SAFETY AND TECHNO-ECONOMIC ANALYSIS OF ETHYLENE TECHNOLOGIES

A Thesis

by

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ABSTRACT

Inherent safety is a concept that enables risk reduction through elimination or reduction of hazards at the grass root level of a process development cycle. This proactive approach aids in achieving effective risk management while minimizing fixed and operating cost. Several indices which quantify the measures of inherent safety have been identified and by applying these techniques on conceptual design stage, an estimate of the inherent risk and additional safety cost measures can be developed. This approach facilitates easy decision making in an early stage, for choosing the best process that is superior in process, economic and safety performance. Yet, these quantitative techniques are not being used effectively in process industries. In this thesis, a comparative approach was developed wherein, two different process technologies producing same chemical were compared through techno-economic and safety analysis, to identify the superior process.

Recent advancements in shale gas monetization have contributed to the growth and expansion of large number of petrochemical plants, particularly the ethylene industry. For this thesis, the production of ethylene through two process technologies were considered, such that one route is the primary process route while other is a novel process that is still in development stage. The process routes identified were ethane steam cracking, a well-established process and “ECLAIRS” (Ethylene from Concentrated Liquid phase Acetylene- Integrated, Rapid and Safe), an emerging Gas to ethylene process. A top level analysis was performed using key quantitative indicators of process, cost and inherent safety. The results show that the state of art technology of ethane cracking has an attractive process and economic potential, while the gas to ethylene technology is more inherently safer. The areas of improvement were identified and critical analysis of metrics was carried out.

DEDICATION

To

My Parents

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First of all, I would like to thank my committee chair, Dr. Mahmoud El-Halwagi for providing continuous, positive support and guidance throughout the course of this research. I would also like to thank my committee members and other department faculty for sharing their knowledge and expertise in the field of chemical engineering. I would also like express my gratitude to Dr. Fadwa El-Jack from Qatar University, for providing valuable inputs on ethylene processes. I sincerely believe that this learning experience has strengthened my fundamental understanding and helped me appreciate new concepts in the field of process safety and chemical engineering.

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CHAPTER I

INTRODUCTION

Process risk management is a fundamental concept of chemical process safety that involves identifying, reducing and managing risks in chemical processes.(Center for Chemical Process, 2008b) Risk is a function of consequence and likelihood of a hazard, where hazard is defined as a potential harm caused by a condition. (Center for Chemical Process, 2008b) In order to effectively manage risks, a thorough hazard analysis must be done to identify all possible hazards produced in a process. Followed by identification, efforts should be taken to reduce those hazards that have high consequences as well as a large likelihood of occurrence. Since, it is impossible to eliminate all the hazards completely in a process, the risk levels should be maintained at a minimum level by continual improvement and effective management. One of those powerful ways of reducing risk is done by eliminating the root cause of hazards in a process. (Center for Chemical Process, 2008b) The approach of identifying the source of hazard and developing methods to eliminate or reduce impact of source is termed as inherent safety approach. (Center for Chemical Process, 2008b)

Hazards of a chemical process are inherent in nature, caused predominantly due to operating conditions, quantities of chemicals, characteristics of chemicals, size and location of unit operations. Consequence of a hazard arising out of an abnormal condition increases with increase in intensity of the above mentioned factors. In addition to these factors there are several other types of hazards such as mechanical hazards of rotary equipment, electrical hazards, safety hazards and few other that can attribute to further severity of hazard consequence.

In order to effectively neutralize the consequence of a hazard, the probability of an abnormal condition is thwarted by following risk reduction in four levels.(Center for Chemical Process, 2008a)

i. Inherent - Reducing or eliminating hazards that are present in the process condition or chemicals involved in processes.
ii. Passive – Eliminating hazards by subduing the impact of an abnormal condition without the use of any human initiated controls or automatic device activation.
iii. Active – Eliminating hazards by thwarting the occurrence of a hazard by initiating manual controls or automatic device activation.
iv. Procedural – Implementing policies, training and other managerial regulations that can effectively help in early identification of a hazard and abnormal situation management, thus preventing an accident from occurring. (Center for Chemical Process, 2008a)

The above mentioned approaches are used in all stages of process development and they seek to address all the hazards present in a process. Though all the methods contribute in increasing overall safety, inherent and passive ways are proven to be the most effective way of risk reduction because they don’t involve any manual or automatic intervention.(Dennis, 2012) Hence, they are considered reliable and robust techniques of risk management.(Dennis, 2012) Inherent safety approach is one such method that can be applied at any stage of a chemical process with ease. However, basic safety of the process is enhanced on implementing the inherent safety approach at the preliminary level of a chemical process life cycle.(Kletz, 1985) This approach is a fundamental and logical way of eliminating risks by removing materials or reducing intensity of process variables that cause significant impact on safety. (Kletz, 1985)

Inherent Safety as defined by CCPS (Center for Chemical Process Safety) is given by: "A chemical manufacturing process is inherently safer if it reduces or eliminates the hazards associated with materials and operations used in the process and this reduction or elimination is permanent and inseparable." (Center for Chemical Process, 2008a) The concept of inherent safety was first introduced by Trevor Kletz, who suggested change in basic technology to remove hazards, rather than adding additional layers to protect the inherent hazards.(Kletz, 1985) Effective inherent safety is achieved with the change or modification done starting from process chemistry followed by change in intensive process parameters and design of equipment. The four main guiding principles of inherent safety approach are defined as follows:(Kletz, 1985)

i. Minimization: Minimizing the inventory of the material, size of equipment, pipeline size can reduce the risk of an incident significantly.

ii. Substitution: Substituting the more hazardous chemical with a less hazardous chemical that gives same or better performance is an effective method of risk reduction. A process that produces more hazardous intermediates or by products that require additional separation processes can be substituted by a less dangerous technology.

iii. Moderation: Moderating the intensity of process parameters such as reduced temperatures and pressure favor in enhancement of safety.

iv. Simplification: A simplified process that has minimum number of equipment not only reduces fixed and operating cost but also enhances safety.

