A is the equipment size in corresponding units; e.g. shell mass in kg for pressure vessels, heat transfer area in m^2 for heat exchangers etc. K_1, K_2 and K_3 are correlation parameters along with the minimum and maximum values of equipment size, which can be found in reference books.

Given As for the equipment in both designs in Figures 4.2a, b and Figures 4.3a, b, now we can calculate the cost of each design (Table 7.11).

Table 7.11: Cost estimations for both hydrogenation design alternatives based on Bare module.

No.	Equipment	Original Design (U$)	Alternative Design (U$)
1	Reactors and Drum Separators	201,200	201,200
2	Air Cooler and Heat Exchangers	1,174,100	1,174,100
3	Storage Tanks and Distillation Columns including Trays	1,393,200	1,322,500
4	Pumps & Compressor	242,000	242,000
TOTAL BARE MODULE COST		**3,010,500**	**2,939,800**
RAW MATERIAL COST		**17,767,470**	**17,767,470**

7.11 PROFITABILITY ANALYSIS

From the above table, it can be observed that the alternative design accompanies with lower fixed cost in terms of total Bare module cost, the revenue from sales in the original design is higher compared to the alternative design.

In order to find out which design is more profitable, a profitability analysis has to be made based on discounted profitability criterion (Table 7.12). The term "Net Present Value" (NPV) is the most important indicator, which shows profitability; i.e. the higher the NPV, the more the profitable the process is.

Table 7.12: Profitability analysis.

Description	Original Design	Alternative Design
Net Present Value-NPV (millions)	U$ 215.1	U$ 180.52
Discounted Cash Flow Rate of Return-DCFROR	233.47%	213.09%
Discounted Payback Period-DPBP (years)	0.1	0.2

This table reveals that the NPV and the DCFROR of the original design is higher and the DPBP is much lower than those of the alternative design. Consequently, although both designs are sustainable and profitable, the original design is much better since it is

environmentally friendlier, inherently safer, and has higher NPV as well as rate of return but lower payback period.

7.12 DISCUSSION

Using the existing (old) methodologies may sometimes be misleading. For instance, based on EIA's and EPA's methods, the difference of energy impacts between original and alternative designs are 80 kg CO_2/h and 6 PEI/h, respectively (Table 7.9). If we had to choose one design based on total Bare module cost, which states that the original design requires about U$ 71,000 more expenditure than the alternative design (Table 7.11), we would opt for the alternative design with 80 kg CO_2/h emission but at lower cost. However, the new energy index shows that the emission reduction from the original design is 334 kg CO_2/h (in addition to other emission) and this reduction leads to revenue for more than U$ 38,000 per year, which means the extra U$ 71,000 capital cost would be compensated in less than two years. So, we may make-up our decision and choose the original design.

The credit for CO_2 emission reduction is $13/ton CO_2 (Ball and Kennet, 2012).

7.13 CONCLUSIONS

The number of operating chemical and refinery plants around the globe is higher than ever before. As such, the frequency of disastrous accidents in the plants handling hazardous chemicals is more than ever before. Today, the chemical and oil & energy industries are on top rank for research investment for sustainable, safer and profitable design.

On one side, at early stage of a chemical process design the detailed data of the process is unavailable. On the other hand, the primitive stage is aligned with the highest impacts of decision making.

Many researchers have been trying to provide new methodologies to overcome this shortcoming. However, these methodologies cannot be used in conceptual design phase due to the following reasons:

- Some of them are qualitative.

- Some of them are quantitative but need several brainstorming meetings, which are either time and cost effective or biased.

- Some need detailed process information, which is lacking during initial design step.

- The data/database used in some of them may not be of good quality.

There is a high demand to a new methodology, which overcomes the above-mentioned constraints yet minimizes the impacts of decision making at conceptual design phase.

This chapter presents a new methodology consisting of composite indices for ranking a variety of process design alternatives without compromising profitability. These **"Must Learn Indices"** enable a process engineer to estimate the impacts of the material and energy of a process on the environment and also to evaluate risks to the process safety during conceptual design as well as operation phases.

Although in the majority of cases, the indices find that the most sustainable design is coined with the most profitable one, in case of any conflicts between both, a multivariable decision making methodology called Analytical Hierarchical Process (AHP) will be used to rank the design array (For more details please refer to Chapter 6).

A simplified hydrogenation process as a case study was selected to apply the new composite indices, because the hydrogenation catalytic reaction is widely used in refineries for economic and environmental purposes.

The composite indices verified that although both design alternatives are sustainable and profitable, the original design with five distinctive products is environmentally friendlier and inherently safer and more profitable.

A highly valuable conclusion from the presented new composite indices is that the art of the new methodology is the meeting of both sustainable and profitable design at no risk, which is so attractive to investors.

Chapter 8

GREEN CHEMISTRY/GREEN DESIGN
ECO-INDUSTRIAL PARK (EIP) DESIGN

Eco-Industrial Park (EIP) is by definition (Saikku, 2006) a set of industries in close proximity where materials, energy and information exchange among companies meets and conceptually, it is an industrial ecology in part.

In this chapter, the background and the constraints of EIP design are briefly reviewed, followed by the introducing a simplified EIP design as a case study using standalone processes, which generate wastes. Then, the new composite indices for both the potential environmental impacts and for the safety risk assessments, which were presented in this thesis, have been applied on the EIP case in order to probe how the new methodology helps to quantify and to appraise different scenarios.

According to Saikku (2006) an EIP brings several benefits to environment, society and economy and can be internationally applied to both existing and new plants, which are in

neighborhood. EIP can be successfully accomplished only when an efficient symbiosis among industries involved is carried out.

From above explanations it can be inferred that EIP has several advantages such as:

- Recycling of by-products (waste) from one company to another as an important raw material.

- Reduction in resource consumption such as water, oil etc.

- Minimization of gas emissions to the environment; e.g. CO_2 and SO_2.

- Enhancement of energy utilization by heat recovery.

- Waste minimization and greatly operational costs reduction.

8.1 THE EIP DESIGN CONSTRAINTS

The new indices have wide variety of applications including EIP; however, there are several serious constraints against an efficient EIP design as a case study including:

1. Usually the plant owners in industrial parks do not disclose their wastes analyses data due to adverse consequences on their profits such as penalties so; these data are either not available or not reliable.

