INCORPORATION OF INHERENT SAFETY AND ENVIRONMENTAL ASPECTS IN PROCESS DESIGN AND SUPPLY CHAIN OPTIMIZATION

A Thesis

by

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ABSTRACT

The integration of inherently safer design and environmental aspects at the early phases of supply chain selection and process design provides significant benefits. It allows the highest ability to positively influence lifecycle safety, environmental impact, and cost of the project. Because of the preliminary nature of conceptual process design, it is crucial to have a simple yet effective approach to evaluate and compare the design alternatives based on the safety and environmental aspects at the early stage of the project when available engineering information and data are limited. This work proposes a framework to incorporating life-cycle safety measures in the supply chain design and the process technologies included in the supply chain.

A hierarchical approach is developed for conceptual-phase engineering project to facilitate the inclusion of safety objectives in the process synthesis and supply chain design engineering work in a consistent manner. Design options are first generated and screened based on economic criteria. Next, safety metrics are used in addition to economic objectives to evaluate the various designs and transportation options. Findings from the hazard and risk assessment are used to generate design alternatives to improve the safety performance. Economic evaluation is updated for acceptable options to guide the decision making.

To demonstrate the approach, a case study is solved for a conceptual design of a high density polyethylene (HDPE) supply chain from shale gas. Various conceptual design options that considered different elements such as process technology, manufacturing

network and capacity were screened and evaluated per proposed framework. A high-level quantitative risk assessment approach was used for assessing the safety aspects of the design options.

DEDICATION

To my parents, my wife, and my children

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NOMENCLATURE

ANP	annual net after-tax profit
AR	total annual revenue
BLEVE	boiling liquid expanding vapor explosion
CEI	chemical exposure index
CEPCI	chemical engineering plant cost index
CISI	comprehensive inherent safety index
CSTR	continuous stirred tank reactor
D	the distance between source port and receiving port
DC	total annual depreciation cost
DME	dimethyl ether
EF	shipping tanker emission factor
EHS	environmental health safety index
EISI	enhanced inherent safety index
F_i	explosion frequency of the process unit i
FBR	fluid bed reactor
FC	shipping vessel fuel consumption factor
FCI	fixed capital investment
FEED	front end engineering design
F&EI	fire & explosion index
F,E&T	fire, explosion and toxicity index

GHG	greenhouse gas
HAZID	hazard identification study
HAZOP	hazard and operability study
HI	hazard index
HDPE	high density polyethylene
HYSYS	hyprotech systems process modeling software by AspenTech
I2SI	integrated inherent safety index
INSET	inherent safety health environment evaluation tool
IRA	inherent risk assessment
ISD	inherently safer design
ISI	inherent safety index
ISIM	inherent safety index module
ISRisk	inherent safety risk for alternative design
$ISBL_i$	the inside battery limits investment of process i
ISPI	inherent safety potential index
IST	inherently safer technology
KPIs	key performance indicators
L_1	manufacturing location 1
L_k	manufacturing location k
LCA	life cycle assessment
LDPE	low-density polyethylene
LLDPE	linear low-density polyethylene

LNG	liquefied natural gas
LOC	loss of containment
M	set of materials
MTO	methanol to olefins
MTP	methanol to propylene
OC	total annual operating cost
$OSBL_i$	the outside battery limits investment of process i
P_{1i}	unit process 1 of process i
P_{2i}	unit process 2 of process i
P_{ni}	unit process n of process i
P_{xi}	unit process x of process i
P_{1j}	unit process 1 of process j
P_{2j}	unit process 2 of process j
P_{mj}	unit process m of process j
P_{yj}	unit process y of process j
P&ID	piping and instrumentation diagram
PE	polyethylene
PI	potential hazard index
PIIS	prototype index for inherent safety
Pre-FEED	pre-front end engineering design
PRI	process route index
PSD	Prevention of Significant Deterioration permitting program

QRA	quantitative risk analysis
RISI	risk-based inherent safety index
$R_{x,y}$	maximum individual risk at specific location x,y of a manufacturing plant
RiskBD	risk for base design
ROI	return of investment
SC	supply chain
SM	the shipping amount of natural gas (in cubic feet) or methanol (in tonnes) shipped between plants
SWeHI	safety weighted hazard index
TCI	total capital investment
UHI	unit inherent hazard index
UPI	unit potential hazard index
$V_{x,y,i}$	Occupant vulnerability at point x,y by the explosion event of the process unit i.
WCI	working capital investment
$T_{x,y}$	Fractional time of attendance at the point x,y; calculated as hours per week/168 hours.
TC	shipping tanker capacity
TR	corporate tax rate

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CHAPTER I

INTRODUCTION

Inherent Safety, also known as Inherently Safer Design, ISD, or Inherently Safer Technology, IST, is a philosophy, a different way of thinking toward safety that is applied to the design and operation of a chemical process. (Hendershot 2006) It is considered the first-order strategy in process risk management. Other strategies of process risk management include passive, active and procedural. (CCPS 2010) Unlike those strategies that accept the hazards and try to control them, the ISD concept is based on avoiding or reducing the hazards associated to the process due to material properties, equipment failures, human error and operational conditions; thus reducing the consequences of the incidents. Similarly, environment friendly design is based on preventing the pollution from the processes.

There are four principles to apply ISD:

- Minimization. Application of this principle is such as using smaller quantities of hazardous substances.
- Substitution. This principle looks for replacing a material with a less hazardous one.
- Moderation. Examples are using less hazardous forms of a material or utilizing process alternatives that operate at less hazardous conditions.
- Simplification. This strategy aims to eliminate unnecessary complexity. (CCPS 2010)

These four strategies help designers identify ISD alternatives. However, a technology cannot be claimed as safer simply by comparing it to other alternatives. In some cases a technological alternative is less safe with respect to certain hazards while proving superior and safer in other aspects. The ultimate decision must be based on the process conditions that apply to each specific design. These conditions can include several elements such as the raw materials used, chemical reaction path, transportation methods and storage arrangements. Therefore the alternative design assessment shall consider all aspects for an accurate and reliable result.

The ISD concept can apply to all stages in a chemical supply chain lifecycle. Applying inherently safer design in the conceptual phase brings with it many significant benefits. (Maher et al. 2012) The most important of which is being the reduction of serious and minor incidents, as well as saving money in the process. Additionally, implementing safer design in the conceptual stage avoids the engineering rework and modifications at later phases. However it is sometimes difficult to analyze the benefits early on in the design due to a lack of available information. Figure I-1 and I-2 illustrate the ability to influence safety, project accumulated cost, level of engineering information detail and the cost accuracy per project phase. The raw material and the chemical route are key factors in creating safer designs. It is crucial to have a simple but effective approach to evaluate and compare the design alternatives based on the overall lifecycle safety and environmental design aspects at the early stage of the project when available data are limited.

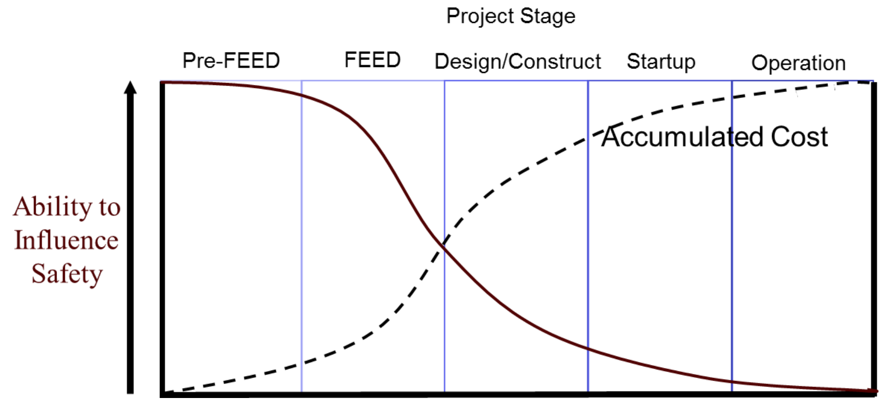

Figure I-1 - Ability to influence safety and cost curve by project phases. Adapted from (Kletz and Amyotte 2010)

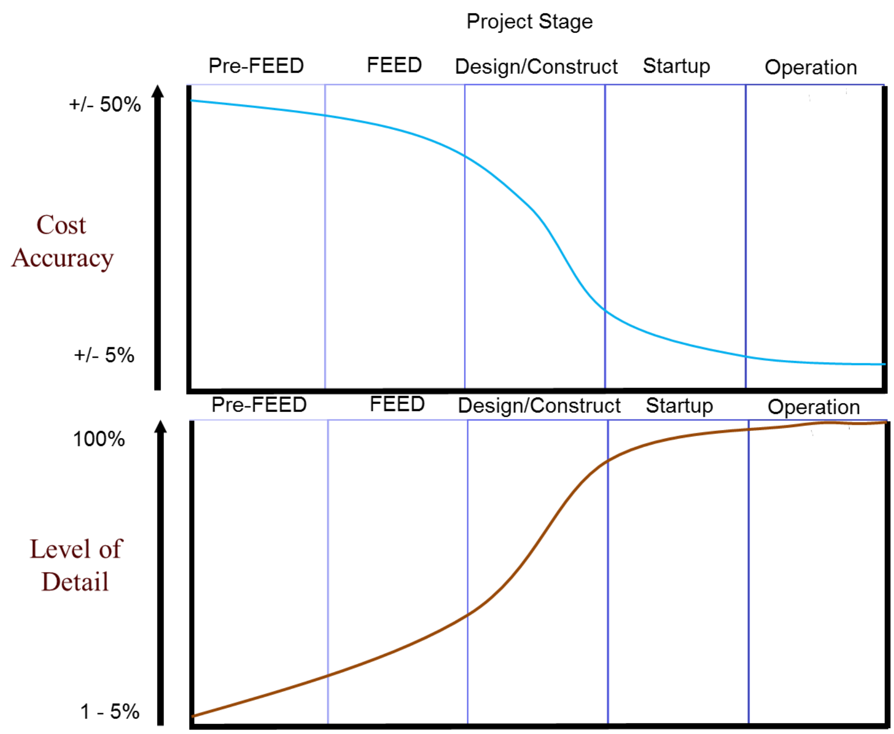

Figure I-2 - Information accuracy and level of detail by project phases.

The main objective of this study is to establish a systematic approach to integrate safety measures to the process and supply chain design in addition to traditional objectives (e.g. economic, environmental) that are used in the early phase of a project. A framework is developed in order to enable process engineering to “do right thing right the first time” by:

- Identifying affordable process technologies and supply chain options that meet business needs. This includes life cycle cost and financial analysis to choose design options.
- Screening and assessing process technology options in term of safety and environment and providing basis for decision making.
- Enabling the project to meet corporate goals on safety and sustainability.

To illustrate the developed framework, a case study is solved for a conceptual design of a high density polyethylene (HDPE) supply chain from shale gas.

CHAPTER II

LITERATURE REVIEWS

Inherent Safety Indices

The ISD concept was first introduced publicly by Dr. Travor Kletz after a catastrophic accident happened in Flixborough, a chemical plant in England in 1974. (Kletz 1978) Since that time, the concept of ISD has been widely studied by industry. There have been relentless efforts from both academic and industrial sectors to develop safety metrics for use in ISD evaluation. Some of them have been applied for years in industries, such as Dow Fire & Explosion Index (F&EI), (AIChE 1994b) Dow Chemical Exposure Index, (AIChE 1994a) Mond Index. (Tyler 1985) Those indices were developed by companies in industry initially for use internally. Later they were adopted by American Institute of Chemical Engineers and published for wider application. Others were developed and proposed from academic fields, such as Prototype Index for Inherent Safety (PIIS), (Edwards and Lawrence 1993) Inherent Safety Index (ISI), (Heikkilä 1999) Expert System for Inherently Safer Process (i-Safe), (Palaniappan et al. 2002a; Palaniappan et al. 2002b) Safety Weighted Hazard Index (SWeHI), (Khan et al. 2001) Integrated Inherent Safety Index (I2SI), (Khan and Amyotte 2005) Fuzzy based Inherent Safety Index, (Gentile et al. 2003) Environmental Health Safety Index (EHS a.k.a SHE), (Koller et al. 2000) Key Performance Indicators (KPIs), (Tugnoli et al. 2007) and much more.

Overall, these metrics were developed for assessing the ISD of a single technology, single plant process or comparing safety of multiple processes/technologies. They employed different approaches such as hazard indices (i.e. fire, explosion and/or toxic hazards) with expert judgment; consequence-based indexes; modeling and simulation. Some indices were proposed to use during process chemical route/process flow sheet development phase and other indexes require intensive data which is only available at the end of detailed engineering design. Table II-1 below summarizes some of the data required in order to do the calculations of some quantitative indexes for ISD assessments. From the table, required data varies from one approach to another. Variations range from a few simple things such as chemical properties, reactions and interactions in the processes, and key operating conditions to more complex changes like complete engineering information (P&ID, layout, equipment design), process information (flow sheet, chemical properties, reactions, material balances) and operation parameters (temperature, pressure, inventory…).

Indices vs. Required Data	Chemical and their properties	Reactions and interactions	Operative conditions	Process Flow Diagram	Equipment inventory	Materials balances	P&ID	Layout definition	Equipment design data	Toxicity	Storage
Dow F&EI (AIChE 1994b)	√	√	√	√	√	√	√	√	√	√	√
Mond Index (Tyler 1985)	√	√	√	√	√	√	√	√	√	√	
Dow CEI (AIChE 1994a)	√		√	√	√	√			√	√	
PIIS (Edwards and Lawrence 1993)	√	√	√								
ISI (Heikkilä 1999)	√	√	√	√	√					√	√
SWeHI (Khan et al. 2001)	√	√	√	√	√	√	√	√			
I2SI (Khan and Amyotte 2004)	√	√	√	√	√	√	√	√		√	
ESH (Koller et al. 2000)	√	√	√	√	√						
KPI (Tugnoli et al. 2007)	√	√	√	√	√	√					
Fuzzy-ISI (Gentile et al. 2003)	√	√	√	√	√		√				
Isafe (Palaniappan et al. 2002a)-(Palaniappan et al. 2002b)	√	√	√	√	√					√	
PRI (Leong and Shariff 2009)	√	√	√	√	√						√
CISI (Gangadharan et al. 2013)	√	√	√	√	√					√	√

Table II-1 – Required data for some ISD metric calculation

Dow Fire and Explosion Hazards Index

A typical complex hazard index was Dow Fire and Explosion Hazards Index. It was applied to quantify the magnitude of potential fires and explosions associated with specific equipment or unit processes in a facility. In order to compute Dow F&EI, the whole process is conceptually divided into separate process units. (AIChE 1994b) The F&EI is the product of a process unit hazard factor (F3) and material factor (MF). The material factor MF of a specific process unit takes into account the most hazardous chemical in the process unit. The MF is obtained from the flammability and reactivity of the substance rating by NFPA. A list of MFs for a number of chemical compounds and materials were also provided in the Dow F&EI guidebook. (AIChE 1994b)

The process unit hazard factor (F3) is the product of the general process hazard factor (F1) and the special process hazard factor (F2). F1 is the sum of all penalties applied to different factors associated with the process: exothermic reactions, endothermic reactions, material handling and transfer, enclosed process units, limited access, drainage of materials, etc. F2 is also the sum of all penalties for toxic materials: operation at vacuum, operation in or near the flammable limits, dust explosion risks, higher pressure than atmospheric pressure, low temperature, quantity of flammable material, corrosion and erosion, leakage around joints and packing, use of fired heaters, hot oil heat exchange systems, large rotating equipment, and more.

Supplementing to Dow F&EI is the Dow Chemical Exposure Index (CEI) which provides rating for potential health hazards associated with possible chemical release incidents. (AIChE 1994a)

One limitation of these indices is that they are only addressing certain hazards, not considering the full range of hazards. (CCPS 2010) Other limitation is the requirement of extensive engineering information and process data in order to compute. It is best used at the end of the design phase of a project when detailed engineering information is available. Other application is to survey the existing plants for hazards identification and safety improvements.

Academia Proposed Inherent Safety Indices

Several inherent safety indices have been developed by researchers around the world in attempt to quantify the inherent safety aspects at early phase of projects. The methods used for indices vary in term of goal, structure, required data and computation technique. Comprehensive reviews and comparative studies on some of these indices can be found in literatures. (Khan et al. 2003; Koller et al. 2001; Rahman et al. 2005; Srinivasan and Natarajan 2012)

The first published index by Edwards and Lawrence proposed an inherent safety index called Prototype Index for Inherent Safety (PIIS). (Edwards and Lawrence 1993) This index was intended for analyzing the choice of a process route, the raw materials used and the sequence of the reaction steps. The PIIS of a process route is calculated by aggregating a Chemical Score and a Process Score. The Chemical Score takes into account inventory, flammability, explosiveness and toxicity, and the Process Score considers temperature, pressure and yield. These factors are scored on a numeric scale corresponding to the ranges of values of the parameter. The route with highest numerical score is considered the least safe route.

Heikkila has extended the PIIS by adding more parameters into the assessment and suggested the Inherent Safety Index (ISI). (Heikkilä 1999) The ISI consists of two indices, a chemical inherent safety index and a process inherent safety index. The chemical inherent safety index has two sub-index groups: one for reaction hazards covering main reaction, side reactions and chemical interaction; the other group for hazardous substances including flammability, explosiveness, toxicity and corrosivity. The process inherent safety index also consists of two sub-indices, one for process conditions (inventory, process temperature and pressure) and the other for the process system (equipment safety and safe process structure). The scoring of the parameters in this method is also based on existing indices such as the Mond Index for toxic exposure and the Dow F&EI for the pressure. Worst case situation basis is assumed for the calculations of the ISI. Similar to the PIIS, a low index value represents an inherently safer process.

Koller and Co-workers have broadened the scope of the assessment with the EHS index that covers environment, health and safety. (Koller et al. 2000) The EHS index is design to apply for the specialty chemical process such as pharmaceuticals, argo and fine chemicals. The safety aspects include mobility, fire and explosion, acute toxicity, reaction and decomposition (the probability for undesired reaction or decomposition and evaluating the probable energy potential). In term of health, two elements were evaluated: irritation and chronic toxicity. For environmental aspects, five areas were analyzed: water-mediated effects, air-mediated effects, solid waste, degradation (persistence of organic substances) and dangerous property accumulation. A flexible approach is used for calculation of individual index value based on availability of information. In case data is not available either from databases or estimation, the index value could be calculated using an error value at the worst case principle.