Inherent safety gained importance after the occurrence of two major accidents in chemical industry: Bhopal Gas tragedy, India (1984) and Explosion at Flixborough, UK.(Kletz, 1985) Both these incidents depict lack of sound process design and illustrate the need for inherently safer design at the initial stage. Following these incidents, continuous efforts have been taken to popularize the concept of Inherently Safer Designs (ISD) and thus improve safety at all levels of a process development. The brief details of the cause and consequence of these two accidents are explained below to understand the need of inherent safety approach.

I.1. Bhopal Gas Tragedy, India (1984)

On December 3, 1984, near Bhopal, India, approximately 41 tonnes of a toxic chemical named Methyl Iso-Cyanate leaked from a chemical plant manufacturing Carbaryl, a pesticide.(Gupta, 2002) This disaster caused approximately 3000+ fatalities and 300,000 injuries.(Gupta, 2002) Methyl Iso-Cyanate, was stored as a chemical intermediate in the process of manufacturing Carbaryl. On the day of the incident, a storage tank containing large quantities of Methyl Iso-Cyanate got contaminated with water which led to an exothermic runaway reaction, causing sudden rise in temperature and pressure.(Kletz, 1985) Increase in pressure caused the pressure relief valve to rupture, causing the toxic gas to be leaked through the flare system.

The release of the toxic gas has been attributed to improper maintenance of safety equipment, lack of proper controls and emergency response, and improper knowledge of chemical.(Browning, 1993) Investigations revealed that the refrigeration system that was designed to cool the storage tank was non-operational as a cost-cutting measure for saving refrigerant. (Browning, 1993) The pressure relief valve of the storage tank was connected to a vent gas scrubber system, followed by a flare system. It was later found that the scrubber system and the flare system were taken offline for maintenance. (Browning, 1993)In addition to negligent use of safety system, the plant personnel were not properly trained to manage emergencies. (Browning, 1993)

This incident is a perfect example of a Swiss-cheese model. When loopholes in each layer of protection align together, then the occurrence of incident is unpreventable. The disadvantage of adding additional layer of protection and the need of more reliable protection is demonstrated in this incident. Studies reveal that Carbaryl can be produced by the same reactants as used in Bhopal chemical plant, but in a different order that avoids the formation of MIC.(Kletz, 2006) Also, if the inventory levels of the plant were reduced, then the disaster could have been possibly avoided. This demonstrates that by applying the key strategies of inherent safety, effective risk management can be achieved.

I.2. Flixborough, UK (1974)

On June 1, 1974, an explosion occurred in a plant manufacturing nylon near Flixborough, UK.(Kletz, 2006) The cause of explosion came from the unit containing six reactors connected in series, in which cyclohexane reacted with oxygen to form cyclohexanol and cyclohexanone mixture.(Kletz, 2006) The reactors were stacked in such as fashion to facilitate the flow of liquid cyclohexane from one reactor to other through gravity.(Kletz, 2006) Leakage of one of the reactors led to removal of that equipment for maintenance. A temporary pipeline was fitted to connect the remaining two reactors in order to keep the production running, but it was not mechanically designed to withstand the sudden rise in pressures in the reactors.(Kletz, 2006) On the day of the incident, the pipeline ruptured and led to a sudden release of flammable cyclohexane in huge quantities that ignited, causing a violent explosion. The explosion killed 28 plant personnel and destroyed the entire plant.(Kletz, 2006) The cause of explosion was attributed to poor mechanical design of the temporary pipeline.(Kletz, 2006) The other underlying reasons of this huge explosion is attributed to large inventory of flammable liquid and the inventory is due to poor conversion rates of each reactor.(Kletz, 2006) This is yet another example showing the need for a different technology that minimizes the use of hazardous materials while increasing or maintaining same production. Studies reveal that by reacting cyclohexane with water and oxygen, a better conversion can be achieved to manufacture the same chemical.(Kletz, 2006) This will ensure reduction in volume of the unit as well as specific consumption of hazardous chemical.

The above mentioned accidents demonstrate how poor process design and inefficient operations affect safety. Soon after these incidents, chemical industries adopted different approaches for replacement of a safer technology to produce the same chemical compound. The lesson to be inferred is that hazards caused by the physical and chemical conditions of materials has to be identified earlier and reduced or modified to attenuate the impact, than by adding additional layers of protection. However, layers of protection are vital in reducing risk and hence, proper and reliable layer of protection is to be used.