2. The companies' owners consider their processes confidential and do not disclose them.

3. The owners usually are not interested in investment in provisions such as new piping and equipment unless they have to.

4. The plants at the same area are not necessarily suitable for EIP since it needs a unique set of companies and technologies to make it possible a sustainable design (Martin et al. 1996).

5. It is difficult to convince the owners for symbiotic relationships within industrial parks. So, in order to design an EIP there is a highly demand to:

6. Regulations and political supports in order to create a business environment to promote sustainable development as well as networking between private and public organizations (Saikku, 2006).

Unfortunately, due to above reasons the existing researches in the field of EIP have lack of process data such as the conditions and the compositions of waste streams. For instance, Brings (2006) has quantitatively studied the steam- and heat-related industrial symbiosis in Kalundborg, Denmark for a reduction in CO_2, SO_2, and NO_x emissions. Although Bring has provided calculations result as e-supplement, the conditions and conditions of waste streams are still missing since, the engineering calculations were left to the companies involved. As such, the wastes (by-products) only include wastewater, cooling water, boiler water, and steam and do not cover other chemical process streams.

A similar study was made by Kim et al. (2010) who optimized a utility network including steam, water and electrical facilities within an industrial complex resulted in high profits and environmental regulations achievements.

8.2 GLAXOSMITHKLINE (GSK) TOOLKIT: A COMBINATION OF ECO-DESIGN AND SUSTAINABILITY IN PHARMACEUTICAL INDUSTRIES

This is a toolkit developed to make GlaxoSmithKline as a leading pharmaceutical company by using the concept of eco-park or eco-design as well as sustainability (González et al., 2009). GSK estimates the environment, health and safety (EHS) impacts from manufacturing of raw materials to the fate of products and non-products just like life cycle assessment (LCA). The GSK is a comprehensive toolkit, which contains five modules;

- **Green Chemistry/Technology Guide**, The guide provides rankings using four categories (a) most used chemistries from GSK chemical synthesis processes, (b) EHS and technology alternatives for processes, (c) metrics for evaluating chemistries, technologies and processes, (d) common issues encountering process design and development.

- **Material Selection Guides:** Primary priority is given to solvent in pharmaceutical industries followed by ranking the solvents based on waste profile, eco-toxicity, flammability, and health impacts, organic and aqueous solvents, solvents LCAs, separation profile (azeotrope formation), physical properties etc.

- **Fast Lifecycle Assessment for Synthetic Chemistry:** It's similar to common LCA but different from WAR algorithm (PEI theory).

- **Green Packaging Guide:** Since packaging is one of the most concerns in pharmaceutical industries. GSK provides guidance for this important manufacturing process.

- **Chemicals Legislation Guide (CLG):** Unlike other parts of the GSK's tool, which are based on the company best practice, CLG is based on the chemicals legislation around the world (Homeland Security Lists, CA Proposition 65, REACH etc.) in order to rank chemical hazards.

This toolkit is accessible only through the GSK's intranet and would be used by different disciplines working together for better design in the course of project stages.

The largest advantage of GSK is that it could be used as a guide for labs and pilot plant design. It also gives the idea to researchers how chemicals and solvents are ranked and summarized based on the applications by GSK. On the other hand, the largest disadvantage of the tool is that the chemical information is limited to company's practice, and hence, may not be commonly applicable in industries. Moreover, its database only covers pharmaceutical applications without any information in the fields of chemical processes like refineries and petrochemicals.

8.3 SIMPLIFIED STAND-ALONE AND COMBINED (EIP) PROCESSES

So, there are serious barriers to design an EIP. However, it is possible to design a simplified process. Figure 8.1 shows the stand alone processes of an industrial park and the individual waste streams.
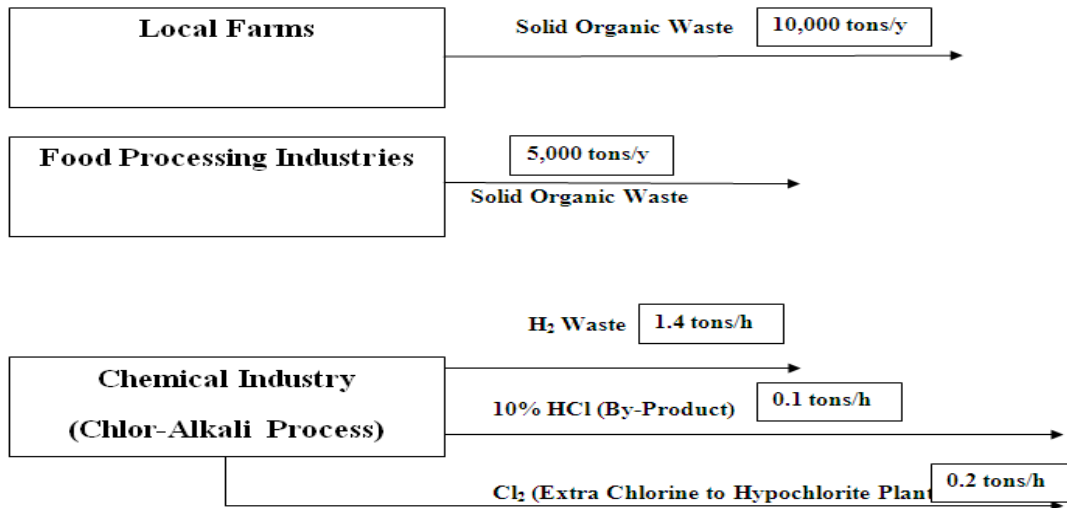
Figure 8.1. Stand Alone Processes. Waste Stream Scheme. No product stream.

This figure is adapted from study made by Martin et al. (1996) since only waste streams are our main concern.

An EIP design is sustainable only when proper technologies are used (Martin et al. 1996); for instance, they enhanced the EIP's profitability by reducing wastes. Technological development makes it possible to bring the industries involved in EIP to efficient symbiotic relationships.