There were some expansions and improved indices over the PIIS and ISI suggested by other researchers such as isafe, (Palaniappan et al. 2002a; Palaniappan et al. 2002b) process route index (PRI), (Leong and Shariff 2009) enhanced inherent safety index (EISI), (Li et al. 2011) comprehensive inherent safety index (CISI). (Gangadharan et al. 2013) In general these index based approaches are based on subjective scaling and weighting, with limited coverage and often unclear granularity. (Srinivasan and Natarajan 2012)

Khan and Amyotte proposed a structured guideword based approach called integrated inherent safety index (I2SI). (Khan and Amyotte 2004; Khan and Amyotte 2005) The I2SI is composed of two main sub-indices: hazard index (HI) and inherent safety potential index (ISPI). The HI measures the damage potential of the process, taking into account the hazard control measures. The process damage potential is assessed in four areas: fire and explosion, acute toxicity, chronic toxicity, and environmental damage. The hazard control measures are quantified subjectively on a scale from 1 to 10 based on process safety expert's experiences. The ISPI addresses the applicability of inherent safety principles to the process, also measured on subjective scaling basis. The I2SI is the combination of ISPI and HI. Inherent safety cost indices were introduced in order to evaluate the economic potential of the option. A conceptual framework was suggested to provide a procedure for calculation of HI and ISPI of process units and cost indices.

Tugnoli et al. used different approach in their recommended Inherent safety key performance indicators (IS KPIs). (Tugnoli et al. 2007; Tugnoli et al. 2012) The IS KPIs is based on the estimated consequences of potential loss of containment (LOC) events associated to equipment and processes. In KPIs, the safety performance of process units are measured by two indices: unit potential hazard index (UPI) and unit inherent hazard index (UHI). The UPI measures the maximum impact area of the worst case scenario while UHI captures the maximum damage area of likely safety scenarios, which takes into account the credibility factors of the equipment in term of safety. The potential hazard index (PI) and inherent hazard index (HI) of a process are the sum of all UPIs and UHIs of all units in the process respectively. Both PI and HI are used to compare the inherent safety of process options; with lower values of PI and HI indicating an inherently safer process.

Although many approaches have been proposed, the methodologies for incorporating ISD into technical, economic, safety and security design considerations are not yet in place.

Quantitative Risk Analysis

The quantitative risk analysis (QRA) is a probabilistic methodology used in industries around the world to quantify overall risk and analyze potential risk reduction strategies. It was considered the best available analytic predictive tool to assess the risks of complex processes, storage facilities, and hazardous material transport systems to contribute to process safety. (Pasman and Reniers 2014) It was recognized as one of useful tool and input in risk-informed decision making process. Many countries and territories require QRA for licensing/permit purposes and provide risk criteria for facilities processing, storage, handling and transportation of hazardous materials. (CCPS 2009)

QRA can be used from the beginning of a project and throughout the life cycle of a facility. (Crowl 2011) Depending on the availability of information for use in the QRA, the depth of study might vary.

There are five major steps to perform a QRA study, including:

1. Defining the potential event consequences and potential incidents.
2. Evaluate the incident consequences. Typical tools such as vapor dispersion modeling and fire and explosion effect modeling can be used.
3. Estimate the potential incident frequencies using fault trees and event trees.
4. Estimate the incident impacts on people, environment and property.
5. Estimate the risk by combining the potential consequence for each event with the event frequency, and summing over all events. (CCPS 2000)

A QRA study requires a major investment of time and effort, especially for a comprehensive study involving the estimation of the frequency and consequences of a range of hazard scenarios and of individual and societal risk. (Mannan and Lees 2005) On the other hand, the uncertainty of the estimated risk could cause argument on the reliability of the result.

Application of QRA in ISD assessment is one of research directions pursued by many academic researchers. Shariff and Leong adopted QRA principles in their proposed inherent risk assessment (IRA) approach by using a risk assessment tool integrated with process design simulator (HYSYS). (Shariff and Leong 2009) Process design data from HYSYS will be used to calculate the probability and the consequences relating to possible risk. The tool is recommended to use at design phase.

Rathnayaka, Khan and Amyotte recently suggested a risk-based inherent safety index (RISI), which is an extension of the I2SI developed earlier. (Rathnayaka et al. 2014) Unlike I2SI which focused on hazard reduction, the authors included estimated occurrence probability in RISI calculation. The index is measured by two risk estimations: risk for base design (RiskBD) and inherent safety risk for alternative design (ISRisk). The RiskDB is estimated based potential damage of major incident hazards in the process, taking into account the probability of occurrence and the risk control measures. Similar to hazard control measures in I2SI, the risk control measures is quantified subjectively based on ten elements with scaling from 1 to 10 for each element. The ISRisk is computed similar to RiskBD with the inclusion of inherent safety applicability factors, which the authors called applicability indices. Two applicability indices were considered: one index accounts for the magnitude of IS principles application to reduce hazard; the other index for the level of applicability of ISD principles to reduce the occurrence probability of accident scenarios. Both indices are subjectively scored on a one-to-ten scale basis. Finally RISI is calculated as ratio between ISRisk and RiskBD. Alternative design with lower RISI is considered inherently safer.

As ISD strategies can help reduce hazards, consequence and probability of the incident, QRA based approaches for ISD are quite promising for assessing and comparison of alternative designs.

Supply Chain Design

Supply network design in the process industry involves some key challenges. Certain strategic configuration decisions need to be made in the early phases of the project such as where to locate the new facilities or how to upgrade or expand of an existing facility; how to assign sources of materials to each manufacturing facility; what are the optimal size and scale of the manufacturing network, and which customer/market region should each manufacturing facility/warehouse distribution serve …(Shah 2005) In addition, the current strong industrial focus on sustainability is broadening the basis for these strategic decisions to include environmental and social aspects in addition to cost.

The inclusion of multiple aspects as design objectives has been considered by various studies on sustainable supply chains. Hugo and Pitstikopoulos developed a methodology to include environmental impact criteria with the traditional economic criteria for deciding location and capacity expansion of facilities, and transportation issues in supply chain design and planning. The proposed multi-objective mixed-integer model aims to maximize profit and minimize the environmental impact of the supply chain using LCA criteria, while satisfying the market demand for products. (Hugo and Pistikopoulos 2005)

El-Halwagi et al. (2013) introduced an approach to include safety criteria into the decision-making process for selection, location, and sizing of a biorefinery supply chain in addition to the techno-economic objectives. Life cycle cumulative risk was considered, covering storage and transportation, process conversion into biofuels or bioproducts, and product storage. (El-Halwagi et al. 2013)

CHAPTER III

A FRAMEWORK FOR SAFETY INTEGRATION IN CONCEPTUAL PROCESS DESIGN

Problem Statement

Consider a conceptual-phase engineering project with the objective of synthesizing and screening flow sheet configurations in a supply chain for the conversion of certain raw materials to certain products and a desired production capacity. The process synthesis and initial conceptual design activities include the generation of design alternatives and the preliminary screening ahead of detailed analysis. In addition to the technical, economic, and environmental criteria used in screening the alternatives, the purpose of this work is to introduce safety considerations early enough in process synthesis and conceptual design. The typical safety analysis follows the initial generation and selection of alternatives and requires relatively extensive data. The objective of this research is to develop a hierarchical approach to the inclusion of safety objectives in process synthesis and conceptual design in a consistent manner to how process engineering work is carried out and using the data that are typically available early enough in design.

Framework

The main objective of the conceptual phase is to define “the best approach” to do the project to meet the business need. Process engineering plays an active role in studying a number of options and determining the viable processes and SC proposal to move forward.

While there are many activities and deliverables which result from the conceptual phase, the proposed work process focuses on five major blocks of activities that process engineering should carry out in conceptual phase, including:

- Initiate process design study.
- Develop options
- Evaluate options
- Refine options
- Summarize and recommend

Figure III-1 illustrates this sequence of activities in graphic form and provides key focuses of each block. Figure III-2 is a systematic approach to integrating safety and environmental objectives in conceptual design. In this framework, design options are first financially evaluated and screened versus economic acceptant criteria. Next, process engineers shall perform hazard and risk evaluation covering safety, health, transportation and environment for those options that pass the initial economic check. Overall risk assessment result will be compiled for each options, then compared with the risk acceptance criteria. The result will also be used to identify and generate design alternatives to improve the safety and environment performances. Cost estimate and economics evaluation will be updated for acceptable options for decision making.

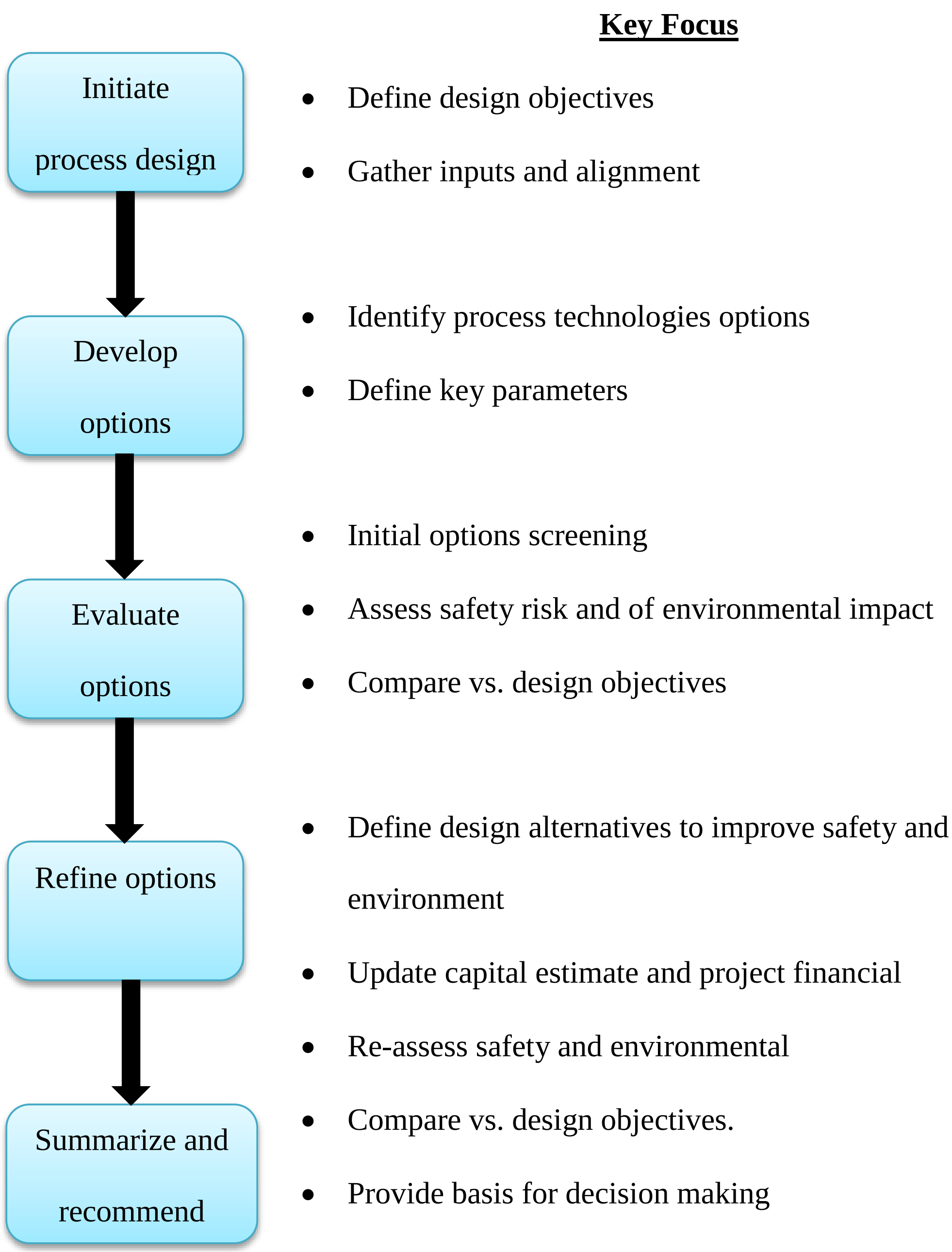

Figure III-1 – Process synthesis and conceptual design block diagram

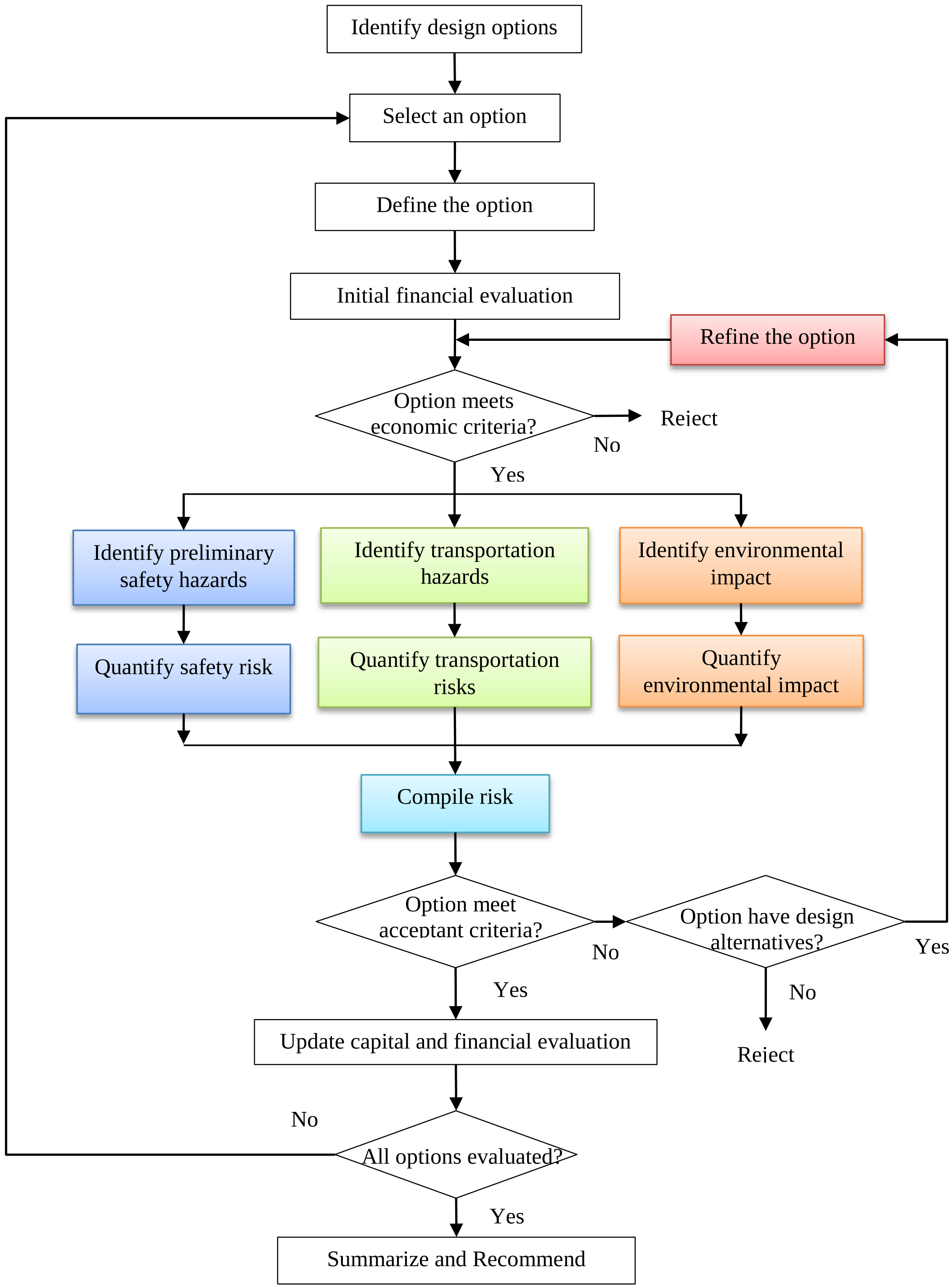

Figure III-2 – Process synthesis and conceptual design framework

Methodology

Process Design Study Initiation

The process engineering initiates the process design work by obtaining following information and inputs:

- Process design objectives.
- Available feedstock sources, characteristics, location and delivery approach (i.e. by pipeline, tank truck, railroad…).
- Corporate's vision, goal, policy and standards on safety and environment; current status and gaps as well as expectations for the project. These inputs are basis for setting up the safety and environment risk acceptant criteria.
- Company's requirement and guidelines on project financial aspect to establish project's economics acceptant criteria.
- Applicable law and regulation as well as company design codes and standards.

Acceptant criteria shall be clearly defined, reviewed and agreed (with senior management) in advance before design can begin.

Option Development

The main focus of this step is generating process design options (process synthesis). Many process synthesis techniques are available in literature and can be utilized, for example Sustainable Design through Process Integration by El-Halwagi. (El-Halwagi 2012)

There are some factors that impact the process synthesis and supply chain design. Generating applicable process design options should consider choices of feedstock, chemical routes and technologies. Other considerations are supply aspects such as size and scale of the process; single manufacturing site versus multiple smaller-capacity sites; consolidated supply chain or dispersed supply chain; size and means of transportation of materials, intermediates and finished products. For example, intermediate products can be produced in one geographic location then shipped to another manufacturing location to process for final products.

Manufacturing location is also an important dimension in generation of supply network design options. There are various factors impacting manufacturing location selection, including the following:

- Availability of materials
- Availability of skilled labors and resource
- Infrastructure
- Availability of transportation and means
- Characteristic of the location and its neighbor whether it's located in adjacent to residential area or in industrial park

Figure III-3 shows a schematic representation of process design alternatives considering 3 dimensions: materials choices, process routes and manufacturing locations.