The typical layers of protection in a chemical process development stage are illustrated below in Figure 1. (S2S-A Gateway for Plant and Process Safety, 2003) Layers of protection provide additional safety measures to suppress the effect of the potential hazards. (Center for Chemical Process, 2008a) These add-on layers do not intend to eliminate hazards, but instead they prevent and control the incidents from happening using manual, automatic and administrative controls. (Center for Chemical Process, 2008a) Every additional layer added reduces the overall risk, but also introduces the need for more reliable equipment. As reliability of equipment increases cost of equipment increases thus, causing a major impact on the fixed and operating cost of the plant. Addition of too many equipment also causes complexity in the process and this increases chances of human and operational error. In order to optimize the reliability and cost of safety, it is important to choose a process that is inherently safe designed so that, safety is ensured with minimal cost of operation and more reliability.

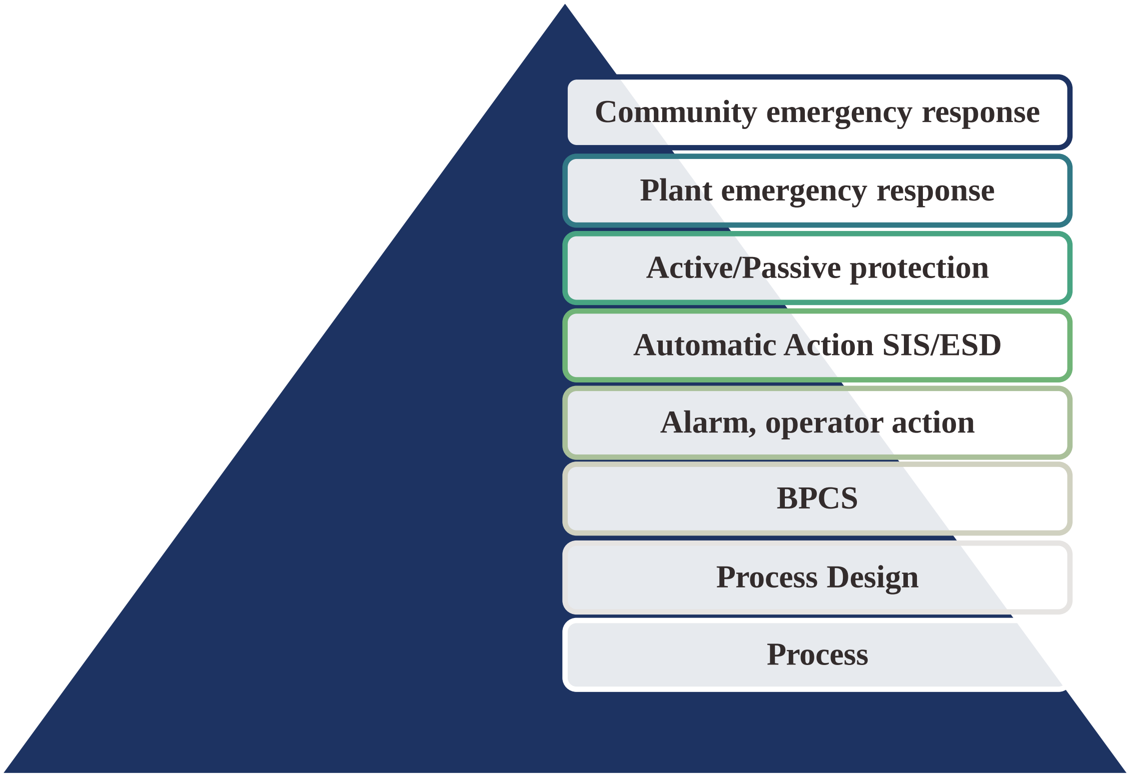


Figure 1: Typical Layers of Protection in a chemical process. Adapted from (S2S-A Gateway for Plant and Process Safety, 2003)

A chemical process development lifecycle is illustrated below in Figure 2. Inherently Safer Design approach is applied at all levels of process development but is cost effective to apply in research and development and conceptual design stage.(Dennis, 2012) This is because in the conceptual design stage after having identified the hazards, there are more opportunities to substitute or modify a process that is not designed and constructed.(Dennis, 2012) In the basic engineering stage, a better picture of process economics and process flow diagram is retrieved, including piping and instrumentation diagram, plant layout, process variables and Layers Of Protection Analysis (LOPA).(Maher, Norton, & Surmeli, 2012) At this stage there are still better opportunities of modification since, more information about the process is obtained. A preliminary Hazards Operability (HAZOP) study identifies all possible hazards and efforts should be taken to reduce the imminent danger in the process than adding layers of protection.(Maher et al., 2012) From the above discussion, it is inferred that the above mentioned process development levels are crucial for determining the safety levels and additional cost of safety to be invested. Applying ISD approach in the later stages can cause time delays, additional cost of redesign and also reduces opportunities of modification.(Dennis, 2012) Nevertheless, ISD can still be applied at all stages such that a good, if not the best process design can be constructed.