Therefore, the above standalone processes can be used to design an EIP when industrial symbiosis is achieved. Figure 8.2 exhibits such a unique set of plants within an EIP to make the most of economic profits out of wastes throughputs from concerned industrial plants and farm lands.
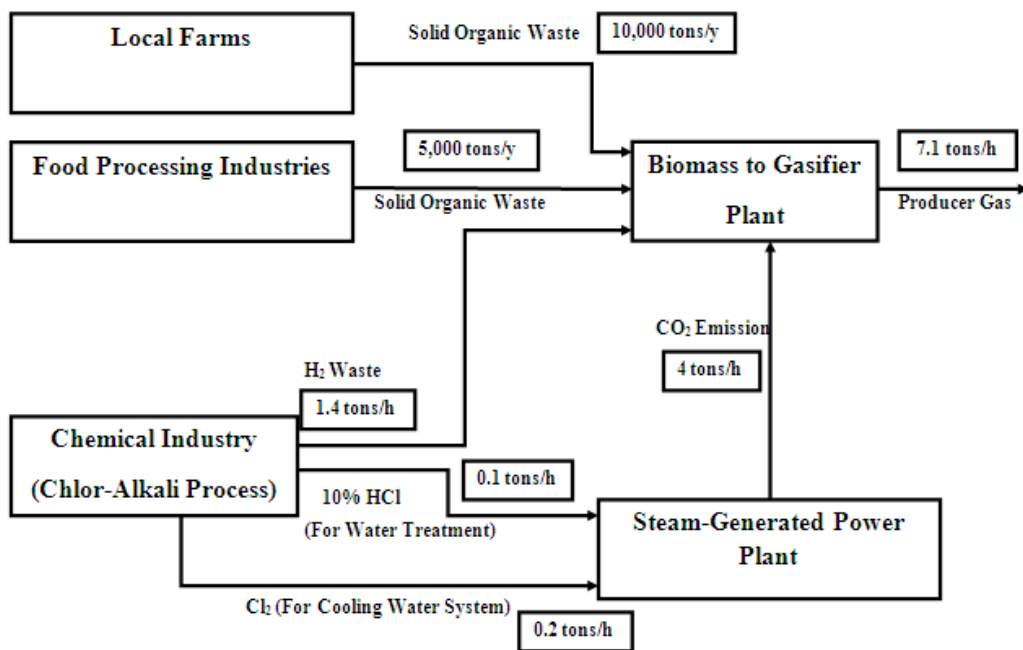
Figure 8.2. Eco-Industrial Park (EIP) Design. Waste Stream Scheme.

As it can be seen from this figure, the addition of a Gasifier technology converts the wastes to the feed material to Fischer-Tropsch process (FTP), which in turn converts the raw material to a wide variety of desired products including bio oil. So, FTP design depends on the product requirements. In the next section, a quick review of Fishcher-Tropsch technology is provided.

This section is regarded as an EIP design, which rather requires true process and technology selection than design a process itself.

8.4 FISCHER-TROPSCH TECHNOLOGY

Combustion in fossil fueled power plant is the main source of gas emissions to atmosphere, which contributes significantly to the global warming phenomenon. Since the combustion may be incomplete due to air to fuel ratios, there is a risk of CO generation and intervention to the environment, which plays an important role in photochemical smog formation.

Fischer-Tropsch Synthesis (FTS) is considered as a process integration methodology. Nowadays, FTS is of great interest to energy industries. The rationale behind it is that FTS converts high H_2/CO ratio syngas to diesel fuel of high cetane number by using biomass and coal. Biomass such as wood chips, solid wastes from farm lands is widely used in gasification process, where it is burnt in gasifiers to produce syngas.

Then, the product of a gasification process is fed to FTS as a raw material. A comparison between coal syngas, biomass syngas and natural gas has been made by Richter (2012) as shown in Table 8.1. Typical composition of a syngas generated from biomass is tabulated in the second column of the above table.

On the other hand, H_2-deficient and CO_2-rich syngas (high carbon utilization) feeding to FTS as raw material is not only economic but it also is sustainable (James et al., 2010). Therefore, the compositions of CO_2-rich syngas may vary from those of above table.

Table 8.1: The compositions of coal syngas, biomass syngas and natural gas (Richter, 2012).

Composition	Coal-Gas	Bio-Gas	Nat-Gas
Hydrogen (H_2)	14.0%	18.0%	--
Carbon Monoxide (CO)	27.0%	24.0%	--
Carbon Dioxide (CO_2)	4.5%	6.0%	--
Oxygen (O_2)	0.6%	0.4%	--
Methane (CH_4)	3.0%	3.0%	90.0%
Nitrogen (N_2)	50.9%	48.6%	5.0%
Ethane (C_2H_6)	--	--	5.0%

In this cases study due to existing hydrogen waste from Chlor-Alkali plant as well as CO_2 from power plant in the feed stream to the gasification process the syngas composition has significantly changed (Table 8.2).

Table 8.2: The composition of biomass syngas of the present case study.

Composition	Case Study
Hydrogen (H_2)	24.0%
Carbon Monoxide (CO)	5.8%
Carbon Dioxide (CO_2)	57.7%
Oxygen (O_2)	0.1%
Methane (CH_4)	0.7%
Nitrogen (N_2)	11.7%

An important part of EIP design is to reduce the amount of CO_2 emission. A syngas or in general a producer gas, which contains a large amount of CO_2, can be converted to variety of products in many different ways using variety of catalysts. Below some of these methods have been provided.

Currently, there are many researchers working on global warming issue mainly caused by CO_2 emissions to the environment as well as the way to capture CO_2. As such, several investigations have been made to convert CO_2 to different hydrocarbons by a wide variety of catalysts and reaction conditions.

Using CO_2-rich syngas as feedstock for FTS, Srinivas et al. (2007) have proposed a kinetic model and a new flow sheet alternative for FTS and reported that new process gives better CO_2 conversion.

Wilhelm et al. (2001) have characterized technologies for syngas generation; e.g. catalytic steam methane reforming SMR, two-step reforming, autothermal reforming ATR, partial oxidation POX , and heat exchange reforming, and discussed the low-cost associated technologies.