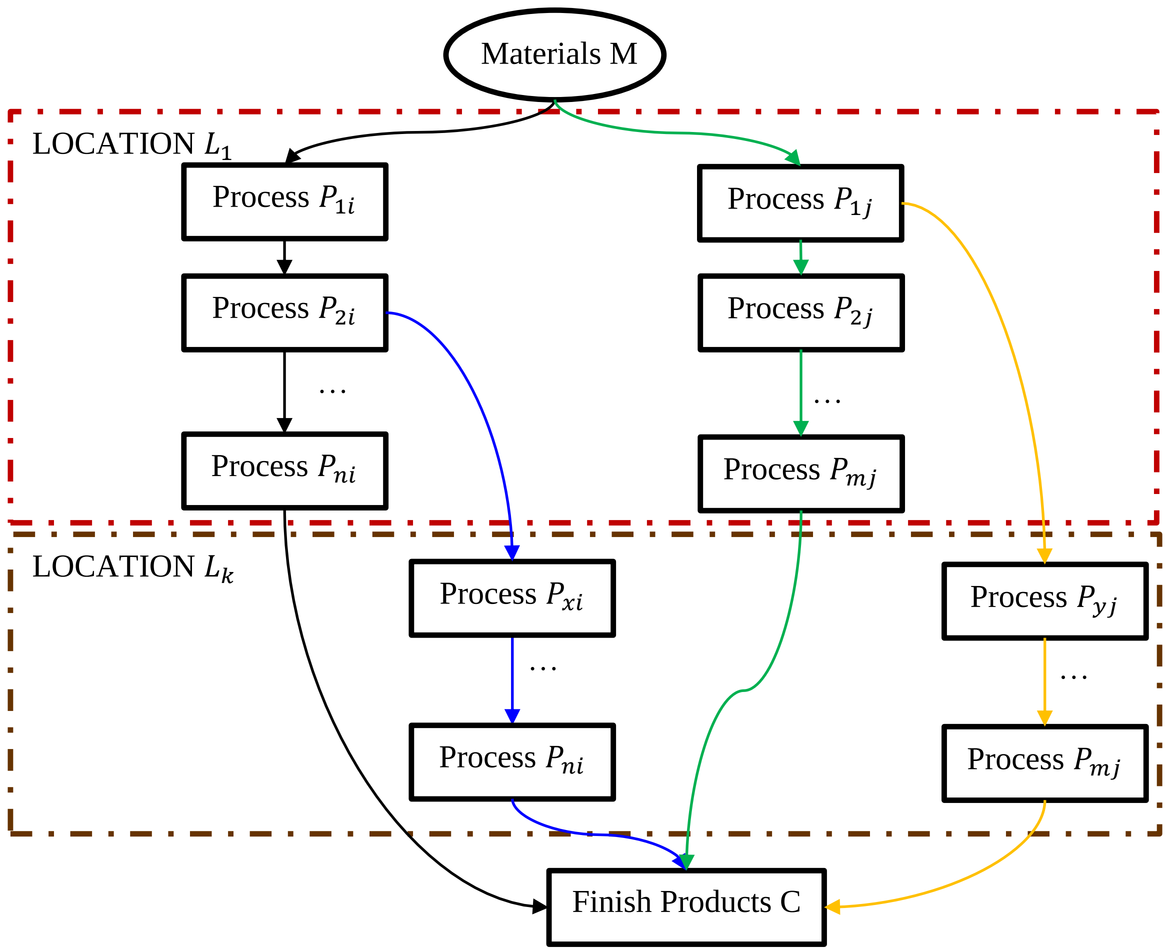

Figure III-3 – Schematic representation of process design alternatives based on materials, chemical routes and manufacturing locations

Essential design information should be developed for each option, including:

- Preliminary process flowsheets with key process conditions and parameters (e.g. flow rate, pressure, temperatures, key equipment size…). Guidelines on how to synthesize a flow sheet could be found in literature (for examples Chemical Engineering Design by Towler and Sinnott; Systematic Methods of Chemical Process Design by Biegler, Grossmann and Westerberg). (Biegler et al. 1997; Towler and Sinnott 2013)

- Rough-cut capacity analysis and material balance
- Physical and chemical properties of feedstock and chemicals used in processes.
- Inventory (feedstock, intermediate, finished product) and frequency of replenishment/shipment
- Information on potential sites where the manufacturing plant might be located, including climate data, seismic conditions, infrastructure and mean of transportation availability.

Option Evaluation

As mentioned earlier, evaluation in this proposed framework includes economic evaluation; hazard and risk assessment, covering safety, health, transportation and environment.

Economic Evaluation

Economic evaluation on generated design options will screen out unattractive cases. This will help focus effort of process engineering on more viable options. Given limited available data at this phase, simple return of investment (ROI) calculation can be used to assess and compare economic yield of the options. The ROI is a ratio of annual net (after-tax) profit (ANP) and total capital investment (TCI). (El-Halwagi 2012)

[III.1] $$\mathrm{ROI} = \frac{\text{Annual Net (after−tax)Profit}}{\text{TCI}} \times 100\%$$

Total capital investment (TCI) is made up of fixed capital investment (FCI) and working capital investment (WCI).

[III.2] TCI = FCI + WCI

A number of methods can be utilized for estimation of capital cost. The following are some of the most commonly used methods:

- Manufacture's quotation.
- Computer-aid tools.
- Capacity ratio with exponent.
- Updates using cost indices.
- Factors based on equipment cost.
- Empirical correlations.
- Turnover ratio. (El-Halwagi 2012)

Based on availability of engineering information, process engineers may choose an appropriate approach to estimate the capital cost. Some cases, combination of these methods can be used.

Annual net (after-tax) profit (ANP) for each option can be calculated given equation below:

[III.3] $$ANP = (AR - OC - DC) \times (1 - TR) + D$$

Where:

AR: total annual revenue

OC: total annual operating cost

DC: total annual depreciation cost

TR: corporate tax rate.

Techniques for estimation of these cost components can be found in literatures, for instant, Chemical Engineering Design by Towler and Sinnott, Sustainable Design through Process Integration by El-Halwagi. (El-Halwagi 2012; Towler and Sinnott 2013)

Safety and Risk Evaluation

Hazard identification (HAZID) shall be performed for each design option that passed the economic screening. Technique for HAZID can be found in literature, for example “Guidelines for Hazard Evaluation Procedures” by Center for Chemical Process Safety. (CCPS 2008)

Hazard and risk evaluation are undertaken using limited information available by the phase data, such as

- Capacity/flow
- Material balance
- Material properties: flammability, toxicity, explosion and reactivity
- Initial flow sheet and key process equipment
- Key process conditions i.e. temperatures, pressure

Hazards and risk evaluation shall consider the entire life cycle of the supply chain option, including storage and transportation.

Figure III-4 illustrates the current ISD assessment methods and their applicable time frame in project life cycle. Depending on scope and type of the process, an appropriate method or combination of multiple approaches may be selected for use.

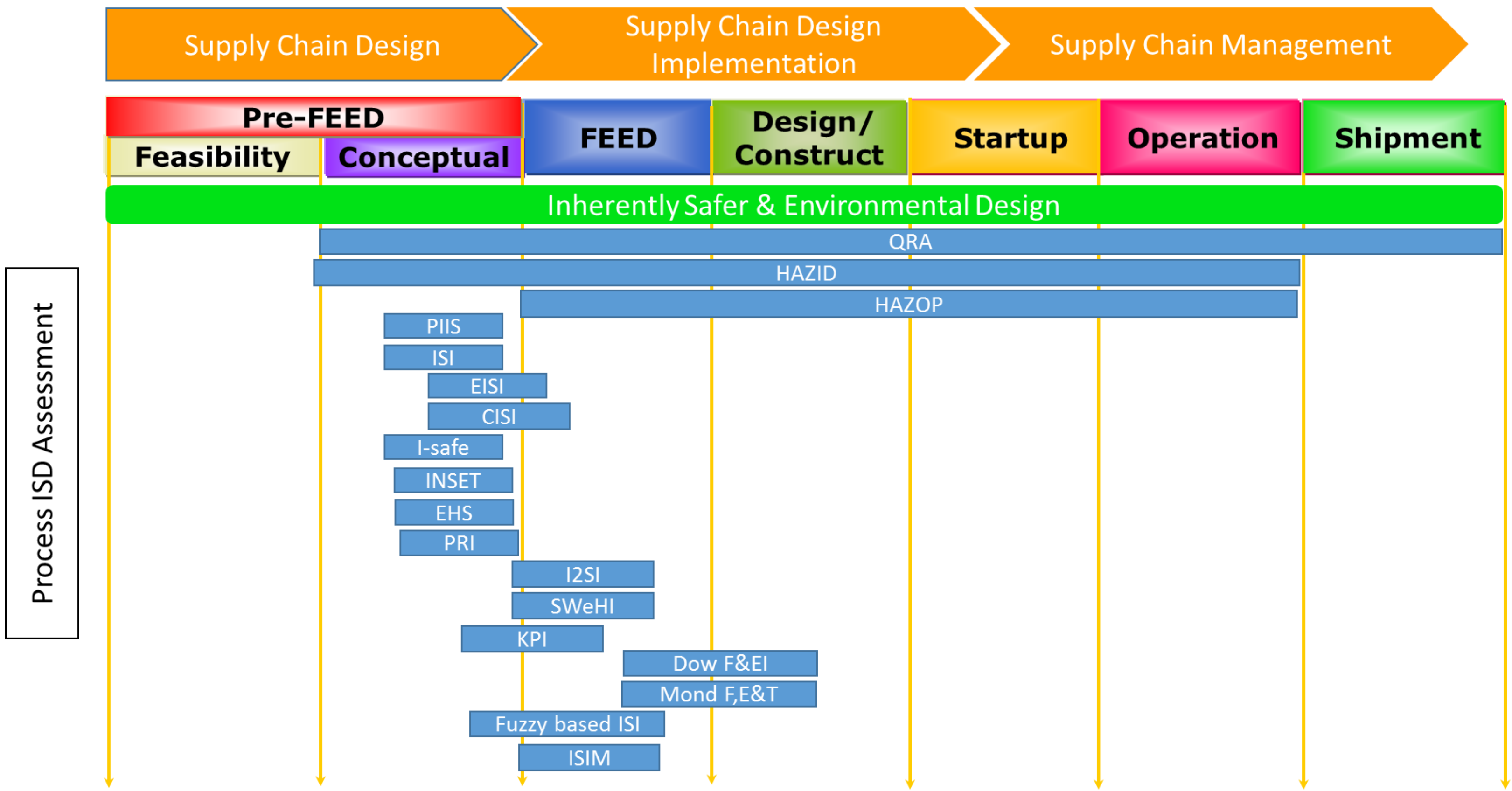

Figure III-4 – Current ISD assessment approaches and applicable time frame in project life cycle

Environmental Evaluation

Environmental assessment for design options can be undertaken in different aspects such as energy, environmental discharge (solid waste, water, air emission) and land use. One or more environmental aspects could be evaluated in corresponding to acceptance criteria. Life cycle approach shall be employed in the context of limited available data at conceptual phase.

Benchmarking technique is widely applied in chemical and petrochemical industries. Many benchmarking studies have been completed on various industry sectors at global level and country basis, especially in energy efficiency and greenhouse gas (GHG) emissions. Best-in-class data from these studies on relevant process technologies and operations could be used for the evaluation.

Option Refinement

Evaluation results and findings from previous steps will be critical inputs for refining options. ISD guide word approach can be used for design alternative identification. Substitution of hazardous materials with less hazardous ones and minimizing hazardous material inventory are usually the most effective ISD strategies applied in conceptual design phase. (Maher et al. 2012) Opportunities on moderation and simplification strategies could also be applied such as less severe operation condition processes or fewer steps processes. Many examples, success stories and case studies of ISD can be found in published literatures for consideration of reapplication, such as “Process Plants: A Handbook for Inherently Safer Design” by Kletz and Amyotte (2010).

Implementation of inherent safety for refining options is not the only risk reduction strategy available. In some cases it may not be the most reasonably practicable application. Combination of various risk management strategies; for instance inherently safer design and additional layers of protection might be used in finding design alternatives to reduce risks to an acceptable level.

One important note that any change to the base design option to form an alternatives could impact the other processes or steps in the entire supply chain. Therefore life cycle re-evaluations on hazards and risk as well as environmental impact are needed.

CHAPTER IV

CASE STUDY

Introduction

Polyethylene (PE) is a thermoplastic polymer ranked number 1 in term of volume and value worldwide. PE is the most popular plastic used in daily life. Applications of PE can be found in different areas such as packaging, consumer products, industrial product, transportation, construction, healthcare… The global market for PE is still growing at pace of about 4% per annum in the period of 2013 – 2018, according to a plastic report article in Pipeline and Gas Journal vol. 241 issue 12. The article is based on the World Polyethylene study from the Freedonia Group, Inc., a Cleveland, OH based market research firm. (Share 2014) This strong growth rate is driven by 1) the robust demand from Asia, especially China and India; 2) the significant improvement in demand from North America; and 3) the lower feedstock cost and availability from U.S. shale gas production.

Item	2008	2013	2018	% Annual growth 2008 – 2013	% Annual growth 2013 – 2018
Polyethylene Demand	67,430	81,785	99,600	3.9	4.0
North America	15,295	16,025	18,130	0.9	2.5
Western Europe	13,885	12,900	13,780	-1.5	1.3
Asia/Pacific	24,730	36,575	47,530	8.1	5.4
Other	13,520	16,285	20,160	3.8	4.4

Table IV-1 – World Polyethylene Demand (thousand tonnes). Source: (Share 2014)

PE is produced by converting ethylene into long-chain polymers. Based on the properties of the product, PE can be classified into three main types:

- Low-density polyethylene (LDPE)
- Linear low-density polyethylene (LLDPE)
- High-density polyethylene (HDPE)

Different types of PE are made based on the conditions of polymerization process. LDPE is produced on free radical processes at high pressure reaction. HDPE and LLDPE are made with coordination catalysts using low pressure processes. Density of LLDPE and LDPE is typically in range of 910 – 940 g/L; of HDPE is at 940 – 970 g/L. LDPE structure contains short chain branches and long chain branches while HDPE and LLDPE generally have short chain branches. (Soares and McKenna 2012)

In industry, ethylene is primarily produced by thermal cracking of natural gas feed stocks (ethane, propane, and butane) and petroleum liquids (naphtha, condensate, and gas oils). Other routes producing ethylene from different feed stocks include catalytic dehydration of bioethanol, (Morschbacker 2009) catalytic conversion of methanol, (Chen et al. 2005) and coal based methanol conversion. Figure IV-2 illustrates the estimated world ethylene production portfolio in 2014 by various feedstock.

This case study addresses the conceptual process design and supply chain of HDPE, the most widely used of the three PE plastics, with natural/shale gas as feedstock source. Overview of process technologies for HDPE and ethylene productions will be discussed in the next section. The case study is solved using the proposed approach discussed previously in the chapter III.

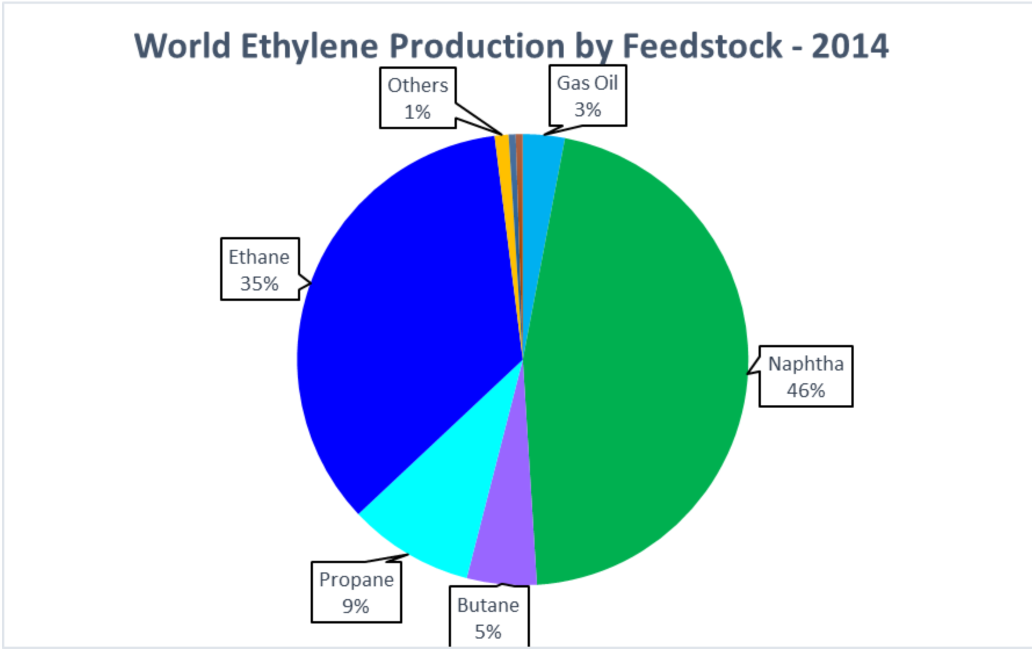

Figure IV-1 – World Ethylene Supply Profile 2014. Source: IHS Chemical. (Petrochemical Conclave 2015)

Technology Overview

HDPE Process Technology

HDPE is manufactured on continuous processes in industry. It can be made as homopolymer, or it can polymerize with addition of very small quantity of comonomer, producing an HDPE copolymer with a slightly lower density and crystallinity. Commonly used comonomers are 1-butene, 1-hexane, and 1-octene. (Soares and McKenna 2012) In general the production processes of PE are classified into three categories based on the polymerization reaction condition:

- Gas phase process
- Slurry phase process

- Solution process

Figure IV-2 represents a simplified process diagram of a slurry phase polymerization process. (Soares and McKenna 2012)

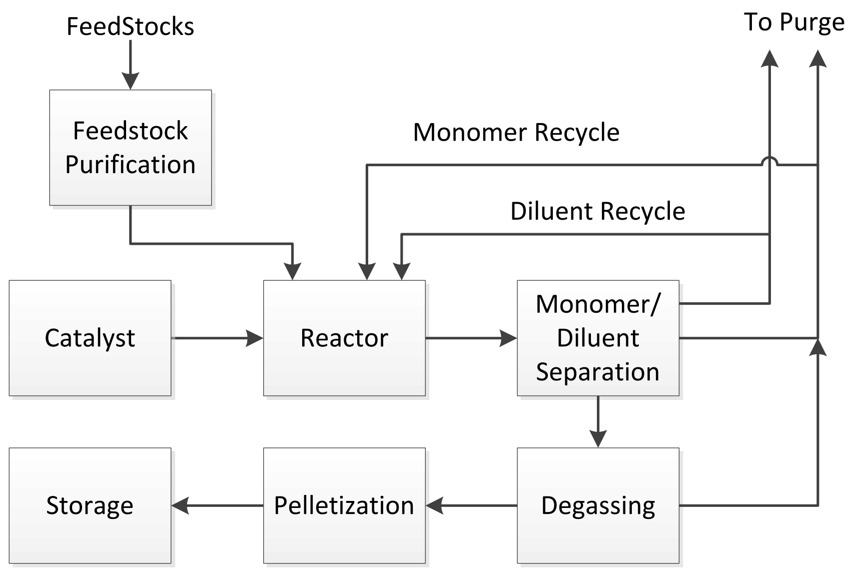

Figure IV-2 – Polymerization simplified process flow diagram – Slurry phase process

The key equipment in the polymerization is the reactor. There are three types of reactor utilized in existing commercially HDPE processes: fluid bed reactor (FBR), continuous stirred tank reactor (CSTR), and loop reactor. Table IV-2, IV-3, IV-4 and IV-5 lists some of major active HDPE process technology licensors today. Note that there are more HDPE process technologies being used globally. However, these processes are no longer active in licensing market. Therefore they are not included in the table.

Most of listed process technologies are capable to produce HDPE and LLDPE (swing process) with wide density range. Different grades of HDPE (regarding density, melt index, mechanical strength…) for various applications can be achieved based on the configurations of reactors (i.e. single or dual, multiple reactors in series) and type of catalyst used. The catalysts used in HDPE processes are Ziegler-Natta catalyst and Chromium based catalyst. Further details of commercial process and catalysts can be found in (Nowlin 2014; Soares and McKenna 2012).

Process	Company	Reactor type	Mode of operation	Reactor temperature (℃)	Reactor pressure (bar)	Residence time
Unipol™	Univation	1 FBR	Condensed	90 – 110	20 – 25	~2 hrs.
Innovene™ G	INEOS	1 FBR	Condensed	90 – 110	20 – 25	~ 2 hrs.
Spherilene	Lyondell Basell	2 FBRs	Dry	70 – 90	20 – 25	~ 1.5 hrs.