Though the concept of ISD clearly carries a lot of benefits, it is not being followed by most of the chemical industries. The reasons are attributed to companies' focus on more productivity, restrictive attitude of exploring new technologies, lack of clarity, ignorance and less time spent on HAZOP in the preliminary stages of design.(Kletz, 1985) Other reasons include conflicting interest between safety and process yield, environmental concerns or economics.(Khan & Amyotte, 2003)

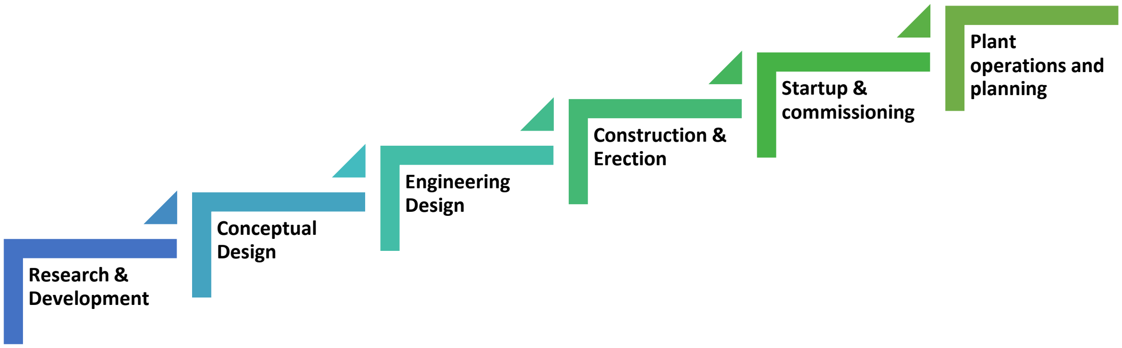


Figure 2: Stages of Chemical Process Development. Adapted from (Bauer & Maciel Filho, 2004)

The above introduction to the concept of inherent safety provides a new route to deal with the hazards identified in a process. This approach provides a wide array of benefits including cost reduction while managing risks and also increase reliability. Yet, the approach is adapted only by a few companies in an effective way. This necessitates development of a problem statement whose principle objective is to apply the inherent safety approach at the conceptual design stage, to demonstrate its merits and method of choosing a safe approach to design. The problem statement can be described as making an effective overall decision between two chemical process routes for producing same chemical compound by analyzing the process technologies, economics of operation and inherent safety levels of the processes. Quantitative measures of all the three key performance factors are evaluated and a top level analysis is performed to select the process having minimum risk at basic level without addition of any layers of protection. The base case product chosen for the study is ethylene and the processes are identified such that one route is a well-established, state of art technology while the other one is a novel technology, that is yet to be commercialized.(Wood, Nwaoha, & Towler, 2012)

The aim of this thesis is to illustrate the idea of inherent safety by doing a top-level quantitative analysis of safety on the base case and comparing the safety levels with the process economics and technology. This study aims to analyze the inherent safety levels of two different process routes producing the same chemical compound and decide on the inherently safer process subject to cost and technological factors. There are several indices that can be used to measure inherent safety and these indices represent the magnitude of potential impact of a process. Another objective of this analysis is to identify areas of process improvement that can help in improving process efficiency as well as safety. This analysis also helps in comparing the operating cost with safety of the plant, so that decisions can be made that are equally beneficial to both the factors. The final aim is to rank all the major equipment/ sections of the plant that impact safety and provide possible recommendations for risk reduction.

The general approach to the problem statement can be illustrated by the Figure 3. Initially, chemical kinetics and general process flow data for both the process technologies are collected from literature. Using this data, a steady state process simulation is carried out with the aid of computational software. From the simulation results, the process parameters, heating and cooling requirements of each unit are calculated. From these results, fixed and operating costs of both the plants are calculated. Energy costs and raw material costs are extracted based on the current prices of natural gas, natural gas liquids and oil. (ICIS, 2015)Following calculation of economic metrics, a basic design analysis is carried out to extract data on size and capacity of unit operations.

After preliminary review of different quantitative hazard indices available, a suitable index is chosen that accounts for intensity of operating conditions and characteristics of chemicals handled. Since ethylene is a derivative of hydrocarbons, a fire and explosion index based on Hazard Identification and Ranking System is chosen as the safety metric.(Khan & Abbasi, 1998) The scope of the safety analysis is restricted to only the process technology (i.e. only process conditions and main stream process flow). Hence the physical location of units and external safety hazards are not considered for analysis. After applying safety metrics on all process units, the indices are ranked according to their level of potential damage or hazard. The economic metrics and safety metrics are compared for each process to identify the process that is inherently safe while being economically beneficial.