Yao et al. (2011) have studied the effect of CO_2 in several mixtures of $H_2/CO/CO_2$ syngas on an iron-based catalyst during FTS at low temperature and found out that CO_2 hydrogenation produces CH_4-rich short chain paraffins. They also found out that at a very high concentration of CO_2 in the $H_2/CO/CO_2$ feed mixture, when $CO_2/(CO+CO_2)$ ratio in the feed gas decreases hydrocarbon reaches at maximum production rate and stays unchanged.

Liu et al. (2008) have studied the effect of co-feeding CO_2 on a Fe–Mn catalyst during FTS by changing the partial pressure of CO_2 added to the feed gas and observed a selectivity decrease in $C19^+$ generation and also an increase in the ratios of olefin/paraffin of low carbon

hydrocarbons. This effect can results in a significant increase in the formation of water and overall oxygenate rates.

The effect of 3% Ru-Al$_2$O$_3$ and 2% Rh-CeO$_2$ catalysts on CH$_4$-CO$_2$ reforming activity using either CO$_2$-rich or CO$_2$-lean model biogas feed was studied (Djinović et al., 2011). The stability of both catalysts at 750 ^{o}C for equimolar CH$_4$/CO$_2$ gas stream was satisfactory. Residence time variations had similar effect on H$_2$ consumption for water formation. CH$_4$/CO$_2$ ratio above 1 has a positive influence on an increase in H$_2$/CO molar ratio within the syngas.

It is also possible now to convert CO$_2$ to CH$_4$ on Ruthenium (Ru) doped cobalt oxide nanorods. Zhuet et al. (2012) have reported that an ultrathin film bimetallic catalyst Co-Ru is formed in the course of reaction to augment reaction selectivity towards methane production compared to cobalt oxide catalyst alone.

Shimura et al. (2013) have employed five types of impregnated Co/TiO$_2$ catalysts with different crystal phases for Fischer–Tropsch Synthesis (FTS) in a stirred slurry tank reactor. They showed that different phases have different CO conversion. Using eleven types of metal ions as additives to TiO$_2$ support, they reported alkali earth metals give high CO conversion, Mn and V increased selectivity rather towards C5$^+$ than CH$_4$, calcium ions resulted in highest CO conversion and about twice higher C5$^+$ than those over the bare Co/TiO$_2$ catalyst.

8.5 RESULT & DISCUSSION

Table 8.3 represents the result of the application of environment and risk indices introduced in this thesis on the simplified EIP design.

As it can be seen from the table, EIP has lower environmental impacts of material by an order of 2. The reason is the wastes are all consumed in gasification process and therefore, the third

column relating to waste stream has null figures for both metrics. As such, the risk to the EIP process safety is almost zero.

Table 8.3: The result of environmental and risk impact assessments (EIP design).

Metrics	Standalone Waste Streams	EIP Design Waste Streams	EIP Design Product Streams
Potential Environmental Impacts, PEI/h	2,280	0	10.4
Risk Index, # Affected People/year	1.4	0	0

In this case study, the concept of symbiosis interaction was used to design a simplified Eco-Industrial Park. The new risk index for inherently safer design as well as the theory of PEI was applied to the simplified EIP design and proved that the EIP is environmentally friendlier and inherently safer design compared to standalone process. It was assumed that the only outlet stream, i.e. syngas or producer gas, is an intermediate product that will bear Fischer-Tropsch reactions. Therefore, in the present EIP design there is no waste stream(s).

Chapter 9

9.1 CONCLUSIONS: BENEFITS OF THE CURRENT RESEARCH

"New Sustainability Indices" were presented in this research. The sustainability indices employ three main metrics to evaluate the process friendliness to the environment and to measure the risks to the process safety; however, depending on the nature of chemical processes other metrics may be used such as product purity, octane number etc. The three principal metrics of the "New Sustainable Indices" are:

1. An existing methodology for the estimation of the Potential Environmental Impacts (PEI) of materials called WAR (WAste Reduction) algorithm.

2. A new methodology for the estimation of the impacts of energy consumption by a process on the environment

3. A new risk assessment methodology for inherent safer design in order to resolve the current environmental and safety issues at early design phase (conceptual design).

The last two methodologies and the selection and the combination of three methodologies are the contributions of the present research.

There are several advantages for individual new indices and combination metrics (Table 9.1).

Table 9.1 Comparison of new methodologies with existing ones.

No.	Metrics	The New Sustainability Indices	The Existing Methodologies	Remarks
1	Energy Impacts on Environment	Based on the Law of Conservation of Material and Energy.	EIA and EPA are both trivial and inventory based. Other methodologies: N/A.	
2		Precision: Estimates the emission rates of all main pollutant gases: (CO_2, SO_2, and NO_2).	EIA: Only estimates CO_2 emission rate. EPA: Estimates emission rate in PEI/h. Other methodologies: N/A.	Refer to Table 4.2
3		Precision: Distinguishes between heat and power consumptions.	EIA: N/A. EPA: N/A. Other methodologies: N/A.	Refer to Table 4.2. The amount of reduction in emission rates (PEI/h) from one design to another in each method (within methods) and compared with other methods (between methods).
4		Accuracy: Considering the efficiency of boiler, turbine, incinerator, gasifier etc.	EIA & EPA: Ignored efficiencies in both methods. Other methodologies: N/A.	
5		Profitability: More revenue out of emission reduction.	EIA: Only estimates CO_2 emission rate. EPA: Estimates emission rate in PEI/h. Other methodologies: Case dependent; e.g. in EPI method, only CO_2 emission rate/year.	U\$13/ton CO_2 and U\$55/ton NO_2 etc. (Ball and Kennett, 2012)
6		Data required: Fossil fuel heat value and chemical composition. Also, heat and power consumptions.	EIA: Energy consumption. EPA: Energy consumption and fuel type. Other methods: Case dependent; e.g. company's energy consumption profile.	
7		Application: 1) Gas, Coal, Oil, Biomass, Any waste subject to burning in incinerators. 2) Conceptual design phase.	EIA: Fossil fuels in general. EPA: Gas, Coal and Oil. Other methods: N/A.	
8		Other advantages: Simplicity, user friendly, quantitative, and independent index from process size, based on engineering laws and standards.	EIA & EPA: Simplicity, user friendly, quantitative etc. Other methodologies: Comprehensive, time consuming, detailed data required, N/A for conceptual design phase.	
9	Risk to Process Safety	Based on risk definition: Risk = f (Frequency, Consequences)	Refer to Table 2.3, which lists and compares the most commonly used hazard and risk assessment methods.	
10		Application: Conceptual design phase, inherent safer process design (ISD).		
11		Advantages: Establishes a linear relationship between mass fraction of hazardous chemicals and risk, a strong tool for screening different processes, simple, user friendly, quantitative, and independent from process size, based on engineering laws and standards.		
12		Reliability of databank from EPA source.		
13	Combined Metrics	Applicable to conceptual design phase.	1) Some of methododlogies are limited to a set of companies conditions such as AIChE SI. 2) Others are good for operating businesses with the main focus on customer satisfaction. 3) Almost all of them are comprehensive, need detailed data, are not applicable at conceptual step of a process design.	
14		Applicable in research, product and process designs, operating plant, EIP design.		
15		Needs minimum available data; i.e. streams compositions and conditions.		
16		Based on reliable databanks.		
17		New sustainability indices are coined to process profitability.		
18		Strong screening tool for decision makers, process engineers, regulators.		
19		Helps Life Cycle Assessment (LCA) in many different ways (Table 9.2).		
20		Reduction in capital and hazardous waste management costs, preservation of resources.		
21		Impressive tool for publicity goals		