Table IV-2 – Major active PE process technology licensing – Gas phase process. Adapted from (Soares and McKenna 2012)

Process	Company	Reactor type	Diluent	Reactor temperature (℃)	Reactor pressure (bar)	Residence time (min)
SCLAIRTECH™	Nova Chemicals	2 CSTRs in parallel/series or 1 CSTR + 1 FBR	Cyclohexane	~300	~138	~30
SCLAIRTECH™ AST	Nova Chemicals	2 CSTRs in parallel/series	Light HC (proprietary)	<200	~138	~5 – 10

Table IV-3 – Major active PE process technology licensing – Solution process. Adapted from (Soares and McKenna 2012)

Process	**Company**	**Reactor type**	**Diluent**	**Reactor temperature (°C)**	**Reactor pressure (bar)**	**Residence time**
MarTECH™	Chevron Phillips	Single loop Dual loop (multilegged)	Isobutane	85 – 100	30 – 40	1 hr.
Hostalen ACP	LyondellBasell	3 CSTR in series	Hexane	75 – 85	5 – 10	1 – 5 hrs. per reactors
Innovene™ S	INEOS	1 – 2 loops	Isobutane	70 – 85	25 – 40	1 hr.
CX	Mitsui	2 CSTR in parallel/series	Hexane	80 – 85	< 8	45 min per reactor

Table IV-4 – Major active PE process technology licensing – Slurry phase process. Adapted from (Soares and McKenna 2012)

Process	**Company**	**Reactor type**	**Diluent**	**Reactor temperature (°C)**	**Reactor pressure (bar)**	**Residence time**
Borstar®	Borealis	Loop + FBR	Supercritical propane (loop)	85 – 100	60 – 65	-

Table IV-5 – Major active PE process technology licensing – Hybrid process. Adapted from (Soares and McKenna 2012)

Thermal Cracking

Ethylene production in U.S is increasing in the last couple years, majority from ethane thermal cracking, thanks to the abundant ethane rich shale gas from U.S. The process is called pyrolysis or steam cracking. Figure IV-3 illustrates a simplified process flow diagram of ethylene steam cracking.

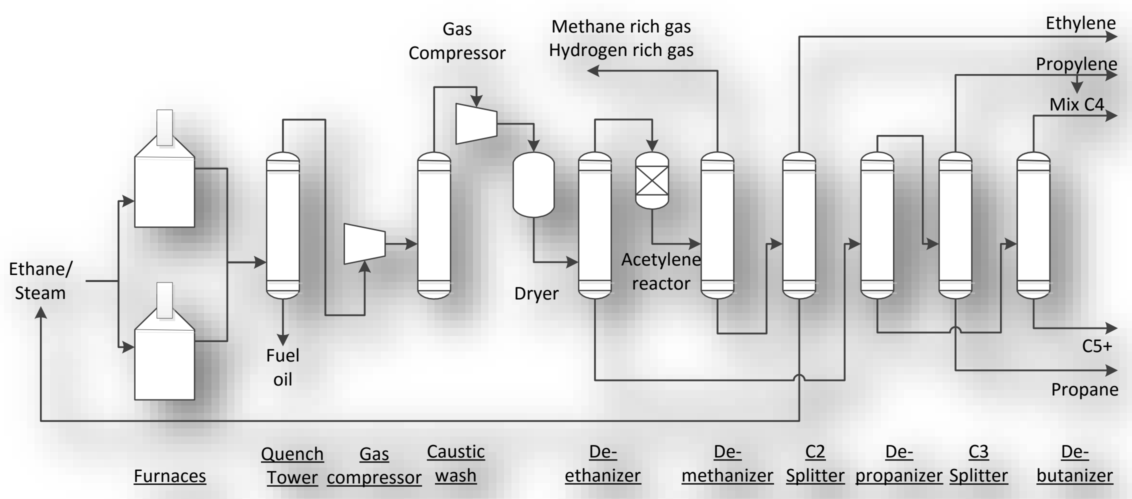

Figure IV-3 – Simplified Process Flow Diagram – Ethane Thermal Cracking

Cracking of ethane is carried out in the cracking furnaces. The ethane stream is heated and mixed with steam then enters a fired tubular reactor (radiant tube or radiant coil) where the pyrolysis happens under controlled residence time, temperature profile, and partial pressure. The design and arrangement of the radiant coil are quite varied from different technology providers. The conversion is highly endothermic, therefore it requires high energy inputs. The reaction products will be quickly cooled down at a water quench tower to prevent degradation of the highly reactive products by secondary reactions. The cracked gas leaving the water quench tower is compressed to 32 – 37 bar in a four-stage centrifugal compressor. Water and acid gas are separated from cracked gas between the stages. After that the dried streams are sent to a series of fractionators that separate the cracked gases into different products such as methane, hydrogen, ethane, propane, propylene… The final ethylene product stream is taken from the C_2 splitter. Typical range of operating parameters of ethylene cracking and fractionation processes are shown in the table IV-6 below.

Parameters	Value
Cracking heater outlet temperature	750 – 900 °C
Cracking heater outlet pressure	1.5 – 2.8 bar (22 – 40 psia)
Dilution steam/hydrocarbon ratio (ethane feed)	0.25 – 0.35 (Zimmermann and Walzl 2000)
Charge gas compressor discharge	30 – 38 bar (425 – 550 psia)
Demethanizer	7 – 32 bar (100 – 465 psia)
Deethanizer	20 – 27 bar (300 – 400 psia)
Depropanizer	10 – 18 bar (150 – 270 psia)
Debutanizer	4 – 6 bar (60 – 90 psia)
Ethylene fractionator	8 – 20 bar (110 – 300 psia)
Propylene fractionator	8 – 20 bar (110 – 300 psia)

Table IV-6 – Typical range of operating parameters – Ethylene Cracking processes (Meyers 2005)

Table IV-7 lists some of major active thermal cracking technology licensing in the industry today with gas feedstock.

Technology	Company	Furnace Radiant coil types	Ethylene Yield (wt%)
SMK™ USC® M-coil	Technip	4-pass coil 6-pass coil	84%
SRT®	CBI	2-pass coil	65 – 75%
SCORE™	KBR	Single Pass Straight Tube Two-pass “U-coil” Serpentine-type “W-coil”	77 - 80%
PYROCRACK®	Linde	4-pass 2 parallel tubes into 2-pass coil 6-pass coil 2-pass 2 parallel tubes into 2-pass coil	84%

Table IV-7 – Major active ethylene thermal cracking process technology licensing (Meyers 2005; Zimmermann and Walzl 2000) (Company websites)

Methanol to Olefins Technology Overview

The methanol to olefins technology is quite new compared to ethylene thermal cracking. The process has only been studied in last four decades. The technology has opened new opportunities for more natural/shale gas utilization since the synthesis of methanol from natural gas feedstock has been widely in production.

The conversion of methanol to olefins is carried out in a fluid bed reactor in the vapor phase. Methanol is converted first to dimethyl ether (DME) intermediate; then the dehydration reaction of DME takes place to produce ethylene and propylene. Similar to ethane cracking process, a series of fractionators are used to further process the reacted effluent to separate the key products from the by-product components. The figure IV-4 below illustrates a simplified process flow diagram of MTO process. (Meyers 2005)

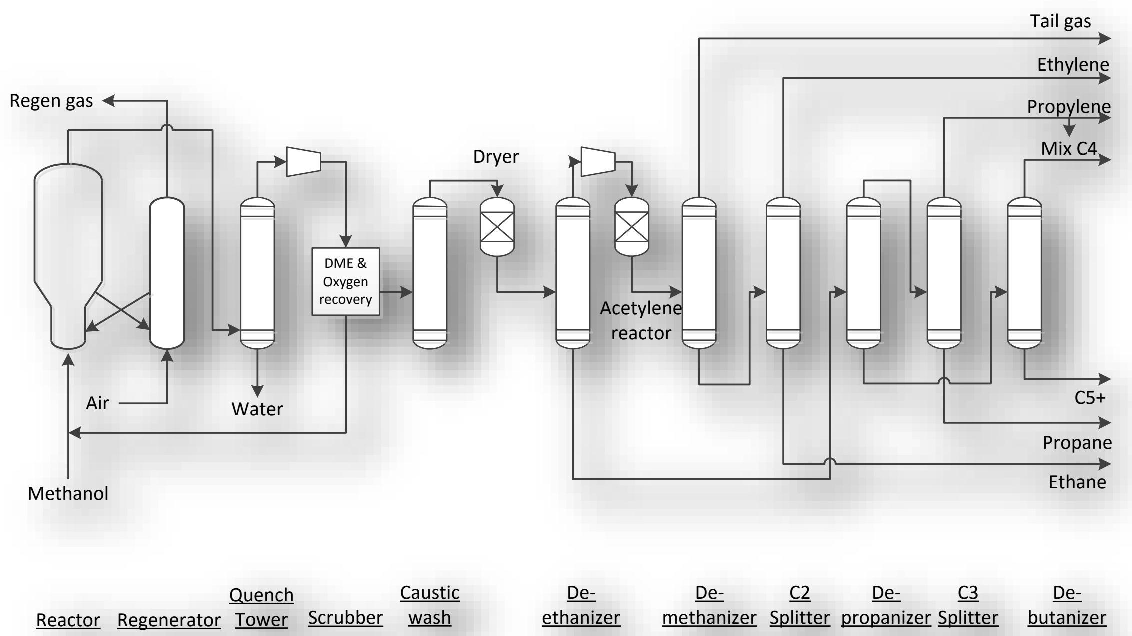

Figure IV-4 – Simplified Process Flow Diagram – MTO process

UOP/Hydro MTO process technology from UOP/INEOS joint venture and Lurgi MTP (methanol to propylene) technology from Air Liquide Company are currently active players in providing licensing technologies for methanol to olefin application. UOP/Hydro MTO process yields both ethylene and propylene at ratio between 0.75 and 1.5. Lurgi MTP process yields primarily propylene product, ethylene product is negligible. Table IV-8 provides a summary of current active MTO process technology licensing and their key process parameters. (Air Liquide Global E&C Solutions 2015; Meyers 2005)

Process	Company	Reactor type	Wt% Yield (Carbon basis)	Reactor temperature (℃)	Reactor pressure (bar g)
UOP/Hydro	UOP LLC/INEOS	FBR	~ 80%	350 – 550	1 – 3
Lurgi MTP	Air Liquide	Fixed bed	NA	400 - 450	1.5

Table IV-8 - Active MTO process technology licensing

Case Study

The case study considers conceptual design for entire high density polyethylene (HDPE) supply chain for primary customers in Asia. Feedstock to be used in this study is U.S. shale gas. Average Barnett shale gas composition is assumed as shown in the table IV-9 below.

Well	C1	C2	C3	CO_2	N_2
1	80.3	8.1	2.3	1.4	7.9
2	81.2	11.8	5.2	0.3	1.5
3	91.8	4.4	0.4	2.3	1.1
4	93.7	2.6	0.0	2.7	1.0
Average	86.7	6.7	2.0	1.7	2.9

Table IV-9 – U.S. Barnett shale gas composition (Bullin and Krouskop 2009)

The objective is to deliver best-in-class safety and environmental performance while maximize supply chain value.

The process synthesis and supply chain option development will take into account following dimensions:

- Choices of chemical pathways: 1) through thermal cracking of ethane to ethylene (ethane cracking route) or 2) reforming of shale gas to syn gas for methanol synthesis then converting methanol to olefins (methanol route).
- Supply chain model and location choices: 1) single manufacturing complex that the entire manufacturing happens at single location close to feedstock source, then ship finished product to customer; or 2) dispersed manufacturing plants that have partial manufacturing carried out in location 1 then intermediate product shipped to location 2 to finish.
- Scale of manufacturing plant: considering throughput options of HDPE at 500 KTA; 1,000 KTA and 1,500 KTA (thousands tonnes per annum).

Given limited available information in literatures and public domain, the case study will not consider the technology choice aspect, but assume the preselected technologies such as HDPE pellets slurry phase polymerization by Phillips, generic ethylene thermal cracking from ethane. LNG processing facility is also included in the scope for ethane thermal cracking route design options in order to maximize the utilization of shale gas. Figure IV-5 provides a schematic representation of process design alternatives considering in this case study based on process routes and manufacturing locations. In total, twelve design options will be evaluated. Table IV-10 illustrates the process design option matrix of the case study. From framework demonstration viewpoint, the case study will cover economic evaluation, safety and risk assessment and environmental impact evaluation only. Design changes and refinement will be not included.

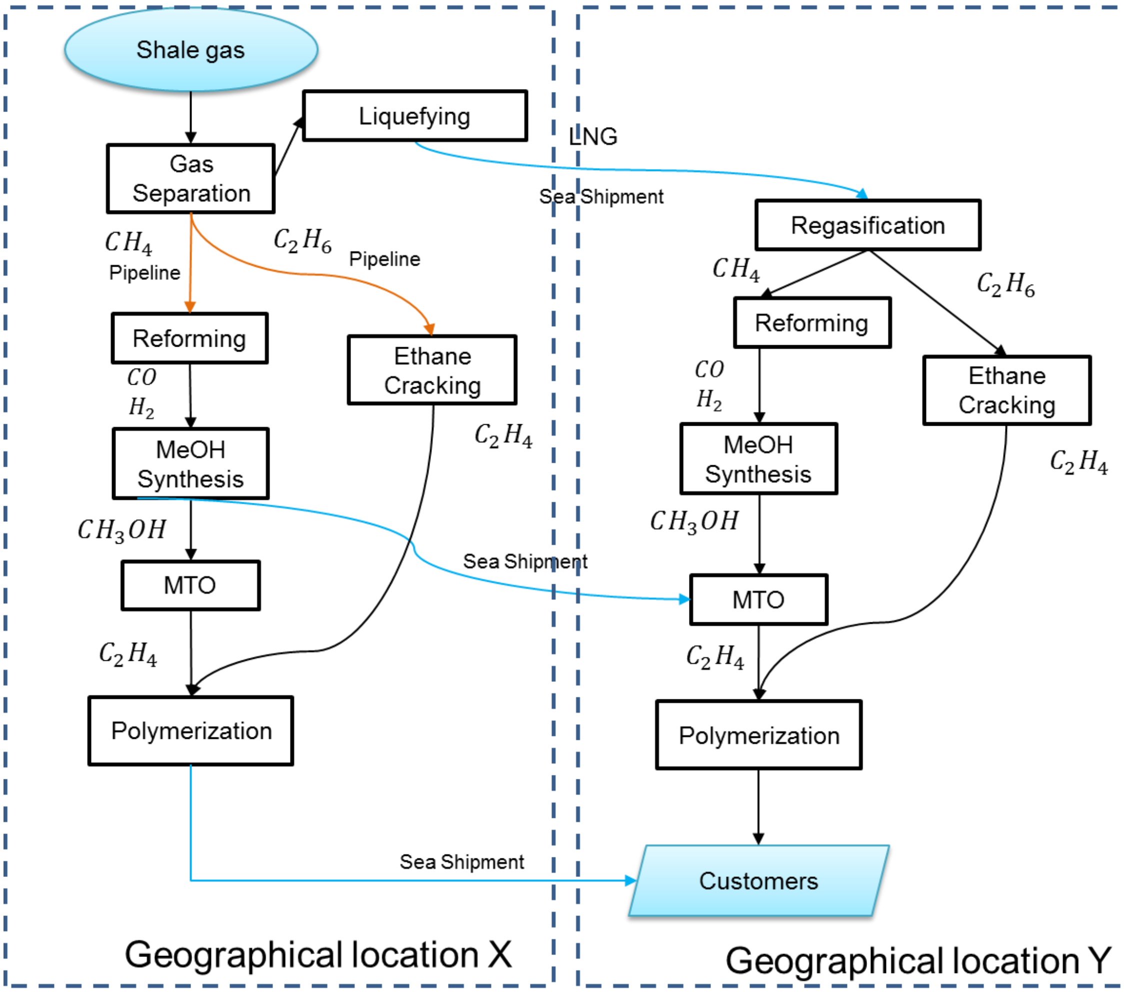

Figure IV-5 – A schematic representation of the case study's process design alternatives

Process Route	Supply Chain Model	Capacity (KTA)		
		500	1000	1500
Methanol Route	Single Complex	Option 1	Option 2	Option 3
	Dispersed mode	Option 4	Option 5	Option 6
Ethane Cracking Route	Single Complex	Option 7	Option 8	Option 9
	Dispersed mode	Option 10	Option 11	Option 12

Table IV-10 – Case study process design option matrix

CHAPTER V

CASE STUDY RESULT AND ANALYSIS

Economic Analysis

The estimated TCI for each design option is calculated based on the following equation:

[V.1] $$TCI = \sum(ISBL_i + OSBL_i)$$

where:

$ISBL_i$: the inside battery limits investment of process i

$OSBL_i$: the outside battery limits investment of process i

The ISBL plant cost is defined as

[V.2] $$ISBL = aS^n$$

where:

S is the desired capacity of the selected process

Parameters a and n are related to the selected process and provided in the table V-1. Process cost correlation for Gas processing and LNG process is estimated based on published information of Chenier Sabine Pass Liquefaction project, $12B investment, 18000 KTA capacity, 4 trains.

Process	ISBL Equation (MM$) (U.S. Gulf Coast basis)	Capacity range	Reference
Gas processing + LNG	$12.603 \times S^{0.7}$	4500 – 18000 KTA	(Cheniere Energy Inc. 2014)
Ethylene by ethane cracking	$9.574 \times S^{0.6}$	500 - 2000 MMlb/y	(Towler and Sinnott 2013) Values in January 2006, CE Index = 478.6
HDPE Pellets by Phillips Slurry process	$3.370 \times S^{0.6}$	300 - 700 MMlb/y	
Ethylene by UOP/Hydro MTO process	$8.632 \times S^{0.6}$	500 - 2000 MMlb/y	
Methanol via natural/shale gas reforming and synthesis	$7.8444 \times S^{0.6}$	5000 tpd	(Ehlinger et al. 2014)

Table V-1 – Process Cost Correlations

The ISBL plant costs take into account the Chemical Engineering Plant Cost Index (CEPCI) of 566.6 as of November 2014.

The OSBL costs are assumed at 50% of ISBL for new plant setup in this case study.

Simple ROI of each option is calculated based on the equation [III.1]. References for the material and finished product's prices are from public internet sources. Shale gas price is assumed at $2.7/MMBtu; HDPE pellets selling price is at $1400 per tonne.

Figure V-1 shows the ROI summary of the twelve design options. The ROI of all design options ranges from 13% to 18%. A minimum ROI of 15% is typically required for most new plant. Therefore 4 out of 12 options fails the criteria. From the result, it is obvious that supply chain model is a critical factor. Higher ROI yield for options with single complex manufacturing model for both methanol route and ethane cracking route than options with dispersed manufacturing model. The single complex manufacturing model eliminates the need for transportation of intermediate between the plants therefore the on-going expenses are lower. The size of manufacturing is another important factor that impact the economic result. High capacity options also yields higher ROI because of the economy of scale impact. Mixed results achieved with chemical route choices. Higher ROI yields for ethane cracking route option at high capacity, yet for methanol route option at low capacity.