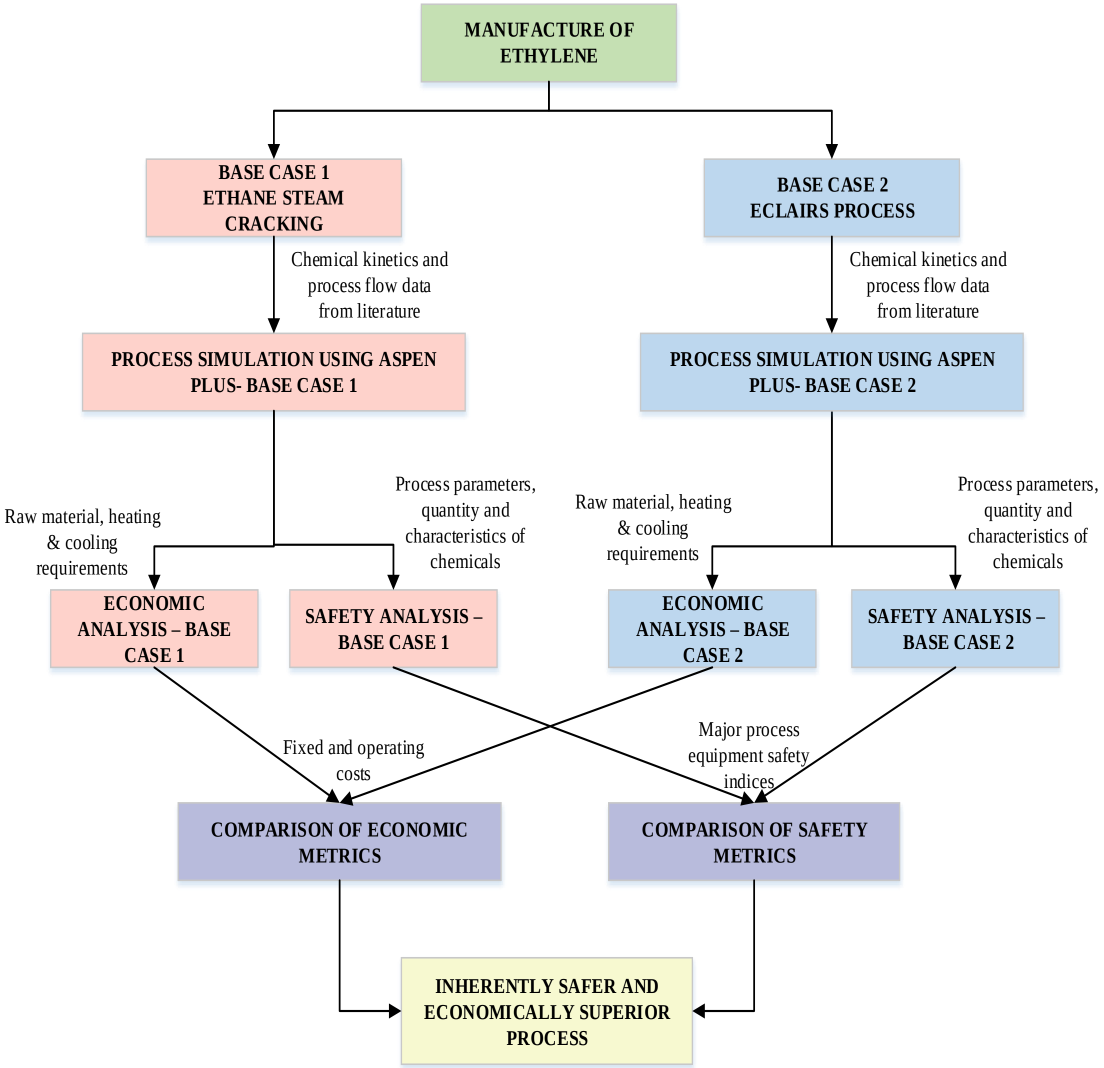


Figure 3: Approach methodology of techno-economic and safety analysis.

CHAPTER II

LITERATURE REVIEW

Recent advancements made in extracting more natural gas from untapped shale gas reserves have opened the door for huge opportunities of shale gas monetization in the petrochemical market. Natural Gas Liquid (NGL) reserves have also increased significantly along with shale gas recoveries and this has led to exploration of opportunities that use NGLs such as ethane, propane and butane as raw materials.(Thomas K. Swift, Martha G. Moore, & Sanchez, 2011) Studies show that ethane, one of the primary components recovered from NGL has a huge market for producing petrochemical intermediates rather than being burnt as a fuel. (Thomas K. Swift et al., 2011)These shale gas developments have led to a 25% increase of ethane supply. (Thomas K. Swift et al., 2011) This increase has created a major growth in petrochemical production capacities, investment in chemical industries, taxes, revenue and economic output.(True, 2013)

One of those petrochemical industry that is undergoing a great deal of expansion is the ethylene industry. Ethylene is a primary petrochemical compound that is used in the manufacture of polyethylene, ethylene dichloride, ethylene oxide, ethyl benzene, vinyl acetate and other miscellaneous chemicals. (Thomas K. Swift et al., 2011) The shale gas boom has led to announcement of 10 new projects to produce ethylene. Table 1 given below shows the major projects announced for expansion of ethylene.

Table 1: Proposed additions of U.S. ethylene production capacity, 2013-2020. (True, 2013)

Company	**Location**	**Proposed capacity in million metric tons per year**
Chevron Phillips	Baytown, TX	1.5
Exxon Mobil	Baytown, TX	1.5
Sasol	Lake Charles, LA	1.4
Dow	Freeport, TX	1.4
Shell	Beaver Co, PA	1.3
Formosa	Point Comfort, TX	0.8
Occidental/Mexichem	Ingleside, TX	0.5
Dow	St. Charles, LA	0.4
LyondellBasell	Laporte, TX	0.4
Aither Chemicals	Kanawha, WV	0.3
Williams/Sabic JV	Geismar, LA	0.2
Ineos	Alvin, TX	0.2
Westlake	Lake Charles, LA	0.2
Williams/Sabic JV	Geismer, LA	0.1
Total		**10.1**

The new projects encompass an additional capacity of 12.5 million tonnes/year, leading to 52 % increase in current US ethylene capacity.(Chang, 2014) This has in turn led to increase in production capacities of important intermediates such as polyethylene, polyvinyl chloride and ethylene glycol. (Chang, 2014) The result of expansion is aimed at meeting the demand for ethylene, and the figure below explains the yearly trend of ethylene production, consumption and demand. From Figure 4 which represents ethylene supply and demand, it is clear that from the year 2013 the capacities of ethylene complexes will be high and the production will be sufficient to meet the demand.