The application of all of the principal metrics of the new sustainability indices to chemical process design and retrofit is strongly recommended since as it was discussed earlier the ignorance of any of them (or all of them) would result in adverse consequences on making decision (Sec. 6.11 and 7.12). ***This is one of the greatest contributions of the present research in chemical engineering and process design. Other contributions include protection of the environment from the emission of polluting gases, inherently safer process design, reduction of energy consumption and gaining revenue out of such reductions.***

As mentioned earlier in Chapter 3, Life Cycle Assessment (LCA) is a well-known methodology widely used across the globe; however, process design and manufacturing is only part of life cycle of a chemical (Figure 3.1) and also to use LCA we need huge data, which may not be available at conceptual design.
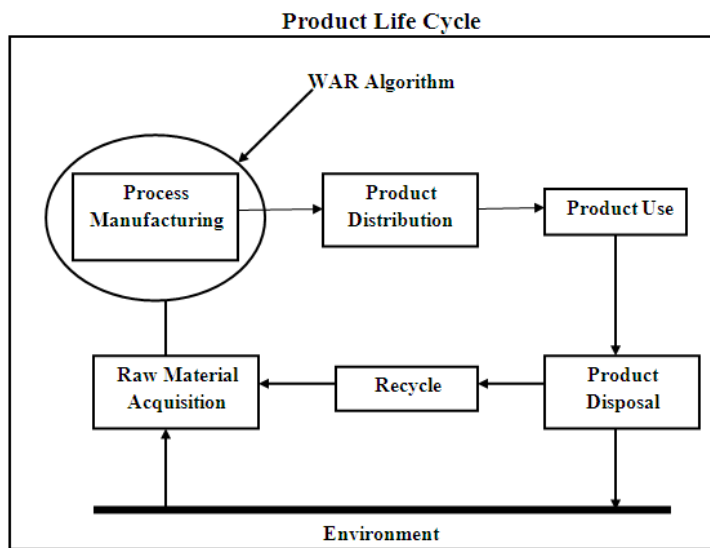

Figure 3.1 The WAR algorithm is concerned only with the processing step of a complete Life Cycle Analysis (LCA), (Young and Cabezas, 1999).

From the above figure, we can explain how it is possible to achieve the LCA goals by employing the "New Sustainability Indices".

In this figure, the "Process Manufacturing" box falls in between "Raw Material Acquisition" and "Product Distribution" boxes. It turns out that there are four possibilities with respect to these boxes, which are summarized in Table 9.2 together with related examples.

The new sustainability indices help process designers evaluate the risks to the process safety and to the environment associated with each input/output streams in different designs in order to find the sustainable processes corresponding to those streams.

Table 9.2 The ways the new sustainable indices are helpful for life cycle assessment (LCA).

Raw Material	Products	Example
Same	Same	Hydrogenation Process

Same	Different	Raw materials: Ethylene & Chlorine
		Products:
		  a. Ethylene DiChloride
		  b. Ethylene Trichloride

Different	Same	Raw materials: a. Ethylene and Chlorine (Direct Chlorination) b. Ethylene and HCl (Oxy-Chlorination) Product: Ethylene DiChloride (EDC)
Different	Different	Gasoline Blends

9.2 FUTURE WORKS

As mentioned above, the present research has several benefits and therefore, there are several potentials to make it always better than before. There are three main areas of improvement:

1. Investor's screening tool: In case of investing on a new chemical or refinery process, my research is very helpful for the people with lack of knowledge about environmental and energy impacts on environment, risks to the process safety and even not about the process itself.

Consider an investing company is willing to establish a new project; for instance, it will receive several proposals through a public tender. Each proposal has minimum data such as overall material and energy balances, flow rates of product (and/or waste) streams and a block flow diagram and of course the total investment cost.

All information will be easily given to new developed software containing new indices and databases and then, the software will calculate the KPI for each proposal vs. costs. Then, the investors (or decision makers) will financially and technically evaluate each design in terms of inherently safest and environmentally friendliest design. As an example, in Chapter 6, different gasoline blends can be named in terms of KPI as:

   a. Isooctane Blend (KPI-SEE):   KPI-I5 (21.8%)-4.2, 10.6, 0

   b. Ethanol Blend (KPI-SEE):   KPI-E5 (25.2%)-16.6, 4.6, 0

   c. Methanol Blend (KPI-SEE):   KPI-M5 (53%)-4.2, 39.8, 0

Where SEE stands for Safety, Environment and Energy, respectively. For example, in case "a" the KPI-I5 is totally 21.8%, 4.2% of which accounts for the ranking of inherent safety design and 10.6% of which exhibits a low ranking of environmentally friendliness of I5 blend.