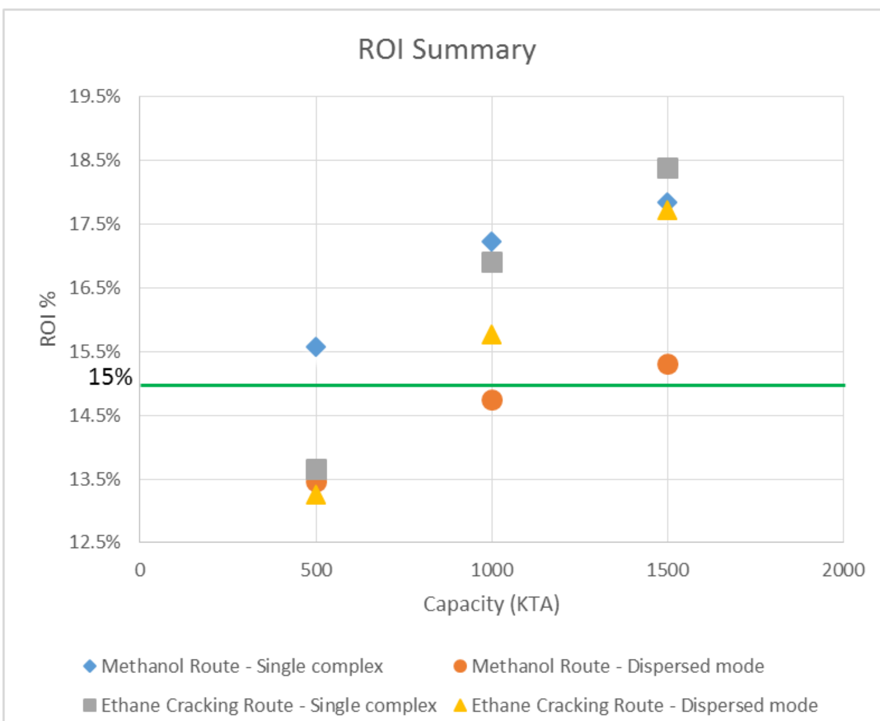

Figure V-1 – ROI summary of the design options

A sensitivity analysis was performed to assess the impact of various feedstock prices and finished product prices to ROI. Table V-2 provides a summary of the ROI of all design options at shale gas price range of 1.7 – 3.7 \$/MMBtu and HDPE price range of 1,200 – 1,600 \$/tonne. More attractive ROIs are attained for lower shale gas prices and higher HDPE selling prices. The ethane cracking route options are still yielded attractive ROIs at lower shale gas prices and lower HDPE selling prices in these range mentioned about. On the other side, at higher shale gas prices the methanol route options could achieve some attractive ROIs with higher HDPE selling price. If the HDPE selling price drops to 900 \$/tonne, both process routes become economically unattractive regardless of the shale gas prices, scale and mode of the manufacturing plant.

Detailed economic analysis of each option is provided in the Appendix A of the thesis.

ROI Criteria	≥ 15%		Shale gas price (1.7 $/MMBtu)			Shale gas price (2.7 $/MMBtu)			Shale gas price (3.7 $/MMBtu)		
HDPE Price ($/tonne)	**Process Route**	**Supply Chain Model**	**Capacity (KTA)**			**Capacity (KTA)**			**Capacity (KTA)**		
			500	**1000**	**1500**	**500**	**1000**	**1500**	**500**	**1000**	**1500**
1200	**Methanol Route**	**Single Complex**	14.7%	16.3%	16.8%	13.8%	15.4%	15.9%	12.9%	14.3%	14.8%
		Dispersed mode	12.6%	13.8%	14.4%	11.8%	13.0%	13.5%	10.9%	12.0%	12.4%
	Ethane Cracking Route	**Single Complex**	15.0%	18.6%	20.2%	13.0%	16.1%	17.5%	10.8%	13.4%	14.5%
		Dispersed mode	14.6%	17.5%	19.5%	12.6%	15.0%	16.8%	10.4%	12.1%	13.9%
1400	**Methanol Route**	**Single Complex**	16.4%	18.1%	18.8%	15.6%	17.2%	17.8%	14.6%	16.2%	16.8%
		Dispersed mode	14.3%	15.6%	16.2%	13.5%	14.8%	15.3%	12.5%	13.8%	14.3%
	Ethane Cracking Route	**Single Complex**	15.7%	19.4%	21.1%	13.7%	16.9%	18.4%	11.5%	14.2%	15.4%
		Dispersed mode	15.3%	18.3%	20.4%	13.3%	15.8%	17.7%	11.0%	12.9%	14.8%
1600	**Methanol Route**	**Single Complex**	18.3%	20.1%	20.8%	17.3%	19.1%	19.8%	16.4%	18.1%	18.7%
		Dispersed mode	16.1%	17.5%	18.2%	15.1%	16.5%	17.2%	14.2%	15.5%	16.1%
	Ethane Cracking Route	**Single Complex**	16.5%	20.4%	22.3%	14.3%	17.7%	19.3%	12.1%	15.0%	16.3%
		Dispersed mode	16.1%	19.4%	21.6%	13.9%	16.6%	18.6%	11.7%	13.7%	15.6%

Table V-2 – Sensitivity analysis for the ROI of all design options at various prices of shale gas and HDPE

Safety and Risk Evaluation

Hazard Identification

A generic hazard identification was performed for the case study process design options using hazard evaluation procedures from the Center for Chemical Process Safety. (CCPS 2008) List of chemicals and substances used or produced in the processes of the case study with their properties are provided in the Appendix B.

In general both ethane cracking and methanol routes have various processes of high flammable gas, flammable and combustible liquids and volatile toxic materials, which have the potential to cause injury, property damage or even fatality. Leaks of hydrocarbons from the process equipment, piping or storage vessels in an abnormal event can lead to a fire, explosions or toxic release that impact plant personnel, property and community surrounding. Tables V-4 and V-5 represent generic process hazards, initiating causes and potential incident outcomes for each process facility of the methanol route and ethane cracking route respectively. All of the processes in this case study are prone to fire and explosion hazards.

Process Plant/ Process hazards	Initiating cause	Incident outcomes
Methanol Synthesis – Hydrocarbon leaks - flammable gases, flammable liquids from reactors, process and storage vessels, pumps, piping and equipment.	Loss of containment caused by corrosion, impact damage, seal failure, operation failure, process upset.	- Pool fire, jet fire, flash fire or vapor cloud explosion possible. - Toxic release
MTO – Hydrocarbon leaks – flammable gases, liquefied flammable gases, flammable liquids from reactors, process and storage vessels, pumps, piping and equipment.	Loss of containment caused by corrosion, impact damage, seal failure, operation failure, process upset	- Pool fire, jet fire, flash fire or vapor cloud explosion possible. - BLEVE possible if pressurized vessel exposed to sufficient heat radiation. - Toxic release
Polymerization - Hydrocarbon leaks - flammable gases, combustible liquids or combustible dust from reactors, pumps, piping and equipment.	Loss of containment caused by corrosion, impact damage, seal failure, operation failure, process upset, runaway reactions	- Jet fire, flash fire or vapor cloud explosion possible. - Dust explosion
Methanol leaks – during tanker loading or unloading	Leak caused by corrosion, impact damage, seal failure, operation failure, process upset	- Pool fire, jet fire, flash fire or vapor cloud explosion possible. - Toxic release

Table V-3 – Generic process hazards of Methanol route

Process Plant/ Process hazards	Initiating cause	Incident outcomes
Gas Processing – Hydrocarbon leaks – flammable gases, liquefied flammable gases, combustible liquids from process and storage vessels, pumps, piping and equipment.	Loss of containment caused by corrosion, impact damage, seal failure, operation failure, process upset.	- Pool fire, jet fire, flash fire or vapor cloud explosion possible. - BLEVE possible if pressurized vessel exposed to sufficient heat radiation.
Ethylene Cracking – Hydrocarbon leaks – flammable gases, liquefied flammable gases, combustible liquids from process and storage vessels, pumps, piping and equipment.	Loss of containment caused by corrosion, impact damage, seal failure, operation failure, process upset.	- Pool fire, jet fire, flash fire or vapor cloud explosion possible. - BLEVE possible if pressurized vessel exposed to sufficient heat radiation.
Polymerization – Hydrocarbon leaks – flammable gases, combustible liquids or combustible dust from reactors, pumps, piping and equipment.	Loss of containment caused by corrosion, impact damage, seal failure, operation failure, process upset, runaway reactions.	- Jet fire, flash fire or vapor cloud explosion possible. - Dust explosion
LNG – LNG leaks during tanker loading or unloading.	Leak caused by corrosion, impact damage, seal failure, operation failure, process upset.	- Pool fire, jet fire, flash fire or vapor cloud explosion possible.

Table V-4 – Generic process hazards of Ethane cracking route

Risk Assessment

A high-level quantitative risk assessment approach was used for assessing and calculating of individual risk of the design options. The approach was adopted from the QRA method described in the CCPS book, "Guidelines for Chemical Process Quantitative Risk Analysis" and the risk-based building siting evaluation for explosion hazards from the CCPS book, "Guidelines for Evaluating Process Plant Buildings". (CCPS 2000; CCPS 2012) For each process design options that passed the economic screening, a risk evaluation was performed at process unit level. Table V-5 shows the incident scenarios included in the risk assessment.

Maximum individual risk was selected to compare among the option. Maximum individual risk is defined as the individual risk to the person exposed to the highest risk in an exposed population. (CCPS 2012) The maximum individual risk of explosion was estimated using equation [V.3]

[V.3] $$R_{x,y} = \sum_{i \in N} F_i V_{x,y,i} T_{x,y}$$

where:

$R_{x,y}$: maximum individual risk at specific location x,y of the manufacturing plant with N process units

F_i: the explosion frequency of the process unit i

$V_{x,y,i}$: Occupant vulnerability at point x,y by the explosion event of the process unit i.

$T_{x,y}$: Fractional time of attendance at the point x,y, calculated as hours per week/168 hours.

	Process Unit	Scenario description	Incident outcome
Methanol route	Shale gas processing	Release of shale gas	Explosion
	Methanol synthesis	Release of methanol	Explosion
	Methanol storage	Release of methanol	Late explosion
	Methanol conversion	Release of reactor's mixture	Explosion
	Ethylene	Release of ethylene	Explosion
	Propylene	Release of propylene	Explosion
	HDPE	Release of ethylene	Explosion
Ethane Cracking route	Shale gas processing	Release of shale gas	Explosion
	LNG production	Release of shale gas	Explosion
	LNG storage	Release of LNG	Explosion
	Steam cracking	Release of cracked gas	Explosion
	Ethylene	Release of ethylene	Explosion
	Propylene	Release of propylene	Explosion
	HDPE	Release of ethylene	Explosion

Table V-5 – Incident scenarios for case study risk assessment

The explosion frequency of each scenario is estimated based on the unit core explosion frequency and adjustment factors: unit capacity, electrical classification, confinement, and management system effectiveness. (Moosemiller 2010) The unit explosion frequency is the product of unit core frequency and the multipliers:

Unit core frequency × throughput multiplier × electrical classification multiplier × indoor multiplier × management system multiplier.

Table V-6 provides the unit core frequency used in the case study. (Moosemiller 2010) Methanol route has a process unit listed in the higher frequency category (1.0×10^{-3} explosion per year for methanol conversion to olefin unit using fluid catalytic cracking); other process units are listed in the medium frequency (ethylene and propylene units), lower frequency (methanol synthesis and HDPE units), and very low frequency categories (gas processing and storage units). Compared to methanol route, the process units of ethane cracking route are not listed in higher frequency category; but medium, lower and very low frequency categories.

	Process Unit	Core explosion frequency per year
Methanol route	Gas processing	3.00E-05
	Methanol synthesis	1.00E-04
	Methanol storage	3.00E-05
	Methanol conversion	1.00E-03
	Ethylene	3.00E-04
	Propylene	3.00E-04
	HDPE	1.00E-04
Ethane Cracking route	Gas processing	3.00E-05
	LNG production	1.00E-04
	LNG storage	3.00E-05
	Steam cracking	3.00E-04
	Ethylene	3.00E-04
	Propylene	3.00E-04
	HDPE	1.00E-04

Table V-6 – Unit core explosion frequency of process units in the case study

Occupant vulnerability was determined based on the consequence analysis of the above release scenarios. Hydrocarbon release quantities were estimated based on nominal flowrates of standard process units. 10-minute release scenarios were assumed. For example, 10-minute release quantity of methanol from 5000 tonne/day methanol synthesis unit is approximately 34700 kg of methanol in vapor phase at 513^{o}K.

The TNT equivalency method was used to estimate the overpressure of the blast wave to the plant buildings. Occupant vulnerability was calculated using probit equation [V.4] for structure damage due to explosion. (Crowl 2011)

[V.4] $$V_{x,y,i} = -23.8 + 2.92 \ln(P_{x,y,i})$$

with $V_{x,y,i}$ is the occupant vulnerability at point x,y by the explosion event of the process unit i; and $P_{x,y,i}$ is the overpressure of the blast wave at the point x,y by the explosion event of the process unit i.

Table V-7 provides the assumption of meteorological data of manufacturing locations included in the consequence models. The assumption on the distances of plant buildings from release points are shown in the table V-8.

	Average temperature	Relative humidity %	Wind velocity (m/s)	Stability class
Location 1	89	70	3.13	D
Location 2	78.8	70	3.6	D

Table V-7 – Assumption on meteorological data of manufacturing locations

	Process Unit	Distance from release points Control room/Lab (m)	Administration (m)
Methanol route	Gas processing	50	150
	Methanol synthesis	75	175
	Methanol storage	150	200
	Methanol conversion	50	150
	Ethylene	75	150
	Propylene	85	150
	HDPE	50	150
Ethane Cracking route	Gas processing	50	150
	LNG production	75	175
	LNG storage	150	200
	Steam cracking	50	150
	Ethylene	75	150
	Propylene	85	150
	HDPE	50	150

Table V-8 – Assumption of distance of plant buildings from release points

Figure V-2 illustrates the maximum individual risk result of the case study. Fire and explosion risk from LNG transportation was assumed at 6.72×10^{-4} fatalities per ship year. (Woodward and Pitblado 2010) Given that there is no published data or literatures found for the risk of methanol tanker ocean shipment, the fatalities rate due to methanol shipment was assumed at 1.109×10^{-5} based on estimation. Detailed assumption and calculation could be found in APPENDIX D.

Storage and transport of methanol is at ambient temperature, with or without nitrogen blanketing. Therefore the explosion risk was very low in this case study. This makes very minor differences between single complex options and dispersed mode options for methanol route.

Most of ethane cracking route options have individual risk exceed 1.0×10^{-3} /year while the methanol route options were below this limit. Comparing the plant processes for single manufacturing complex supply chain model, the maximum individual risk of ethane cracking route options were higher than of methanol route options as they included additional risk of LNG production, storage and shipment. Without LNG scopes, the risks of ethane cracking route options are lower than of the methanol route options (Figure V-3). Process design changes or further risk investigation are required in order to reduce the risk.

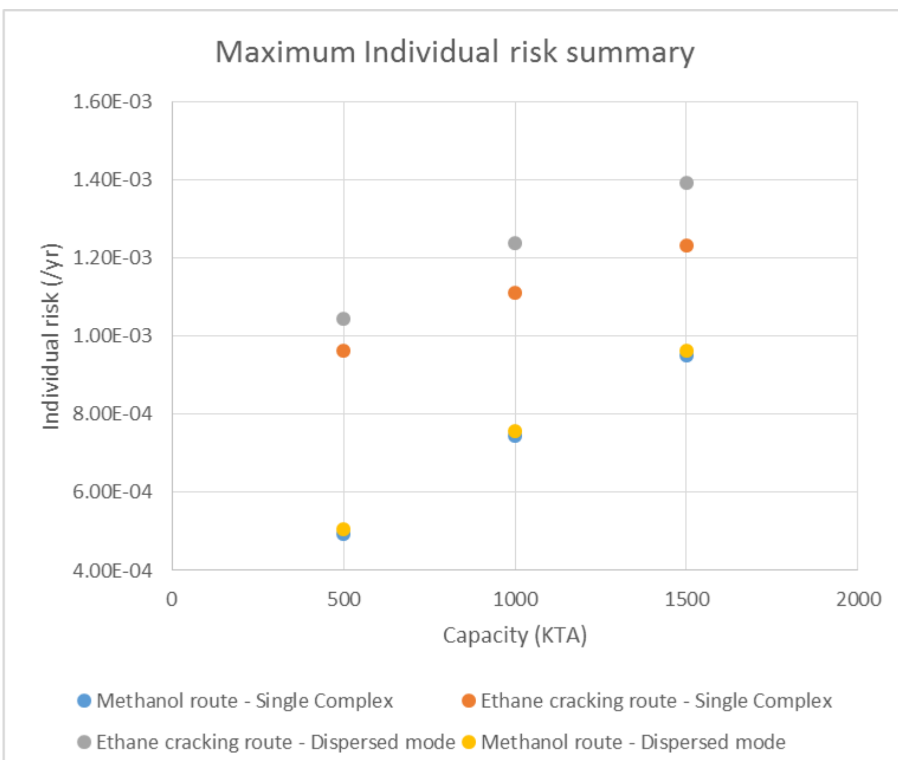

Figure V-2 – Maximum individual risk summary

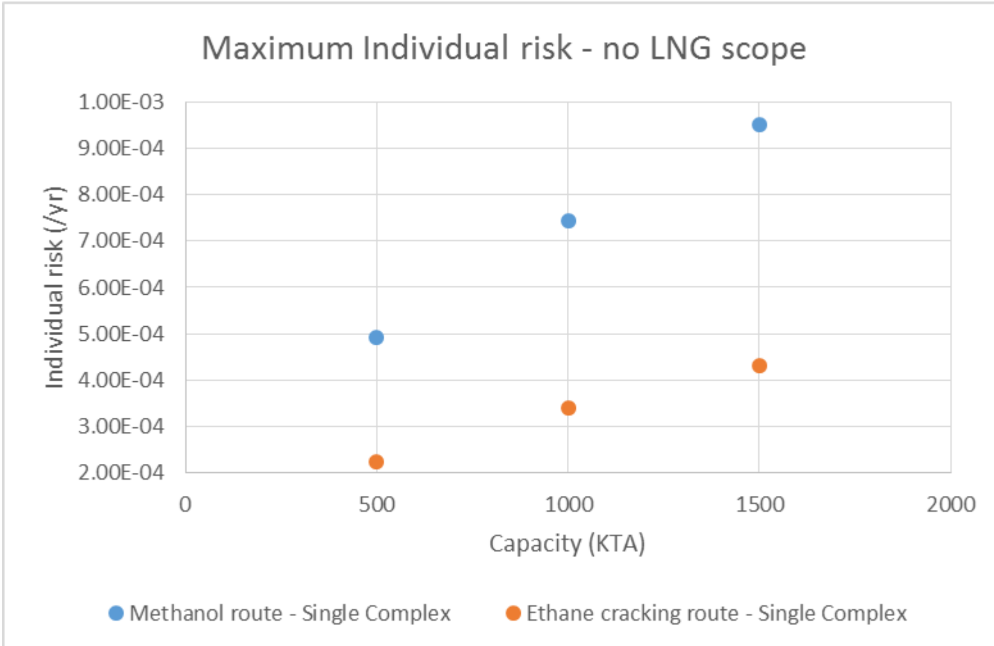

Figure V-3 – Maximum individual risk – no LNG scope for ethane cracking route

Environmental Impact

In this case study, greenhouse gas (GHG) emission was selected for environmental impact analysis. GHG is one of pollutants included in Prevention of Significant Deterioration (PSD) permitting program under the Environmental Protection Agency (EPA) administration for new and modified major sources of air pollution such as power plants, manufacturing facilities, and other facilities that emit air pollution. Benchmarking approach was used to quantify lifecycle emissions from all stages of production in the options. CO_2 emission was calculated based on total energy use in the process including transportation. Energy use of each process was identified based on published literatures.