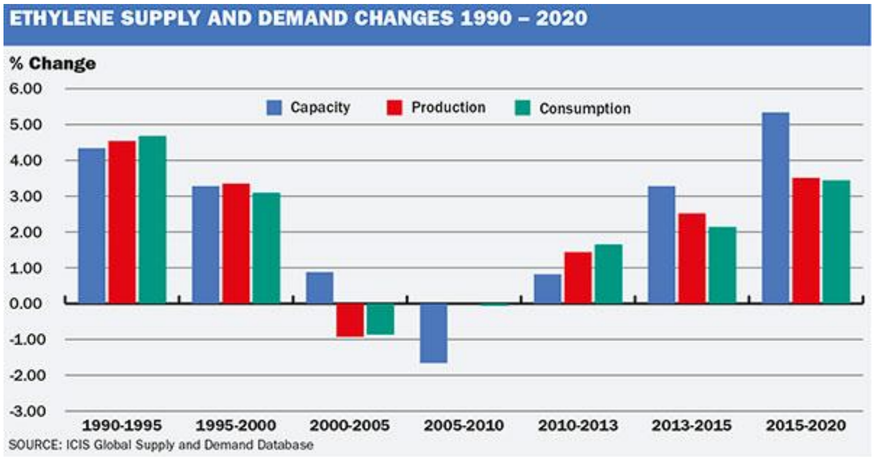
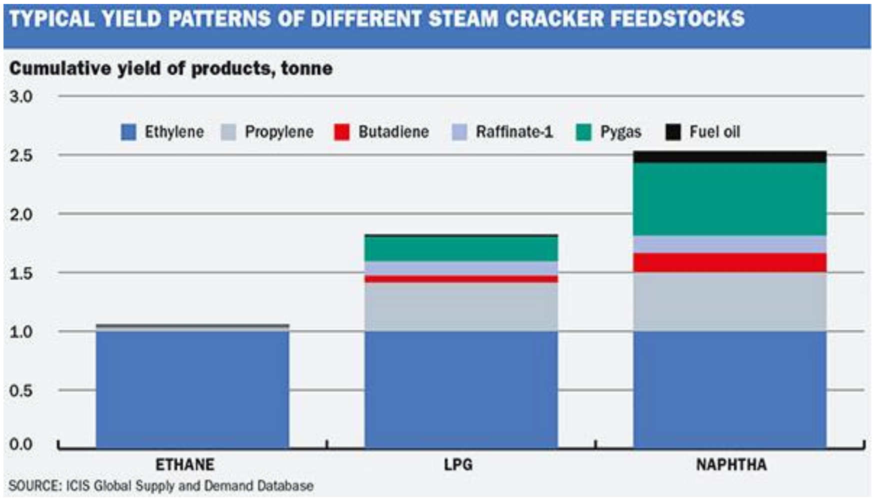


Figure 4: Ethylene supply and demand change. (ICIS, 2015)

Ethylene is primarily manufactured through steam cracking of naphtha or ethane, and this is the oldest and most established technology for producing ethylene. (Thomas K. Swift et al., 2011) Over 85% of ethylene is derived from ethane feedstock. (Thomas K. Swift et al., 2011) With more availability of ethane, steam cracking of ethane is gaining more importance. Moreover, the excess supply has made prices of ethane cheaper than naphtha and hence, a lot of projects are already underway to convert naphtha crackers to gas crackers.(True, 2013) Literature studies also reveal that specific consumption of ethane is much lower than that of naphtha.(Ren, Patel, & Blok, 2006) Other advantages of using ethane feedstock are low CO2 emission, high ethylene and hydrogen yield and less heaviers.(Ren et al., 2006) The Figure 5 shown below illustrates the comparison of different feed stocks of cracker. Since ethane cracking is already a fully matured technology, it offers less of a chance for exploring modifications in the process for improving safety. Hence, this base case will serve as an excellent basis for comparison of other new technologies.



SOURCE: ICIS Global Supply and Demand Database

Figure 5: Yield patterns of different steam cracking feed stocks. (ICIS, 2015)

Another competing technology is a novice technology called “ECLAIRS,” which involves usage of natural gas as the raw material.(Gattis, Peterson, & Johnson, 2004) Natural gas also serves as an excellent raw material due to the abundant supply and cheap price. Pyrolysis of methane to acetylene, followed by selective hydrogenation to ethylene is the main chemistry.(Gattis et al., 2004) This new gas to ethylene technology is currently designed and operated by Synfuels International Inc. at a test scale level.(Gattis et al., 2004) Since it is a new technology, more opportunities exist to identify areas that lack safety and demonstrate the idea of inherent safety effectively. Hence, a safety techno-economic comparison of this process with the state of art ethane cracking technology will help in identifying dark areas and will deliver clear benefits of choosing one over the other.

II.1. Safety Metrics

Literature review shows a wide array of systematic quantitative tools adopted for measuring the risk and inherent safety of a process. Quantitative metrics are objective based and are more effective since they represent the magnitude of impact. Moreover, the scale of improvement achieved by modifying a process or operating variables is well interpreted by a quantitative measure such as a safety or a hazard index and this facilitates continual improvement. Thus, these indices can be useful in capturing the application of inherent safety design principles. Safety indices are simple to use in the early stage of design for hazard identification since they do not require detailed process information and are also cheaper than the more traditional approaches such as HAZOP, FTA (Fault Tree Analysis) and FMEA (Failure Mode and Effect Analysis).(Khan, Sadiq, & Amyotte, 2003) They are easy to calculate and enable easy comparison between processes.(Khan et al., 2003) A list of most commonly used safety metrics is discussed below.