On the other hand, M5 blend has the highest KPI and the lowest environmental impacts and a moderate inherently safety design. This kind of report will tell us that E5 is safest product with highest potential environmental impacts, while M5 is the environmentally

friendliest product with the same safety risk as of I5. The difference between sum of SEE and total KPI is related to other metrics, in our case octane number, mileage loss etc.

The energy impacts of the product have been initially set to zero during products simulation. It is obvious that the summation of KPIs is 100%. From above figures it can be surprisingly concluded:

$$KPI\text{-}M5 \quad > \quad (KPI\text{-}I5 + KPI\text{-}E5) \quad ; \quad KPI\text{-}M5 + KPI\text{-}I5 + KPI\text{-}E5 = 1.00$$

2. Designer's screening tool: Similar approach is applied to a process designer. At design stage, many brain storming meetings take place in engineering offices, which may or may not be biased. The new indices are highly accurate and unbiased due to its historical and world widely accepted data especially those provided by EPA. Using the new indices a process designer can examine as many design alternatives as he can at any stage of the process design for screening purposes at maximum credibility. In this way, such brain storming meetings will be dramatically minimized.

3. A code based evaluation of different process alternatives, as in other engineering codes such as in piping discipline. KPI 1234 (234, 500, 500); where 234, 500 and 500 are the contribution of energy impacts, environmental impacts and safety risks to the process design, respectively.

The indices can be used by government to penalize plants who has more than a certain level of impacts to the environment.

APPENDIX A

ECONOMIC ANALYSIS

A.1 CAPITAL COST ESTIMATION

Total capital investment equals to fixed capital investment plus working capital (Douglas, 1998):

Total Capital Investment (TCI)=Fixed capital investment (FCI)+Working Capital investment (WC) (A.1)

The Fixed Capital Investment is the sum of design, construction and installation expenditures of a plant and consists of the costs of the plant, auxiliary equipment and buildings; e.g. utility, engineering, construction and contingency. The Working Capital is the extra money for starting up and the operation of the plant until the plant earns revenue and includes raw materials, products and by-products inventory, and cash in hand, receivable account, spare parts etc. (Towler and Sinnot, 2008).

There are several methods for the estimation of capital costs of a chemical process, depending on the stage of a process design and operation. Table A.1 shows several stages of process design and corresponding cost estimations.

In this research, I have used definitive estimation or class 3 when PFDs have been generated and rough equipment sizing has been made. Therefore, the below equation has been used to decide if the new design is economical (Towler and Sinnot, 2008).

$$C_e = a + b\ S^n \tag{A.2}$$

where C_e is the cost of the equipment in U\$. The letters "a, b and n" are parameters which can be found from the relevant tables in reference books (Seider et al., 2003; Towler and Sinnot, 2008). S is the size of equipment and varies from equipment to equipment. For instance, S is the shell mass in kg for pressure vessels, and for heat exchangers, S is heat transfer area in m^2.

Table A.1: Cost estimation methods (adapted from Towler and Sinnot (2008))

TYPE OF ESTIMATE	ACCURACY	REMARKS
Order of Magnitude (Ballpark, Guesstimate, Class 5)	±30% - 50%	Based on similar process costs (historic data is required not design information).
Preliminary (Feasibility, Study, Class 4)	±30%	Based on lack of data from cost and detailed design. PFD is required. (Factored Estimate).
Definitive (Budgeting, Authorization, Class 3)	±10-15%	Based on a rough equipment sizing, large contingency factor. Authorizes the fund to proceed with the design to a more detailed extend.
Detailed (Quotation, Tender, Firm, Class 2)	± 5-10%	Used in project cost control, fixed price contracts estimation. Based on near complete process design, P&ID, quotes for equipment, purchased list, complete DWGs, specifications, site survey.
Check (As-Bid, Class 1)	± 5-10%	Same as detailed estimate + delivery. Based on completed design and procurement of specialized items.

The breakdown of total capital investment and start-up costs has been provided by Douglas (1998), which gives an estimate of the cost of each project activity based on fixed capital investment (FCI). In a sense the FCI is broken down to the following items (Douglas, 1998):

- Direct costs (70-85% of FCI),
- Indirect costs (15-30% of FCI).

Direct costs include onsite costs or Inside of Battery Limit (ISBL) and Offside cost or Outside of Battery Limit (OSBL). Indirect costs include expenditures other than material and labour such as engineering, construction, contingency etc.

The fixed capital investment (FCI) is estimated using Lang factor given the total purchased equipment costs (Towler and Sinnot, 2008):

$$C = F \left(\Sigma \, C_e \right) \tag{A.3}$$

where C is the total capital cost of *ISBL*; $\Sigma \, C_e$ is total cost of shipped equipment; e.g. reactor, tank, pump etc. F is installation (or Lang) factor.

Each of these components consists of several items, which are related to FCI. For instance, the factors for equipment erection, piping instrumentation & control, electrical, civil, structures & buildings are 0.3, 0.8, 0.3, 0.2, 0.3 and 0.2, respectively. Then, C_e for all equipment is estimated using these factors (Towler and Sinnot, 2008).

In the present research, the equations (A.2) and (A.3) have been used for estimation of the equipment costs, fixed capital costs and total capital costs

A.2 PROFITABILITY ANALYSIS

Cost estimation is very important in all business types, especially in process plant design; however, profitability analysis is more important for decision makers in order to address the questions: When the investment will be recovered from the process plant? Is the design profitable? How attractive is that for investors?

Profitability analysis for large projects as well as process improvement and retrofitting is most commonly done by cash flow diagram (CFD). Two distinctive methods are employed for this reason: Cumulative CFD and Discrete CFD.

Following assumptions are made for economic evaluation of projects (Turton et al., 2012):

1. The land is purchased at time zero.

2. The construction will start right after land purchase.

3. The construction duration is from six months to three years depending on project size. In the present research two years suffice from construction phase to start-up.

4. The fixed capital expenditure for equipment bidding, purchase and installation is larger in the first year compared to the second year of construction.

5. The working capital investment will appear right after the end of construction phase when the plant is commissioned.

6. The working capital (salaries, raw material inventories, contingencies, etc.) is considered as onetime payment recoverable when the plant life comes to its end.