Table V-9 lists the assumptions and data used in the process GHG emission calculation. Process and energy efficiency opportunities were not considered in this exercise. Emission factor is assumed 0.053 tonne CO_2e per 1 MMBtu energy consumed.

CO_2 emission related to tanker transportation of LNG was calculated using the equation [V.5] (Jaramillo et al. 2007)

[V.5] $$CO2 = (EF)(2 \times roundup\left(\frac{SM}{TC}\right) \times \frac{D}{TS} \times FC \times \frac{1}{24}$$

Where:

EF: the shipping tanker emission factor of 3,200 kg CO_2/tonne of fuel consumed;

2: the number of trips each tanker does for every load (one bringing the chemicals and one going back empty);

SM: the shipment amount of natural gas (in cubic feet) or methanol (in tonnes) shipped between plants;

TC: the shipping tanker capacity; assumed to be 120,000 cubic meters of LNG (1 m3 LNG = 21,537 ft3 NG); and 20,000 tonnes of methanol.

D: the distance between source port and receiving port; 10015 nautical miles assumed in this case study (port of Freeport, Texas – port of Incheon, S. Korea);

TS: the tanker speed of 14 Knots;

FC: shipping vessel fuel consumption factor of 41 tonnes of fuel per day;

24: hours per day.

Process Plant	Energy consumption	Reference
Gas processing + LNG production	10% of feed gas	(PetroWiki 2015)
Regasification	3% of feed gas	(Jaramillo et al. 2007)
Ethane cracking	17 – 21 GJ/t ethylene	(Ren et al. 2006)
Methanol from natural/shale gas	10 GJ/t methanol	(Ren et al. 2008)
MTO Process	13 GJ/t ethylene	(Ren et al. 2008)
HDPE Slurry phase process	7.6 GJ/t HDPE	(International Energy Agency 2007)

Table V-9 – Process plant energy consumption

The emissions of each design options are summarized in the table V-10 & V-11. For both ethane cracking and methanol routes, single manufacturing complex model yield less CO_2 emission than dispersed mode because of no intermediate transport and processing activities. In order to reduce the pollutant, especially for mega capacity supply chain, it is better off having a single manufacturing location than dispersing the supply network. This model also enable ongoing cost savings for transportation as mentioned in the economic analysis above.

		Volume		
	Process Plant	**500 KTA**	**1000 KTA**	**1500 KTA**
Methanol route -Single Complex (MM tonne CO2e/year)	Methanol Synthesis	1.15	2.29	3.44
	MTO	0.33	0.66	0.99
	Polymerization	0.19	0.38	0.57
	Total	**1.67**	**3.34**	**5.01**
Methanol route - Dispersed mode (MM tonne CO2e/year)	Methanol Synthesis	1.15	2.29	3.44
	MTO	0.33	0.66	0.99
	Polymerization	0.19	0.38	0.57
	Methanol Shipment	0.90	1.79	2.68
	Total	**2.57**	**5.13**	**7.69**

Table V-10 – GHG emissions result for methanol route options

		Volume		
	Process Plant	**500 KTA**	**1000 KTA**	**1500 KTA**
Ethane Cracking route - Single Complex (MM tonne CO2e/year)	Gas Processing/LNG	1.52	3.03	4.55
	Ethane Cracking	0.51	1.02	1.53
	Polymerization	0.19	0.38	0.57
	LNG Shipment	0.64	1.28	1.93
	Total	**2.86**	**5.72**	**8.58**
Ethane Cracking route - Dispersed mode (MM tonne CO2e/year)	Gas Processing/LNG	1.52	3.03	4.55
	Ethane Cracking	0.51	1.02	1.53
	Polymerization	0.19	0.38	0.57
	LNG Shipment	0.73	1.44	2.17
	Regasification	0.43	0.86	1.29
	Total	**3.37**	**6.74**	**10.11**

Table V-11 – GHG emission results for ethane cracking route options

Although the absolute emissions of the ethane cracking route options are higher than of methanol option, it does not mean that the processes of ethane cracking route emit more GHG than processes of methanol route. Since the quantities of gas feed for two process routes are different, it is worth to view the GHG emission per MMBtu feed gas (table V-12). Among the options, the single manufacturing complex model for ethane cracking route has lowest emission per unit feed gas, while the dispersed manufacturing mode for methanol is highest in term of GHG emission.

	Supply Chain model	CO2e Emission (T CO2e/MMBtu feed gas)
Methanol Route	Single Complex	0.037
	Dispersed mode	0.056
Ethane Cracking Route	Single Complex	0.010
	Dispersed mode	0.012

Table V-12 – GHG emission result per MMBtu feed gas

CHAPTER VI

CONCLUSION AND FUTURE WORK

Conclusions

Incorporation of safety aspects in early stage of process synthesis and conceptual design of supply chains is challenging but important for generating valuable insights early enough in the project. A hierarchical approach has been developed to enable process engineers to include safety objectives in the design of a supply chain and the processes within the supply chain design. According to this framework, the design options are first generated and screened based on economic criteria. Economically infeasible options are removed from further consideration. Next, safety criteria are coupled with the economic metrics to assess the various designs and transportation options. The results of the risk assessment for each options are checked versus acceptable limits to remove unacceptable options. Findings from the hazard and risk assessment are used to generate design alternatives to improve the safety performance. Economic evaluation is updated for acceptable options to guide the decision making. The developed framework was applied to a case study on conceptual design of HDPE supply chain from shale gas. Various conceptual design options that considered different elements such as process technology, supply chain network and capacity were screened and evaluated per proposed framework. The safety aspects of the design options were evaluated by utilizing a high-level quantitative risk assessment approach with the limited engineering information that was available by the project phase.

Future work

This research can be expanded to include a multi-objective approach in conjunction with an algorithmic model to explore an optimum solution for process design and supply chain considering the multiple aspects as outlined in this research. Other direction is the integration of feedstock distribution that takes into account the capacity of supply sources, safety, risk and cost of transportation. Finally, mass and energy integration can be used to methodically generate and optimize design alternatives.

REFERENCES

AIChE (1994a) Dow's Chemical Exposure Index Guide. 1st edn. American Institute of Chemical Engineers, New York, NY

AIChE (1994b) Dow's Fire & Explosion Index Hazard Classification Guide. 7th edn. John Wiley & Sons, Inc., New York, NY

Air Liquide Global E&C Solutions (2015) Methanol-to-Propylene - Lurgi MTP Process. http://www.engineering-solutions.airliquide.com/file/otherelementcontent/pj/42/9e/ec/af/methanol-to-propylene%20flyer5517811988317851881.pdf. Accessed Sep 18, 2015

Biegler L. T., Grossmann I. E., Westerberg A. W. (1997) Systematic Methods of Chemical Process Design. Prentice Hall International Series in the Physical and Chemical Engineering Sciences. Prentice Hall, Upper Saddle River, NJ

Bullin K. A., Krouskop P. E. (2009) Compositional Variety Complicates Processing Plans for US Shale Gas, *Oil & Gas Journal* 107:50-55

CAMEO Chemicals (2015) Database of Hazardous Materials. http://cameochemicals.noaa.gov/. Accessed Aug 28, 2015

CCPS (2000) Guidelines for Chemical Process Quantitative Risk Analysis (2nd Edition). Center for Chemical Process Safety/AIChE, New York, NY

CCPS (2008) Guidelines for Hazard Evaluation Procedures (3rd Edition). Center for Chemical Process Safety/AIChE, New York, NY

CCPS (2009) Guidelines for Developing Quantitative Safety Risk Criteria. Center for Chemical Process Safety/AIChE, New York, NY

CCPS (2010) Inherently Safer Chemical Processes - A Life Cycle Approach. 2nd edn. John Wiley & Sons, Inc., New York, NY

CCPS (2012) Guidelines for Evaluating Process Plant Buildings for External Explosions, Fires, and Toxic Releases. 2nd edn. John Wiley & Sons, Inc., New York, NY. doi:10.1002/9781118312995.ch9

Chen J. Q., Bozzano A., Glover B., Fuglerud T., Kvisle S. (2005) Recent Advancements in Ethylene and Propylene Production Using the UOP/Hydro MTO Process, *Catalysis Today* 106:103-107 doi:http://dx.doi.org/10.1016/j.cattod.2005.07.178

Cheniere Energy Inc. (2014) Cheniere Energy Analyst/Investor Day. http://media.corporate-ir.net/media_files/IROL/10/101667/Analyst_Day_Presentation_WEBrev.pdf. Accessed Feb 19, 2015

Crowl D. A. (2011) Chemical Process Safety : Fundamentals with Applications. 3rd edn. Prentice Hall, Upper Saddle River, NJ

Edwards D. W., Lawrence D. (1993) Assessing The Inherent Safety of Chemical Process Routes: Is There a Relation Between Plant Costs and Inherent Safety?, *Process Safety and Environmental Protection* 71b:252 - 258

Ehlinger V. M., Gabriel K. J., Noureldin M. M. B., El-Halwagi M. M. (2014) Process Design and Integration of Shale Gas to Methanol, *ACS Sustainable Chemistry & Engineering* 2:30-37 doi:10.1021/sc400185b

El-Halwagi A. M., Rosas C., Ponce-Ortega J. M., Jiménez-Gutiérrez A., Mannan M. S., El-Halwagi M. M. (2013) Multiobjective Optimization of Biorefineries with Economic and Safety Objectives, *AIChE Journal* 59:2427-2434 doi:10.1002/aic.14030

El-Halwagi M. M. (2012) Sustainable Design Through Process Integration : Fundamentals and Applications to Industrial Pollution Prevention, Resource Conservation, and Profitability Enhancement. Elsevier Butterworth-Heinemann, Boston, MA

Gangadharan P., Singh R., Cheng F., Lou H. H. (2013) Novel Methodology for Inherent Safety Assessment in the Process Design Stage, *Industrial & Engineering Chemistry Research* 52:5921-5933

Gentile M., Rogers W. J., Mannan M. S. (2003) Development of a Fuzzy Logic-Based Inherent Safety Index, *Process Safety and Environmental Protection* 81:444-456

Heikkilä A. M. (1999) Inherent Safety in Process Plant Design: An Index-based Approach. D.Sc.Tech., Teknillinen Korkeakoulu (Helsinki) (Finland)

Hendershot D. C. (2006) An Overview of Inherently Safer Design, *Process Safety Progress* 25:98-107

Hugo A., Pistikopoulos E. N. (2005) Environmentally Conscious Long-range Planning and Design of Supply Chain Networks, *Journal of Cleaner Production* 13:1471-1491 doi:http://dx.doi.org/10.1016/j.jclepro.2005.04.011

International Energy Agency (2007) Tracking Industrial Energy Efficiency and CO2 Emissions. International Energy Agency, France

Jaramillo P., Griffin W. M., Matthews H. S. (2007) Comparative Life-Cycle Air Emissions of Coal, Domestic Natural Gas, LNG, and SNG for Electricity Generation, *Environmental Science & Technology* 41:6290-6296 doi:10.1021/es063031o

Khan F. I., Amyotte P. R. (2004) Integrated Inherent Safety Index (I2SI): A Tool for Inherent Safety Evaluation, *Process Safety Progress* 23:136-148 doi:10.1002/prs.10015

Khan F. I., Amyotte P. R. (2005) I2SI: A Comprehensive Quantitative Tool for Inherent Safety and Cost Evaluation, *Journal of Loss Prevention in the Process Industries* 18:310-326

Khan F. I., Husain T., Abbasi S. A. (2001) Safety Weighted Hazard Index (SWeHI), *Process Safety and Environmental Protection* 79:65-80

Khan F. I., Sadiq R., Amyotte P. R. (2003) Evaluation of Available Indices for Inherently Safer Design Options, *Process Safety Progress* 22:83-97 doi:10.1002/prs.680220203

Kletz T. A. (1978) What You Don't Have, Can't Leak, *Chemistry and Industry*:287-292

Kletz T. A., Amyotte P. R. (2010) Process Plants: A Handbook for Inherently Safer Design, 2nd Edition. CRC Press, Taylor & Francis Group,

Koller G., Fischer U., Hungerbühler K. (2000) Assessing Safety, Health, and Environmental Impact Early during Process Development, *Industrial & Engineering Chemistry Research* 39:960-972

Koller G., Fischer U., Hungerbühler K. (2001) Comparison of Methods Suitable for Assessing the Hazard Potential of Chemical Processes During Early Design Phases, *Process Safety and Environmental Protection* 79:157-166 doi:http://dx.doi.org/10.1205/095758201505119393

Leong C. T., Shariff A. M. (2009) Process Route Index (PRI) to Assess Level of Explosiveness for Inherent Safety Quantification, *Journal of Loss Prevention in the Process Industries* 22:216-221

Li X., Zanwar A., Jayswal A., Lou H. H., Huang Y. (2011) Incorporating Exergy Analysis and Inherent Safety Analysis for Sustainability Assessment of Biofuels, *Industrial & Engineering Chemistry Research* 50:2981-2993 doi:10.1021/ie101660q

Maher S. T., Norton K. D., Surmeli S. (2012) Design an Inherently Safer Plant, *Chemical Engineering Progress* 108:43-47

Mannan S., Lees F. P. (2005) Lees' Loss Prevention in the Process Industries: Hazard Identification, Assessment, and Control. 3rd edn. Elsevier Butterworth-Heinemann, Boston, MA

Methanol Institute (2013) Methanol Safe Handling Manual. http://www.methanol.org/getattachment/05f122f1-c9d3-47d8-8c16-5a5d39717cbe/Methanol-Safe-Handling-Manual-Final---English.pdf.aspx. Accessed Sep 6, 2015

Methanol Market Services Asia (MMSA) (2013) Methanol Shipping: A Snapshot. http://www.methanolmsa.com/wp-content/uploads/2013/11/Karan-Grover.pdf. Accessed Feb 25, 2015

Meyers R. A. (2005) Handbook of Petrochemicals Production Processes. McGraw-Hill, New York, NY

Moosemiller M. (2010) Development of Algorithms for Predicting Ignition Probabilities and Explosion Frequencies, *Process Safety Progress* 29:155-161 doi:10.1002/prs.10360

Morschbacker A. (2009) Bio-Ethanol Based Ethylene, *Polymer Reviews* 49:79-84 doi:10.1080/15583720902834791

Nowlin T. E. (2014) Business and Technology of the Global Polyethylene Industry : An In-depth Look at the History, Technology, Catalysts, and Modern Commercial Manufacture of Polyethylene and Its Products. Scrivener Publishing, Beverly, MA

Palaniappan C., Srinivasan R., Tan R. B. (2002a) Expert System for the Design of Inherently Safer Processes. 1. Route Selection Stage, *Industrial & Engineering Chemistry Research* 41:6698-6710

Palaniappan C., Srinivasan R., Tan R. B. (2002b) Expert System for the Design of Inherently Safer Processes. 2. Flowsheet Development Stage, *Industrial & Engineering Chemistry Research* 41:6711-6722

Pasman H., Reniers G. (2014) Past, Present and Future of Quantitative Risk Assessment (QRA) and the Incentive It Obtained from Land-Use Planning (LUP), *Journal of Loss Prevention in the Process Industries* 28:2-9

Petrochemical Conclave (2015) Outlook for Olefins and Polyolefins...and the Great Energy Price Deflation. http://petrochemconclave.com/presentation/2015/Mr.TPotter.pdf. Accessed Aug 21, 2015

PetroWiki (2015) Liquified Natural Gas (LNG). http://petrowiki.org/Liquified_natural_gas_(LNG). Accessed Feb 18, 2015

Rahman M., Heikkilä A.-M., Hurme M. (2005) Comparison of Inherent Safety Indices in Process Concept Evaluation, *Journal of Loss Prevention in the Process Industries* 18:327-334 doi:http://dx.doi.org/10.1016/j.jlp.2005.06.015

Rathnayaka S., Khan F., Amyotte P. (2014) Risk-based Process Plant Design Considering Inherent Safety, *Safety Science* 70:438-464 doi:http://dx.doi.org/10.1016/j.ssci.2014.06.004

Ren T., Patel M., Blok K. (2006) Olefins from Conventional and Heavy Feedstocks: Energy Use in Steam Cracking and Alternative Processes, *Energy* 31:425-451 doi:http://dx.doi.org/10.1016/j.energy.2005.04.001

Ren T., Patel M. K., Blok K. (2008) Steam Cracking and Methane to Olefins: Energy Use, CO2 Emissions and Production Costs, *Energy* 33:817-833 doi:http://dx.doi.org/10.1016/j.energy.2008.01.002

Shah N. (2005) Process Industry Supply Chains: Advances and Challenges, *Computers & Chemical Engineering* 29:1225-1235 doi:http://dx.doi.org/10.1016/j.compchemeng.2005.02.023

Share J. (2014) Global Demand for Polyethylene to Reach 99.6 Million Tons in 2018, *Pipeline & Gas Journal* 241:52

Shariff A. M., Leong C. T. (2009) Inherent Risk Assessment—A New Concept to Evaluate Risk in Preliminary Design Stage, *Process Safety and Environmental Protection* 87:371-376 doi:http://dx.doi.org/10.1016/j.psep.2009.08.004

Soares J. B. P., McKenna T. F. L. (2012) Polyolefin Reaction Engineering. Wiley-VCH Verlag GmbH & Co. KGaA. doi:10.1002/9783527646944.ch4

Srinivasan R., Natarajan S. (2012) Developments in Inherent Safety: A Review of the Progress During 2001–2011 and Opportunities Ahead, *Process Safety and Environmental Protection* 90:389-403 doi:http://dx.doi.org/10.1016/j.psep.2012.06.001

Towler G., Sinnott R. (2013) Chemical Engineering Design. 2nd edn. Elsevier Butterworth-Heinemann, Boston, MA