II.1.1. Dow Fire and Explosion Index

Dow fire and explosion index is the most commonly used index in chemical industries.(Khan et al., 2003) This index has been revised seven times with the latest published in 1994.(Khan et al., 2003) This index is primarily calculated after the basic engineering stage when all the design parameters, layout, spacing, controls and detection systems are added.(AichE, 1994) The information needed for evaluating fire and explosion index are plot plan, process flow diagram, replacement cost data of equipment and details of all layers of protection.(AichE, 1994). Initially, a parameter called Material Factor (MF) which measures the hazard potential in terms of flammable and reactive characteristics of the material is calculated.(AichE, 1994) This is followed by calculation of general and special process hazards. General process hazards (F1) account for penalties due to exothermic and endothermic reactions, material transfer, access, enclosed units and drainage and spill control of chemical.(AichE, 1994) Special process hazards (F2) include penalties for hazardous operating conditions, process parameters, quantity, corrosion and types of equipment used in operation.(AichE, 1994) The above mentioned process hazards are multiplied to get process unit hazards factor (F3), which is again multiplied with material factor to get the fire & explosion index.(AichE, 1994) Later, Loss Control Credit Factor (LCCF) is calculated by multiplying credits assigned on the basis of availability of process controls, material isolation techniques and fire protection added.(AichE, 1994) Finally, from the calculated Fire and Explosion Damage Index (FEDI), a radius of exposure, area exposed to the hazard and the replacement cost of all equipment in that area are calculated.(AichE, 1994)

Damage radius = 0.84* FEDI

Additional factor called a damage factor, which represents the degree of loss exposure is calculated based on MF and F3. This damage factor multiplied with value of area exposed gives base Maximum Probable Property Damage (MPPD).(AichE, 1994)

By applying loss credit factor to this value, the actual MPPD is determined. Subsequently, maximum probable day's outage and the business interruption in terms of monetary value are calculated.(AichE, 1994) The penalties and credits are based on designated ranges of parameters calculated using expert-based knowledge. The advantage of using this index is that it accounts for all design details and correlates the damage incurred to monetary value. But, from the above calculation method, it is clear that Dow index is a very comprehensive and laborious process of hazard identification. It is also expensive due to the amount of data required and additionally, it requires technical expertise to decide on the penalty and credit values.

II.1.2. Mond Index

The Mond fire, explosion and toxicity index was developed by Mond division at ICI.(Khan et al., 2003) The approach and principles of calculation are similar to Dow index, except that Mond index includes additional hazards.(Khan et al., 2003) The major changes incorporated in Mond index are that it includes a wider range of storage and process facilities, processing of explosive chemicals, toxicity hazards index, deviating effects of good design, extended plant layout, indices to account for fire, aerial and internal explosion.(Lewis, 1979) The initial procedure of hazard assessment due to fire and explosion are the same as Dow index except for some additional factors included in the assessment. An additional toxicity index is included, which is based on toxic characteristics of the chemical, quantity in use and health implications.(Khan et al., 2003) Fire, explosion and toxicity indices calculated are analyzed and compared with the acceptable risk standards.(Lewis, 1979) Following this, reviews of the hazard factors namely the general and special process hazards are done to implement design changes that would reduce the risk levels.(Lewis, 1979) Finally, credits for implementation of preventive control features are accounted and final indices are recalculated.(Lewis, 1979) Thus, this index carries an additional advantage of accounting for special hazard considerations. However, it carries the same disadvantage as that of Dow index because this procedure is also time-consuming and comprehensive.

II.1.3. Inherent Safety Index (ISI)

Inherent safety index is used for measuring the inherent safety potential of a process. ISI is a modified version of Prototype Index of Inherent Safety (PIIS).(Heikkilä, Hurme, & Järveläinen, 1996) The PIIS introduced by Edward & Lawrence was mainly reaction-oriented and failed to include other processes into consideration.(Edwards & Lawrence, 1993) ISI accounts for all the process attributes combined with the chemical characteristics.(Heikkilä et al., 1996) This index is effective for making business decisions for choosing process alternatives producing the same product. The total inherent safety is represented by the below mentioned formula:(Heikkilä et al., 1996)

$I_{TI} = I_{CI} + I_{PI}$

I_{CI} (chemical inherent safety index) represents the value contributed by chemicals and chemical characteristics while I_{PI} (Physical inherent safety index) represents process parameters and other physical factors.(Heikkilä et al., 1996) The addition of these sub-indices form the total inherent safety index (I_{TI}) which depicts the basic hazard potential of the process.(Heikkilä et al., 1996) The chemical inherent safety index is addition of individual scores assigned to 7 categories, namely heat of reaction, heat of side reaction, flammability, toxicity, explosiveness, corrosiveness and chemical interactions.(Heikkilä et al., 1996) The process inherent safety is the addition of individual scores assigned to five categories namely inventory, pressure, temperature, equipment safety and safety of process structure.(Heikkilä et al., 1996) The approach uses different databanks for each sub-category to extract information about them.(Heikkilä et al., 1996) The scores are based on experienced based ranges of values for each sub-category. The scale of score varies such that the smaller score represents a highly safe process and vice versa.(Heikkilä et al., 1996) Hence, the process with higher I_{TI} value indicates that it is more hazardous. The advantage of using this index is that due to the requirement of basic information on chemicals and process, it can be easily applied during the conceptual stage of design for choosing better alternatives. The disadvantage is that the index is subjective type and is based on a semi-quantitative scoring pattern which might yield different results for different users based on their experience.