7. After the plant is put into operation, the selling of finished products generates revenue.

8. The revenue is usually less at the beginning of production but increases in subsequent years.

9. Due to depreciation effects, the cash flow decreases over the time. Capital depreciation is defined as the difference between the initial investment and scarp value of equipment.

10. A life time for each project is assumed for profitability evaluation; e.g. 10, 12, etc., which is usually different from project working life and from the time of depreciation allowance.

11. It is assumed that the project will be closed down after its life time (item 10). Then, the land and equipment will be sold for salvage/scrap and both fixed as well as working capital costs are recovered (additional cash flow at project closing down time).

Based on the above assumptions, it is now possible to calculate and compare the overall earnings during project life time with initial investment. So, the estimation of time value of money is crucial for estimation of project profitability.

There are three criteria for profitability analysis: time, cash and interest rate. Two methods of the profitability evaluation are non-discounted and discounted techniques; the former is used in process retrofitting and does not consider the time value of money, while the latter should be employed in new large projects (Table A.2). Moreover, for the discounted method yearly cash flows is discounted back to time zero.

Table A.3 Three criteria for each of two methods of profitability assessment.

	Non-Discounted Criteria	Discounted Criteria
Time	Payback period (PBP) = The time duration for fixed capital investment (FCI) recovery after start-up of project.	Discounted payback period (DPBP) = The time duration for fixed capital investment (FCI) recovery after start-up of project with all cash flows discounted back to time zero.
Cash	Cumulative cash position (CCP) = project worth at the end of its life. $$CCR = \frac{\sum All\ Positive\ Cash\ Flows}{\sum All\ Negative\ Cash\ Flows}$$ Process is profitable if CCR > 1	Discounted cumulative cash position, or net present value (NPV) = end of project's cumulative discounted cash position. For projects comparison purposes at different levels present value ratio (PVR) is better criterion: $$PVR = \frac{Pressnt\ value\ of\ All\ Positive\ Cash\ Flows}{Present\ value\ of\ All\ Negative\ Cash\ Flows}$$ At break even situation; PVR =1.
Interest Rate	Rate Of Return On Investment (ROROI) = Non-discounted rate at which there will be earning out of FCI. $$ROROI = \frac{Average\ Annual\ Net\ Profit}{FCI}$$ Average Annual Net Profit over the life of the project after starting-up.	Discounted cash flow rate of return (DCFROR) = the interest rate where all cash flows are discounted to set the project's NPV=0, thus, DCFROR is the highest after-tax interest rate (discount rate) where the project can break down. Note1: When comparing alternative investments, the higher the DCFROR, the more attractive the project. But the highest DCFROR is not recommended. However, in case of mutually exclusive investment comparison, pick the project with highest NPV.

APPENDIX B

The study of the environmental impact categorization was first made by three research groups called CML (Centre of Environmental Science), TNO (Netherlands Organization for Applied Scientific Research) and B&G (Fuel and Raw Materials Bureau) and the result was issued by Heijungs et al. (1992). This classification was improved to use in process design. The WAR algorithm theory employs eight environmental impact categories for the assessment of PEI indices (Young et al., 2000), which are classified into two areas of concerns:

B.1 Global atmospheric impact categories:

Below is the list of four corresponding categories:

B.1.1 Global warming potential (GWP):

CO_2 in the atmosphere has two different performances with respect to the light wavelength coming to the earth from the sun. It is fairly transparent to short wavelength UV and let it go to the earth surface and warm it up. However, it absorbs the long wavelength coming out from the earth surface by radiation and then emits it, meaning that it limits heat loss from the earth. Although global warming effect is known as the immediate outcome of CO_2 emissions to the atmosphere, the emission of other gases such as methane, nitrous oxide (N_2O) and CFCs have also similar influence (Davis and Masten, 2004b). These gases are also referred

to as "greenhouse gases". N_2O and CH_4 contents in emission gases are reported to be as little as 0.86% on CO_2 equivalent basis in the USA (EPA, 2011).
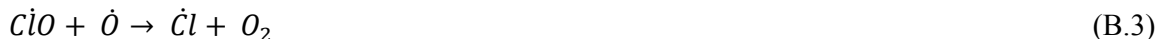
CO_2 is produced by combustion of fossil fuels such as natural gas, oil, coal etc. These fuels are mainly used in large amounts by different sectors of industries all around the world such as power plants, oil and gas companies, mining industries, chemical and other industrial plants, cars and other vehicles, ships and vessels, aircrafts, and also by civilians; e.g. for heating their house.

The comparison of the extent of a unit mass of a chemical, which absorbs infrared (IR) rays, during its atmospheric life time to the extent of a unit mass of CO_2, which absorbs IR too, over its relevant lifetime, determines the GWP value. The half-life of the chemicals was factored into calculations for GWP determination; however, as the GWP of chemicals with different half-lives in atmosphere changes over the time length the comparison is made, the time base was chosen to be 100 years (Young and Cabezas, 1999) for this database.

B.1.2 Ozone depletion potential (ODP):

Ozone makes it possible for living creatures to live on the earth. Therefore without it, the temperature of the earth would be high enough to burn almost everything on the earth and ruin the life. The small UV radiation to the earth causes summer season while too much exposure to this small rays causes skin cancer. It is reported that a 5% depletion in ozone layer leads to a 10% increase in skin cancer (Davis and Masten, 2004b).

Thus, the function of ozone is to absorb the UV radiation coming from sun light. However, some chemicals can violate its function. CFCs in general have detrimental effects on ozone layer by the following chemical chain reactions, which take place in atmosphere (Davis and Masten, 2004b):

$$CCl_3F + h\gamma \rightarrow C\dot{C}l_2F + \dot{C}l \qquad \text{(B.1)}$$

$$\dot{C}l + O_3 \rightarrow C\dot{l}O + O_2 \qquad \text{(B.2)}$$

$$C\dot{l}O + \dot{O} \rightarrow \dot{C}l + O_2 \qquad \text{(B.3)}$$

This is a chain reaction in that $\dot{C}l$ attacks O_3 as in chemical reaction (2) and consumes it continuously.

The comparison of the reaction rate of a unit mass of a chemical and ozone to produce oxygen molecule to a unit mass of CFC-11 and ozone to produce oxygen molecule determines the value of ODP (Young and Cabezas, 1999).