Tugnoli A., Cozzani V., Landucci G. (2007) A Consequence Based Approach to the Quantitative Assessment of Inherent Safety, *AIChE Journal* 53:3171-3182

Tugnoli A., Landucci G., Salzano E., Cozzani V. (2012) Supporting the Selection of Process and Plant Design Options by Inherent Safety KPIs, *Journal of Loss Prevention in the Process Industries* 25:830-842 doi:http://dx.doi.org/10.1016/j.jlp.2012.03.008

Tyler B. J. (1985) Using the Mond Index to Measure Inherent Hazards, *Plant/Operations Progress* 4:172-175 doi:10.1002/prsb.720040313

Woodward J. L., Pitblado R. M. (2010) LNG Risk Based Safety. John Wiley & Sons, Inc. doi:10.1002/9780470590232.ch4

Zimmermann H., Walzl R. (2000) Ethylene. In: Ullmann's Encyclopedia of Industrial Chemistry. Wiley-VCH Verlag GmbH & Co. KGaA. doi:10.1002/14356007.a10_045.pub3

APPENDIX A

DETAILED ECONOMIC ANALYSIS

OPTION 1 - Single Complex - 500 KTA						
			Methanol Synthesis	MTO	Polymerization	Total
	Capacity		2,280 KTA	510 KTA	500 KTA	
CAPEX	ISBL	MM$	2,085	690	352	
	OSBL	MM$	-	345	176	
	Total	MM$	2,085	1,035	528	3,648
Mater	Material	MM$	(123)			(123.32)
	Catalyst & Chemical	MM$	(14)		(25)	(38.70)
Revenue	Main Product	MM$			700.00	700
	By-product					
	Methane/LNG	MM$	-			-
	Propane	MM$	-			-
	Propylene	MM$		441.02		441.02
	Gasoline	MM$		101.22		101.22
	Fuel oil	MM$		-		-
	Fuel gas	MM$		0.69		0.69
Operating Cost	Labor	MM$	41.38	41.38	27.59	
	Maintenance	MM$	20.85	10.35	7.04	
	Utilities	MM$	21.65	18.76	10.81	
	Property Tax + Insurance	MM$	20.85	6.90	3.52	
	Environmental Charge	MM$	41.69	20.69	10.56	
	Rent	MM$	20.85	10.35	5.28	
	Total Operation Cost	MM$	167.27	108.42	64.80	(340.49)
	Depreciation	MM$	208.47	103.46	40.03	(364.76)
	Regasification	MM$				-
Transport	HDPE transport cost	MM$				(57.50)
	Methanol transport cost	MM$				-
	BT profit	MM$				318.16
	AATP	MM$				568.38
	ROI					15.6%

Table A-1 – Option 1 economic analysis

OPTION 2 - Single Complex - 1000 KTA						
			Methanol Synthesis	MTO	Polymerization	Total
	Capacity		4,570 KTA	1015 KTA	1000 KTA	
CAPEX	ISBL	MM$	3,716	1,379	704	
	OSBL	MM$	-	690	352	
	Total	MM$	3,716	2,069	1,056	6,842
Mater	Material	MM$	(247)			(246.65)
	Catalyst & Chemical	MM$	(27)		(50)	(77.41)
Revenue	Main Product	MM$			1,400.00	1,400
	By-product					
	Methane/LNG	MM$	-			-
	Propane	MM$	-			-
	Propylene	MM$		882.04		882.04
	Gasoline	MM$		202.44		202.44
	Fuel oil	MM$		-		-
	Fuel gas	MM$		1.39		1.39
Operating Cost	Labor	MM$	55.17	55.17	41.38	
	Maintenance	MM$	37.16	20.69	14.09	
	Utilities	MM$	43.30	37.51	21.62	
	Property Tax + Insurance	MM$	37.16	13.79	7.04	
	Environmental Charge	MM$	74.33	41.38	21.13	
	Rent	MM$	37.16	20.69	10.56	
	Total Operation Cost	MM$	284.28	189.25	115.82	(589.35)
	Depreciation	MM$	371.63	206.92	40.03	(684.19)
	Regasification	MM$				-
Trans port	HDPE transport cost	MM$				(115.00)
	Methanol transport cost	MM$				-
	BT profit	MM$				773.27
	AATP	MM$				1,179.08
	ROI					17.2%

Table A-2 – Option 2 economic analysis

OPTION 3 - Single Complex - 1500 KTA						
			Methanol Synthesis	MTO	Polymerization	Total
	Capacity		6,850 KTA	1525 KTA	1500 KTA	
CAPEX	ISBL	MM$	5,814	1,759	982	
	OSBL	MM$	-	880	491	
	Total	MM$	5,814	2,639	1,473	9,927
Mater	Material	MM$	(370)			(369.97)
	Catalyst & Chemical	MM$	(41)		(25)	(116.11)
Revenue	Main Product	MM$			2,100.00	2,100
	By-product					
	Methane/LNG	MM$	-			-
	Propane	MM$	-			-
	Propylene	MM$		1,323.05		1,323.05
	Gasoline	MM$		303.65		303.65
	Fuel oil	MM$		-		-
	Fuel gas	MM$		2.08		2.08
Operating Cost	Labor	MM$	82.76	82.76	55.17	
	Maintenance	MM$	58.14	26.39	19.64	
	Utilities	MM$	64.95	56.27	32.42	
	Property Tax + Insurance	MM$	58.14	17.59	9.82	
	Environmental Charge	MM$	116.29	52.78	29.46	
	Rent	MM$	58.14	26.39	14.73	
	Total Operation Cost	MM$	438.43	262.19	161.25	(861.87)
	Depreciation	MM$	581.44	263.91	40.03	(992.67)
	Regasification	MM$				-
Transport	HDPE transport cost	MM$				(172.50)
	Methanol transport cost	MM$				-
	BT profit	MM$				1,215.68
	AATP	MM$				1,770.70
	ROI					17.8%

Table A-3 – Option 3 economic analysis

OPTION 4 - Dispersed Mode - 500 KTA						
			Methanol Synthesis	MTO	Polymerization	Total
	Capacity		2,2800 KTA	510 KTA	500 KTA	
CAPEX	ISBL	MM$	2,085	766	391	
	OSBL	MM$	-	383	195	
	Total	MM$	2,085	1,148	586	3,819
Mater	Material	MM$	(123)			(123.32)
	Catalyst & Chemical	MM$	(14)		(25)	(38.70)
Revenue	Main Product	MM$			700.00	700
	By-product					
	Methane/LNG	MM$	-			-
	Propane	MM$	-			-
	Propylene	MM$		441.02		441.02
	Gasoline	MM$		101.22		101.22
	Fuel oil	MM$		-		-
	Fuel gas	MM$		0.69		0.69
Operating Cost	Labor	MM$	41.38	24.83	16.55	
	Maintenance	MM$	20.85	11.48	7.82	
	Utilities	MM$	21.65	18.76	10.81	
	Property Tax + Insurance	MM$	20.85	7.66	3.91	
	Environmental Charge	MM$	41.69	22.97	11.73	
	Rent	MM$	20.85	11.48	5.86	
	Total Operation Cost	MM$	167.27	97.18	56.68	(321.12)
	Depreciation	MM$	208.47	114.84	40.03	(381.95)
	Regasification	MM$				-
Trans port	HDPE transport cost	MM$				-
	Methanol transport cost	MM$				(171.28)
	BT profit	MM$				206.56
	AATP	MM$				514.15
	ROI					13.5%

Table A-4 – Option 4 economic analysis

OPTION 5 - Dispersed Mode - 1000 KTA						
			Methanol Synthesis	MTO	Polymerization	Total
	Capacity		4,570 KTA	1015 KTA	1000 KTA	
CAPEX	ISBL	MM$	3,716	1,531	782	
	OSBL	MM$	-	766	391	
	Total	MM$	3,716	2,297	1,173	7,186
Mater	Material	MM$	(247)			(246.65)
	Catalyst & Chemical	MM$	(27)		(50)	(77.41)
Revenue	Main Product	MM$			1,400.00	1,400
	By-product					
	Methane/LNG	MM$	-			-
	Propane	MM$	-			-
	Propylene	MM$		882.04		882.04
	Gasoline	MM$		202.44		202.44
	Fuel oil	MM$		-		-
	Fuel gas	MM$		1.39		1.39
Operating Cost	Labor	MM$	55.17	33.10	24.83	
	Maintenance	MM$	37.16	22.97	15.64	
	Utilities	MM$	43.30	37.51	21.62	
	Property Tax + Insurance	MM$	37.16	15.31	7.82	
	Environmental Charge	MM$	74.33	45.94	23.45	
	Rent	MM$	37.16	22.97	11.73	
	Total Operation Cost	MM$	284.28	177.80	105.07	(567.16)
	Depreciation	MM$	371.63	229.68	40.03	(718.57)
	Regasification	MM$				-
Trans port	HDPE transport cost	MM$				-
	Methanol transport cost	MM$				(342.56)
	BT profit	MM$				533.52
	AATP	MM$				1,060.02
	ROI					14.8%

Table A-5 – Option 5 economic analysis

OPTION 6 - Dispersed Mode - 1500 KTA						
			Methanol Synthesis	MTO	Polymerization	Total
	Capacity		6,850 KTA	1525 KTA	1500 KTA	
CAPEX	ISBL	MM$	5,814	1,953	1,090	
	OSBL	MM$	-	976	545	
	Total	MM$	5,814	2,929	1,635	10,379
Mater	Material	MM$	(370)			(369.97)
	Catalyst & Chemical	MM$	(41)		(75)	(116.11)
Revenue	Main Product	MM$			2,100.00	2,100
	By-product					
	Methane/LNG	MM$	-			-
	Propane	MM$	-			-
	Propylene	MM$		1,323.05		1,323.05
	Gasoline	MM$		303.65		303.65
	Fuel oil	MM$		-		-
	Fuel gas	MM$		2.08		2.08
Operating Cost	Labor	MM$	82.76	49.65	33.10	
	Maintenance	MM$	58.14	29.29	21.80	
	Utilities	MM$	64.95	56.27	32.42	
	Property Tax + Insurance	MM$	58.14	19.53	10.90	
	Environmental Charge	MM$	116.29	58.59	32.71	
	Rent	MM$	58.14	29.29	16.35	
	Total Operation Cost	MM$	438.43	242.63	147.29	(828.35)
	Depreciation	MM$	581.44	292.94	40.03	(1,037.90)
	Regasification	MM$				-
Trans port	HDPE transport cost	MM$				-
	Methanol transport cost	MM$				(513.84)
	BT profit	MM$				862.63
	AATP	MM$				1,589.98
	ROI					15.3%

Table A-6 – Option 6 economic analysis

OPTION 7 - Single Complex - 500 KTA						
			Gas Processing/ Liquefraction	Cracking	Polymerization	Total
	Capacity		286 Tcf	510 KTA	500 KTA	
CAPEX	ISBL	MM$	5,166	765	352	
	OSBL	MM$	2,583	382	176	
	Total	MM$	7,749	1,147	528	9,425
Mater	Material	MM$	(773)			(772.64)
	Catalyst & Chemical	MM$	(86)		(25)	(110.85)
Revenue	Main Product	MM$			700.00	700
	By-product					
	Methane/LNG	MM$	3,010.12			3,010.12
	Propane	MM$	77.09			77.09
	Propylene	MM$		6.78		6.78
	Gasoline	MM$		0.34		0.34
	Fuel oil	MM$		0.07		0.07
	Fuel gas	MM$		17.64		17.64
Operating Cost	Labor	MM$	55.17	41.38	27.59	
	Maintenance	MM$	51.66	11.47	7.04	
	Utilities	MM$	85.85	36.95	10.81	
	Property Tax + Insurance	MM$	51.66	7.65	3.52	
	Environmental Charge	MM$	154.98	22.95	10.56	
	Rent	MM$	77.49	11.47	5.28	
	Total Operation Cost	MM$	476.80	131.88	64.80	(673.48)
	Depreciation	MM$	774.88	114.75	40.03	(942.45)
	Regasification	MM$				-
Trans port	HDPE transport cost	MM$				(57.50)
	LNG transport cost	MM$				(715.92)
	BT profit	MM$				539.19
	AATP	MM$				1,287.54
	ROI					13.7%

Table A-7 – Option 7 economic analysis

OPTION 8 - Single Complex - 1000 KTA						
			Gas Processing/ Liquefraction	Cracking	Polymerization	Total
	Capacity		572.4 Tcf	1015 KTA	1000 KTA	
CAPEX	ISBL	MM$	8,392	1,160	704	
	OSBL	MM$	4,196	580	352	
	Total	MM$	12,588	1,739	1,056	15,384
Mater	Material	MM$	(1,545)			(1,545.27)
	Catalyst & Chemical	MM$	(172)		(50)	(221.70)
Revenue	Main Product	MM$			1,400.00	1,400
	By-product					
	Methane/LNG	MM$	6,020.23			6,020.23
	Propane	MM$	154.18			154.18
	Propylene	MM$		13.57		13.57
	Gasoline	MM$		0.67		0.67
	Fuel oil	MM$		0.14		0.14
	Fuel gas	MM$		35.27		35.27
Operating Cost	Labor	MM$	68.97	55.17	41.38	
	Maintenance	MM$	83.92	17.39	14.09	
	Utilities	MM$	171.70	73.90	21.62	
	Property Tax + Insurance	MM$	83.92	11.60	7.04	
	Environmental Charge	MM$	251.76	34.79	21.13	
	Rent	MM$	125.88	17.39	10.56	
	Total Operation Cost	MM$	786.14	210.24	115.82	(1,112.19)
	Depreciation	MM$	1,258.80	173.93	40.03	(1,538.37)
	Regasification	MM$				-
Trans port	HDPE transport cost	MM$				(115.00)
	LNG transport cost	MM$				(1,431.83)
	BT profit	MM$				1,659.70
	AATP	MM$				2,600.58
	ROI					16.9%

Table A-8 – Option 8 economic analysis

OPTION 9 - Single Complex - 1500 KTA						
			Gas Processing/ Liquefraction	Cracking	Polymerization	Total
	Capacity		858.5 Tcf	1525 KTA	1500 KTA	
CAPEX	ISBL	MM$	11,146	1,951	982	
	OSBL	MM$	5,573	976	491	
	Total	MM$	16,719	2,927	1,473	21,120
Mater	Material	MM$	(2,318)			(2,317.91)
	Catalyst & Chemical	MM$	(258)		(25)	(332.55)
Revenue	Main Product	MM$			2,100.00	2,100
	By-product					
	Methane/LNG	MM$	9,030.35			9,030.35
	Propane	MM$	231.27			231.27
	Propylene	MM$		20.35		20.35
	Gasoline	MM$		1.01		1.01
	Fuel oil	MM$		0.21		0.21
	Fuel gas	MM$		52.91		52.91
Operating Cost	Labor	MM$	110.34	82.76	55.17	
	Maintenance	MM$	111.46	29.27	19.64	
	Utilities	MM$	257.55	110.85	32.42	
	Property Tax + Insurance	MM$	111.46	19.51	9.82	
	Environmental Charge	MM$	334.39	58.54	29.46	
	Rent	MM$	167.19	29.27	14.73	
	Total Operation Cost	MM$	1,092.40	330.20	161.25	(1,583.85)
	Depreciation	MM$	1,671.94	292.71	40.03	(2,111.97)
	Regasification	MM$				-
Transport	HDPE transport cost	MM$				(172.50)
	LNG transport cost	MM$				(2,147.75)
	BT profit	MM$				2,769.57
	AATP	MM$				3,884.50
	ROI					18.4%

Table A-9 – Option 1 economic analysis

OPTION 10 - Dispersed Mode - 500 KTA						
			Gas Processing/ Liquefraction	Cracking	Polymerization	Total
	Capacity		286 Tcf	510 KTA	500 KTA	
CAPEX	ISBL	MM$	5,166	849	391	
	OSBL	MM$	2,583	425	195	
	Total	MM$	7,749	1,274	586	9,609
Mater	Material	MM$	(796)			(795.82)
	Catalyst & Chemical	MM$	(86)		(25)	(110.85)
Revenue	Main Product	MM$			700.00	700
	By-product					
	Methane/LNG	MM$	3,103.21			3,103.21
	Propane	MM$	77.09			77.09
	Propylene	MM$		6.78		6.78
	Gasoline	MM$		0.34		0.34
	Fuel oil	MM$		0.07		0.07
	Fuel gas	MM$		17.64		17.64
Operating Cost	Labor	MM$	55.17	24.83	16.55	
	Maintenance	MM$	51.66	12.74	7.82	
	Utilities	MM$	85.85	36.95	10.81	
	Property Tax + Insurance	MM$	51.66	8.49	3.91	
	Environmental Charge	MM$	154.98	25.47	11.73	
	Rent	MM$	77.49	12.74	5.86	
	Total Operation Cost	MM$	476.80	121.22	56.68	(654.69)
	Depreciation	MM$	774.88	127.37	40.03	(960.89)
	Regasification	MM$				(81.18)
Trans port	HDPE transport cost	MM$				-
	LNG transport cost	MM$				(811.80)
	BT profit	MM$				489.91
	AATP	MM$				1,274.43
	ROI					13.3%

Table A-10 – Option 10 economic analysis

OPTION 11 - Dispersed Mode - 1000 KTA						
			Gas Processing/ Liquefraction	Cracking	Polymerization	Total
	Capacity		572.4 Tcf	1015 KTA	1000 KTA	
CAPEX	ISBL	MM$	8,392	1,287	782	
	OSBL	MM$	4,196	644	391	
	Total	MM$	12,588	1,931	1,173	15,691
Mater	Material	MM$	(1,592)			(1,591.63)
	Catalyst & Chemical	MM$	(177)		(50)	(226.85)
Revenue	Main Product	MM$			1,400.00	1,400
	By-product					
	Methane/LNG	MM$	6,206.42			6,206.42
	Propane	MM$	154.18			154.18
	Propylene	MM$		13.57		13.57
	Gasoline	MM$		0.67		0.67
	Fuel oil	MM$		0.14		0.14
	Fuel gas	MM$		35.27		35.27
Operating Cost	Labor	MM$	68.97	33.10	24.83	
	Maintenance	MM$	83.92	19.31	15.64	
	Utilities	MM$	257.55	73.90	21.62	
	Property Tax + Insurance	MM$	83.92	12.87	7.82	
	Environmental Charge	MM$	251.76	38.61	23.45	
	Rent	MM$	125.88	19.31	11.73	
	Total Operation Cost	MM$	871.99	197.10	105.07	(1,174.16)
	Depreciation	MM$	1,258.80	193.06	40.03	(1,569.13)
	Regasification	MM$				(162.36)
Trans port	HDPE transport cost	MM$				-
	LNG transport cost	MM$				(1,672.30)
	BT profit	MM$				1,413.83
	AATP	MM$				2,473.98
	ROI					15.8%