B.1.3 Acidification potential (AP):

Acidification potential influences directly on the air quality through gas emissions. Emissions such as CO_2, SO_2, NO_x, Volatile Organic Compounds (VOCs), etc. to the atmosphere are converted to acidic compounds thru chemical reactions (Davis and Masten, 2004b) and increase the acidity of rain or decreases the PH of the rain (called acid rain or acid deposition) and in turns the acid deposition has adverse effects on lakes, forests, fishes, agriculture etc.

PH is an indicator of the acidity of a liquid such as water. PH of pure water is 7.0; however, natural and unpolluted rain is fairly acidic, about 5.6, since CO_2 produced from ecosystem goes to the air and is dissolved in rain to produce carbonic acid. Therefore, PH is used for the measurement of the acidity of rain.

Acid rain refers to a mixed dry and wet deposition from the air containing nitric and sulfuric acid. In the USA 2/3 of SO_2 and ¼ of NO_x are generated in power plants due to combustion of fossil fuels (EPA, 2010a). All of these compounds in the air affect on the PH of the rain. In 2000, the average PH amount in the USA was around 4.3 (EPA, 2010b).

B.1.4 Photochemical oxidation (or smog formation) potential (PCOP):

During the Second World War, a new type of pollution was found which caused eye and skin irritation as well as plant damage. Further investigation addressed a new source of pollutants; i.e. internal combustion engine (Schnelle and Brown, 2002a). It also causes smog production, which reduces visibility and this is why it is called either photochemical oxidation or smog formation. This effect is visible in the upper layer of atmosphere where brown mist or smog appears. The following compounds react to produce smog:

NO_x, SO_2, VOCs, peroxyacetyl nitrate (PAN) and peroxybenzoyl nitrate (PBN).

NO and NO_2 are primary pollutants among other nitrogen oxides with respect to smog production. In fact NO is converted to NO_2 , which contributes in smog formation and gives colour to smog as it does to flue gas coming out of stacks. NO_x and VOCs take part in complex photochemical reactions in the presence of sunlight, which result in smog production. The smog contains ozone, NO_2, PAN, PBN and other oxidizing agents in trace quantities (Schnelle and Brown, 2002b).

The comparison of the reaction rate of a unit mass of a chemical and a hydroxyl radical $\dot{O}H$ to a unit mass of ethylene and a hydroxyl radical $\dot{O}H$ determines the value of smog formation potential or PCOP (Young and Cabezas, 1999).

The effects of smog formation or photochemical oxidation include reduction of plant growth and damage to leaf tissue. The unit of the relevant impacts to the environment is in ppb ozone (by volume) produced by the substances released into the atmosphere.

B.2 Local toxicological impacts categories:

Below is the list of four corresponding categories:

B.2.1 Human toxicity potential by ingestion (HTPI):

HTPI is concerned with a chemical within a liquid or solid phase at $0^{o}C$ and atmospheric pressure with an exposure potential, while HTPE is concerned with a chemical in gas phase at the same conditions as mentioned above (Young and Cabezas, 1999). Ingestion and inhalation (or dermal) exposure are considered all of the main routes of a chemical exposure with respect to human; therefore, both HTPI and HTPE categories are used for toxicity evaluation.

The human toxicity potential (HTP) is a calculated index, which exhibits the potential impact of a unit of chemical released into the environment. There are two types of experiments for HTP; LD_{50} and OSHA for HTPI and HTPE, respectively. In order to protect the employees from exposure to hazardous materials, OSHA (Occupational Safety & Health Administration) put Permissible Exposure Limits (PELs) into effect. They are thresholds of substances in the air and based on an 8-hour time weighted average (TWA) exposure. PELs standards vary depending on general industry, shipyard employment, and the construction industry (US Department of Labor, 2012).

So, HTP is based on both the toxicity of a compound and its potential dose, which is used to weight emissions recorded as part of a life-cycle assessment (LCA) or in the toxics release inventory (TRI) and to aggregate emissions in terms of a reference compound. Total emissions can be evaluated in terms of benzene equivalence (carcinogens) and toluene equivalents (noncarcinogens). The potential dose is calculated using a generic fate and exposure model, which determines the distribution of a chemical in a model environment and accounts for a number of exposure routes such as inhalation, ingestion of products, fish, and meat, and dermal contact with water and soil.

B.2.2 Human toxicity potential by exposure (HTPE):

See Section 2.4.2.1.

B.2.3 Terrestrial toxicity potential (TTP):

The measurement of a contaminant concentration does not itself represent its potential impacts on the environment. However, by toxicity test, one can determine whether or not the concentration of toxic agent at a level to have adverse effects on organisms present in site's media. When a contaminant is bioavailable in an ecosystem, it will have toxic influence on the environment. Bioavailable means that a material has a shape and conditions that life form can start (EPA, 1994). Thus, in order to estimate the contamination impacts on the organisms' performance such as growth, they are subjected to a toxic medium; e.g. soil, water etc., known as toxicity tests. They determine lethal and sublethal influences on the organisms, known as measurement endpoints. There are a wide range of toxicity tests; however, two fundamental tests are carried out to measure the effects of exposure on the organisms: "acute" and "chronic" tests, which are short-term tests at high toxic concentration and long-term tests at low toxic concentration, respectively.

An acute toxicity test exposes organisms to a series of samples site's medium at different concentrations and over a period of time; i.e. 24 to 96. The results are in terms of the concentration of the medium at which half of the organisms died, represented by LC_{50}. Alternatively,

Terrestrial toxicity concerns with potential impacts of a chemical, which have adverse effects on aquatic organisms living on land with respect to their life-cycle, no matter entirely or predominantly.

B.2.4 Aquatic toxicity potential (ATP):

Aquatic toxicity concerns with potential impacts of a chemical, which have adverse effects on aquatic organisms living in water with respect to their life-cycle, no matter entirely or predominantly.

Some researchers consider both safety risks evaluation and environmental impact assessment (EIA) as a tool for the evaluation of the friendliness of a process to the environment, plant equipment and workers. Regardless of the similarity of "environmental protection" and "safety improvement" in terms of the preventing the hazardous chemicals to be released to the environment, there are considerable differences between them.

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