Table A-11 – Option 11 economic analysis

OPTION 12 - Dispersed Mode- 1500 KTA						
			Gas Processing/ Liquefraction	Cracking	Polymerization	Total
	Capacity		858.5 Tcf	1525 KTA	1500 KTA	
CAPEX	ISBL	MM$	11,146	2,166	1,090	
	OSBL	MM$	5,573	1,083	545	
	Total	MM$	16,719	3,249	1,635	21,604
Mater	Material	MM$	(2,387)			(2,387.45)
	Catalyst & Chemical	MM$	(258)		(75)	(332.55)
Revenue	Main Product	MM$			2,100.00	2,100
	By-product					
	Methane/LNG	MM$	9,309.64			9,309.64
	Propane	MM$	231.27			231.27
	Propylene	MM$		20.35		20.35
	Gasoline	MM$		1.01		1.01
	Fuel oil	MM$		0.21		0.21
	Fuel gas	MM$		52.91		52.91
Operating Cost	Labor	MM$	110.34	49.65	33.10	
	Maintenance	MM$	111.46	32.49	21.80	
	Utilities	MM$	257.55	110.85	32.42	
	Property Tax + Insurance	MM$	111.46	21.66	10.90	
	Environmental Charge	MM$	334.39	64.98	32.71	
	Rent	MM$	167.19	32.49	16.35	
	Total Operation Cost	MM$	1,092.40	312.13	147.29	(1,551.81)
	Depreciation	MM$	1,671.94	324.91	40.03	(2,160.38)
	Regasification	MM$				(243.54)
Trans port	HDPE transport cost	MM$				-
	LNG transport cost	MM$				(2,435.39)
	BT profit	MM$				2,604.28
	AATP	MM$				3,827.11
	ROI					17.7%

Table A-12 – Option 12 economic analysis

APPENDIX B

CASE STUDY CHEMICALS AND THEIR PROPERTIES

Chemical Name	CAS Number	Physical State	NFPA 704			
			H	F	R	Special
Diethanolamine, $C_4H_{11}NO_2$	111-42-2	Liquid	3	1	0	
Dimethyl Ether, DME, C_2H_6O	115-10-6	Gas	2	4	1	
Ethane, C_2H_6	74-84-0	Gas	1	4	0	
Ethanolamine, C_2H_7NO	141-43-5	Liquid	3	2	0	
Methylethanolamine, C_3H_9NO	109-83-1	Liquid	3	2	0	
Ethylene, C_2H_4	74-85-1	Gas	2	4	2	
Fuel Oil No.1		Liquid	2	2	0	
Gasoline	86290-81-5	Liquid	1	3	0	
Glycol, Diethylene, $C_4H_{10}O_3$	111-46-6	Liquid	1	1	1	
Glycol, Ethylene, $C_2H_6O_2$	107-21-1	Liquid	2	1	0	
Glycol, Tetraethylene, $C_8H_{18}O_5$	112-60-7	Liquid	1	1	0	
Glycol, Triethylene, $C_6H_{14}O_4$	112-27-6	Liquid	1	1	0	
Hydrogen Sulfide; H_2S	7783-06-4	Gas	4	4	0	
Hydrogen, H_2	1333-74-0	Gas	0	4	0	
Isobutane, C_4H_{10}	75-28-5	Gas	0	4	0	
Liquefied Natural Gas	74-82-8	Liquid	3	4	0	
Methane, CH_4	74-82-8	Gas	2	4	0	
Methanol, CH_3OH	67-56-1	Liquid	1	3	0	
Natural Gas	74-82-8	Gas	3	4	0	
Nitrogen, N_2	7727-37-9	Gas	NA	NA	NA	
Oxygen, Liquid, O_2	7782-44-7	Liquid	3	0	0	OX
Polyethylene, High Density	9002-88-4	Solid	NA	NA	NA	
Propane, C_3H_8	74-98-6	Gas	2	4	0	
Propylene, C_3H_6	115-07-1	Gas	1	4	1	
Sulfur Dioxide, SO_2		Gas	3	0	0	
Sulfur Trioxide, SO_3		Liquid	3	0	2	
Sulfur, S		Liquid	1	1	0	
Water, H_2O		Liquid	0	0	0	

Table B-1 – Case study chemicals and their properties (CAMEO Chemicals 2015; Crowl 2011)

Chemical Name	CAS Number	Physical State	Flash Pt. °F(°C)	Auto-Ignition Temp. °F(°C)	Flammable Limits	Lower Heat of Combustion (kJ/mol)
Diethanolamine, $C_4H_{11}NO_2$	111-42-2	Liquid	279	1224	1.6%-9.8%	
Dimethyl Ether, DME, C_2H_6O	115-10-6	Gas	25	662	2%-50%	
Ethane, C_2H_6	74-84-0	Gas	-211	940	2.9%-13%	-1428.6
Ethanolamine, C_2H_7NO	141-43-5	Liquid	200	770	5.5%-17%	
Methylethanolamine, C_3H_9NO	109-83-1	Liquid	165	NA	NA	
Ethylene, C_2H_4	74-85-1	Gas	-213	842	2.75%-28.6%	-1322.6
Fuel Oil No.1		Liquid	100	444	0.7%-5%	
Gasoline	86290-81-5	Liquid	-36	853	1.4%-7.4%	
Glycol, Diethylene, $C_4H_{10}O_3$	111-46-6	Liquid	290	NA	1.6%-10.8%	
Glycol, Ethylene, $C_2H_6O_2$	107-21-1	Liquid	232	775	3.2%- NA-%	
Glycol, Tetraethylene, $C_8H_{18}O_5$	112-60-7	Liquid	360	NA	NA	
Glycol, Triethylene, $C_6H_{14}O_4$	112-27-6	Liquid	330	NA	0.9%-9.2%	
Hydrogen Sulfide; H_2S	7783-06-4	Gas	NA	500	4.3%-45%	
Hydrogen, H_2	1333-74-0	Gas	NA	1065	4%-75%	-241.8
Isobutane, C_4H_{10}	75-28-5	Gas	-117	890	1.8%-8.4%	-2649
Liquefied Natural Gas	74-82-8	Liquid	NA	999	5.3%-14%	
Methane, CH_4	74-82-8	Gas	-306	1004	5%-15%	-802.3
Methanol, CH_3OH	67-56-1	Liquid	52	867	6%-36.5%	-631.1
Natural Gas	74-82-8	Gas	NA	NA	NA	
Nitrogen, N_2	7727-37-9	Gas	NA	NA	NA	-
Oxygen, Liquid, O_2	7782-44-7	Liquid	NA	NA	NA	
Polyethylene, High Density	9002-88-4	Solid	430	NA	NA	
Propane, C_3H_8	74-98-6	Gas	-156	842	2.1%-9.5%	-2043.1
Propylene, C_3H_6	115-07-1	Gas	-162	851	2%-11.1%	-1925.7
Sulfur Dioxide, SO_2		Gas	NA	NA	NA	
Sulfur Trioxide, SO_3		Liquid	NA	NA	NA	
Sulfur, S		Liquid	370	450	NA	
Water, H_2O		Liquid	NA	NA	NA	

Table B-1 – Case study chemicals and their properties (cont'd) (CAMEO Chemicals 2015; Crowl 2011)

Chemical Name	CAS Number	Physical State	PHYSICAL PROPERTIES			
			Molecular Wt.	Boiling Point °F(°C)	Melting Point °F(°C)	Heat of Vaporization (BTU/lb)
Diethanolamine, $C_4H_{11}NO_2$	111-42-2	Liquid	105.14	516.40	82.0	
Dimethyl Ether, DME, C_2H_6O	115-10-6	Gas	46.07	-8.00	-217.3	
Ethane, C_2H_6	74-84-0	Gas	30.07	-127.50	-279.9	210.41
Ethanolamine, C_2H_7NO	141-43-5	Liquid	61.08	338.00	50.5	
Methylethanolamine, C_3H_9NO	109-83-1	Liquid	75.11	316.00	23.9	
Ethylene, C_2H_4	74-85-1	Gas	28.05	-154.70	-272.4	
Fuel Oil No.1		Liquid	170	380-560	-55	70.19
Gasoline	86290-81-5	Liquid	72	140 - 390	NA	67.89
Glycol, Diethylene, $C_4H_{10}O_3$	111-46-6	Liquid	106.12	473.00	14.0	393
Glycol, Ethylene, $C_2H_6O_2$	107-21-1	Liquid	62.07	387.70	9.0	449
Glycol, Tetraethylene, $C_8H_{18}O_5$	112-60-7	Liquid	194.23	621.00	24.8	273
Glycol, Triethylene, $C_6H_{14}O_4$	112-27-6	Liquid	150.17	545.00	24.3	270
Hydrogen Sulfide; H_2S	7783-06-4	Gas	34.08	-76.59	-121.9	235.6
Hydrogen, H_2	1333-74-0	Gas	2.016	-423.00	-434	194
Isobutane, C_4H_{10}	75-28-5	Gas	58.12	10.80	-427.5	
Liquefied Natural Gas	74-82-8	Liquid	>16	-258	-296	
Methane, CH_4	74-82-8	Gas	16.04	-258.70	-296.5	219.22
Methanol, CH_3OH	67-56-1	Liquid	32.04	148.30	-144	
Natural Gas	74-82-8	Gas	NA	NA	NA	NA
Nitrogen, N_2	7727-37-9	Gas	28.013	-320.10	-354	85.6
Oxygen, Liquid, O_2	7782-44-7	Liquid	32	-297.30	-361	91.6
Polyethylene, High Density	9002-88-4	Solid	0000 - 5000	NA	185 - 230	
Propane, C_3H_8	74-98-6	Gas	44.097	-43.8	-305.9	185
Propylene, C_3H_6	115-07-1	Gas	42.08	-53.9	-301.4	
Sulfur Dioxide, SO_2		Gas	64.05	14.00	-104.8	166.7
Sulfur Trioxide, SO_3		Liquid	80.06	112.60	62.2	235.3
Sulfur, S		Liquid	32.06	279.22	233-246	651.6
Water, H_2O		Liquid	18.015	212.00	32.0	970.3

Table B-1 – Case study chemicals and their properties (cont'd) (CAMEO Chemicals 2015; Crowl 2011)

Chemical Name	CAS Number	Physical State	PHYSICAL PROPERTIES		
			Specific Gravity (7)	Vapor Pressure mm Hg	Vapor Density (related to air)
Diethanolamine, $C_4H_{11}NO_2$	111-42-2	Liquid	1.095	5.000	3.650
Dimethyl Ether, DME, C_2H_6O	115-10-6	Gas	0.724	2.128	1.617
Ethane, C_2H_6	74-84-0	Gas	0.546	NA	NA
Ethanolamine, C_2H_7NO	141-43-5	Liquid	1.016	0.4	2.100
Methylethanolamine, C_3H_9NO	109-83-1	Liquid	0.941	0.7	2.590
Ethylene, C_2H_4	74-85-1	Gas	0.569	NA	NA
Fuel Oil No.1		Liquid	0.81-0.85	5.000	NA
Gasoline	86290-81-5	Liquid	0.7321	382.58	NA
Glycol, Diethylene, $C_4H_{10}O_3$	111-46-6	Liquid	1.118	< 0.01	3.660
Glycol, Ethylene, $C_2H_6O_2$	107-21-1	Liquid	1.115	0.060	2.140
Glycol, Tetraethylene, $C_8H_{18}O_5$	112-60-7	Liquid	1.120	NA	NA
Glycol, Triethylene, $C_6H_{14}O_4$	112-27-6	Liquid	1.125	< 0.001	5.170
Hydrogen Sulfide; H_2S	7783-06-4	Gas	0.916	15200.000	1.190
Hydrogen, H_2	1333-74-0	Gas	0.071	NA	NA
Isobutane, C_4H_{10}	75-28-5	Gas	0.557	3.100	NA
Liquefied Natural Gas	74-82-8	Liquid	0.415 - 0.45	NA	NA
Methane, CH_4	74-82-8	Gas	0.422	258574	0.550
Methanol, CH_3OH	67-56-1	Liquid	0.792	100 - 237.87	1.110
Natural Gas	74-82-8	Gas	NA	NA	NA
Nitrogen, N_2	7727-37-9	Gas	0.807	NA	NA
Oxygen, Liquid, O_2	7782-44-7	Liquid	1.140	NA	NA
Polyethylene, High Density	9002-88-4	Solid	0.920	NA	NA
Propane, C_3H_8	74-98-6	Gas	0.590	9823.000	1.500
Propylene, C_3H_6	115-07-1	Gas	0.609	760.000	1.460
Sulfur Dioxide, SO_2		Gas	1.434		
Sulfur Trioxide, SO_3		Liquid	1.840		
Sulfur, S		Liquid	0.234		
Water, H_2O		Liquid	1.000		

Table B-1 – Case study chemicals and their properties (cont'd) (CAMEO Chemicals 2015; Crowl 2011)

APPENDIX C

CASE STUDY DETAILED INDIVIDUAL RISKS OF PROCESS OPTIONS

		500 KTA		1000 KTA		1500 KTA	
	Process Unit	Control room	Admin	Control room	Admin	Control room	Admin
Single complex	Natural gas processing	9.80E-06	6.23E-06	1.48E-05	9.39E-06	1.89E-05	1.20E-05
	Methanol synthesis	3.27E-05	0.00E+00	4.93E-05	0.00E+00	6.29E-05	0.00E+00
	Methanol storage	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Methanol conversion	2.97E-04	0.00E+00	4.49E-04	0.00E+00	5.73E-04	0.00E+00
	Ethylene	7.30E-05	0.00E+00	1.10E-04	0.00E+00	1.41E-04	0.00E+00
	Propylene	4.75E-05	0.00E+00	7.17E-05	0.00E+00	9.16E-05	0.00E+00
	HDPE	2.68E-05	0.00E+00	4.07E-05	0.00E+00	5.17E-05	0.00E+00
	Subtotal	4.87E-04	6.23E-06	7.35E-04	9.39E-06	9.39E-04	1.20E-05
	Total	4.93E-04		7.45E-04		9.51E-04	

Table C-1 – Detailed individual risks of methanol route single complex manufacturing options

		500 KTA		1000 KTA		1500 KTA	
	Process Unit	Control room	Admin	Control room	Admin	Control room	Admin
Location 1	Natural gas processing	9.80E-06	6.23E-06	1.48E-05	9.39E-06	1.89E-05	1.20E-05
	Methanol synthesis	3.27E-05	0.00E+00	4.93E-05	0.00E+00	6.29E-05	0.00E+00
	Methanol storage	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
Location 2	Methanol storage	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Methanol conversion	2.97E-04	0.00E+00	4.49E-04	0.00E+00	5.73E-04	0.00E+00
	Ethylene	7.30E-05	0.00E+00	1.10E-04	0.00E+00	1.41E-04	0.00E+00
	Propylene	4.75E-05	0.00E+00	7.17E-05	0.00E+00	9.16E-05	0.00E+00
	HDPE	2.68E-05	0.00E+00	4.07E-05	0.00E+00	5.17E-05	0.00E+00
	Subtotal	4.87E-04	6.23E-06	7.35E-04	9.39E-06	9.39E-04	1.20E-05
	Total	4.93E-04		7.45E-04		9.51E-04	
	Methanol transportatio	1.109E-05		1.109E-05		1.109E-05	

Table C-2 – Detailed individual risks of methanol route dispersed manufacturing options

		500 KTA		1000 KTA		1500 KTA	
	Process Unit	**Control room**	**Admin**	**Control room**	**Admin**	**Control room**	**Admin**
Single complex	Gas processing	8.92E-06	8.30E-06	1.35E-05	1.26E-05	1.73E-05	1.61E-05
	LNG production	2.97E-05	2.29E-05	4.50E-05	3.47E-05	5.76E-05	4.43E-05
	LNG storage	8.38E-06	4.86E-06	1.27E-05	7.36E-06	1.62E-05	9.42E-06
	Steam cracking	1.28E-04	0.00E+00	1.94E-04	0.00E+00	2.47E-04	0.00E+00
	Ethylene	5.18E-05	0.00E+00	7.91E-05	0.00E+00	1.01E-04	0.00E+00
	Propylene	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	HDPE	2.68E-05	0.00E+00	4.07E-05	0.00E+00	5.17E-05	0.00E+00
	Subtotal	2.54E-04	3.61E-05	3.85E-04	5.46E-05	4.91E-04	6.98E-05
	Total	2.90E-04		4.39E-04		5.60E-04	
	LNG Transportation	6.72E-04		6.72E-04		6.72E-04	

Table C-3 – Detailed individual risks of ethane cracking route single complex manufacturing options

		500 KTA		1000 KTA		1500 KTA	
	Process Unit	**Control room**	**Admin**	**Control room**	**Admin**	**Control room**	**Admin**
Location 1	Gas processing	8.92E-06	8.30E-06	1.35E-05	1.26E-05	1.73E-05	1.61E-05
	LNG production	2.97E-05	2.29E-05	4.50E-05	3.47E-05	5.76E-05	4.43E-05
	LNG storage	8.38E-06	4.86E-06	1.27E-05	7.36E-06	1.62E-05	9.42E-06
Location 2	Steam cracking	1.28E-04	0.00E+00	1.94E-04	0.00E+00	2.47E-04	0.00E+00
	Ethylene	5.18E-05	0.00E+00	7.91E-05	0.00E+00	1.01E-04	0.00E+00
	Propylene	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00	0.00E+00
	Gas processing	8.92E-06	8.30E-06	1.35E-05	1.26E-05	1.73E-05	1.61E-05
	LNG production	2.97E-05	2.29E-05	4.50E-05	3.47E-05	5.76E-05	4.43E-05
	LNG storage	8.38E-06	4.86E-06	1.27E-05	7.36E-06	1.62E-05	9.42E-06
	HDPE	2.68E-05	0.00E+00	4.07E-05	0.00E+00	5.17E-05	0.00E+00
	Subtotal	3.01E-04	7.21E-05	4.56E-04	1.09E-04	5.82E-04	1.40E-04
	Total	3.73E-04		5.65E-04		7.21E-04	
	LNG Transportation	6.72E-04		6.72E-04		6.72E-04	

Table C-4 – Detailed individual risks of ethane cracking route dispersed manufacturing options

APPENDIX D

METHANOL TANKER SHIPMENT FATALITY RATE ESTIMATION

Worldwide, by 2013 there were roughly 4100 ships capable for methanol ocean shipment. (Methanol Market Services Asia (MMSA) 2013)

According to Methanol Institute, there were 22 incidents related to methanol transport in period of 1998 – 2011, resulted in 14 fatalities. (Methanol Institute 2013) In these 22 incidents, 12 incidents were fire and explosion. However further detailed data was not given for fatalities rate associated with type of transportation (i.e., ocean tanker, barge, tanker truck, or railroad). These data were compiled based on information collected from internet. Therefore, for maximum fatalities rate related to ocean tanker methanol transport, it was assumed to use 14 facilities in this period.

The potential loss of life per ocean tanker ship year was calculated as below:

$$\frac{14\ fatalities}{22\ incidents} \times \frac{1}{14\ years} \times \frac{1}{4100\ ships} = 1.109\ \times 10^{-5}/ship\ year$$