II.1.4. Safety Weighted Hazard Index (SWeHI)

SWeHI is an advanced and modified version of its predecessor index, HIRA (Hazard Identification and Ranking). This index aims to capture the entire picture of a process by including all factors such as process, environment and society and how they impact safety.(Khan, Husain, & Abbasi, 2001) Quantitatively, it represents the radius of area that is hazardous, caused due to operating and environmental conditions of a particular unit/ section.(Khan et al., 2001) The formula for calculating the SWeHI index is given as follows:(Khan et al., 2001)

$SWeHI = B/A$

In the above formula, B represents the damage caused due to fire, explosion or toxic release of a particular unit under the assumption of a 50% probability of damage. ‘A’ represents the credits gained due to the safety measures and controls adopted for either preventing occurrence of an accident or reducing the frequency.(Khan et al., 2001) Thus, if the control measures are low, the value of index will be high suggesting that the unit or process is not safe. This type of analysis is best suited for identifying, comparing and ranking different units within a process, so that maximum focus can be given on the more hazardous equipment for safety improvement. The method of approach and calculation of B is identical to the calculation of the HIRA index except for addition of two penalties; one accounts for external factors such as earthquakes and floods while the other accounts for vulnerability of surroundings such as accident and societal clashes.(Khan et al., 2001) The calculation of A is done by considering two subgroups: one that measures the controls adopted and the other that reduces the frequency of occurrence. The general formula is given by:(Khan et al., 2001)

$A = 0.15*\sum (1+cr_i)$

In the above mentioned formula, credits are included to account for emergency response planning, disaster management planning, other control measures such as foam, water and fire extinguishing materials available, control systems, detecting systems, emergency control measures, human error and human reliability.(Khan et al., 2001) Each of these categories is further divided into sub categories that are additive and the final number is calculated by using the above mentioned formula. All the quantification methods used in the calculation of B are derived from thermodynamic, empirical models, National Fire Protection Agency (NFPA) rankings, American Petroleum Institute (API) standards, process safety design codes, storage area classification guidelines and Dow index.(Khan et al., 2001) The calculation of A is based on expert decisions, literature studies on controls, detection and human error.(Khan et al., 2001) Thus, this index has attempted to quantify factors predominantly based on objective type data. Hence, it is reliable and is very effective in specifically identifying areas where safety controls need to be added. However, the disadvantage of this index is that it can be applied only for a fully designed or an existing plant, thus failing to fetch opportunities of improving the actual process.

II.1.5. Hazard Identification and Ranking System (HIRA)

The Hazard Identification and Ranking System introduced by Khan and Abbasi in the year 1998 is a systematic and comprehensive methodology of hazard identification.(Khan & Abbasi, 1998) This method aims to be more sensitive to process parameters and is accurate since the quantification is made using thermodynamic and fluid dynamics models. The index accounts for impact of hazards posed by a unit at elevated temperatures due to environmental factors and surroundings.(Khan & Abbasi, 1998) Hence, it is accurate in describing the hazard potential of a unit. This index is unique from other indices such that it considers different classes of equipment according to the hazards specific to it, thus accounting for all kinds of hazards of each unit.(Khan & Abbasi, 1998) The various units that are classified based on their special hazards are:(Khan & Abbasi, 1998)

i. Storage units
ii. Physical units with operations such as pumping, mass and heat transfer and compression.
iii. Unit having chemical reactions
iv. Transportation units
v. Other hazardous units such as boilers, furnaces and fired heaters

The HIRA index is a combination of two other indices: Fire and Explosion Damage Index (FEDI) and Toxicity Damage Index (TDI).(Khan & Abbasi, 1998) The estimation of FEDI is based on several penalties and energy factors. Finally, a damage potential is calculated from which the FEDI is estimated using the following formula:(Khan & Abbasi, 1998)

$\text{FEDI} = 4.76 * (\text{Damage potential})^{1/3}$

FEDI is the damage radii represented in meters. The semi-quantitative ranking is given by Table 2.

Table 2: Semi-quantitative hazard ranking of FEDI. (Khan & Abbasi, 1998)

Fire and Explosion damage Index (FEDI)	Hazard Characterization
FEDI>500	Extremely hazardous
500>FEDI>400	Highly hazardous
400>FEDI>200	Hazardous
200>FEDI>100	Moderately hazardous

Table 2: Continued.

Fire and Explosion damage Index (FEDI)	Hazard Characterization
100>FEDI>20	Less hazardous
else	No hazard

An illustrative diagram describing the various penalties and energy factors is given in Figure 6. The algorithm for calculating temperature and pressure penalties for different classes of units vary depending on the equipment class specific guidelines. Other penalties calculated include that for location of nearest hazardous units, capacity, characteristics of chemicals, density of units, physical state of chemical during transport, quantity of fuel used in furnaces, type of reaction and probability of side or runaway reactions.(Khan & Abbasi, 1998) These penalties are included in the estimation of FEDI depending on their applicability to that particular class of equipment. All the values of penalties obtained are from thermodynamic, empirical models, API standards, NFPA rankings, Dow index and other quantitative relationships derived from literature studies.(Khan & Abbasi, 1998)

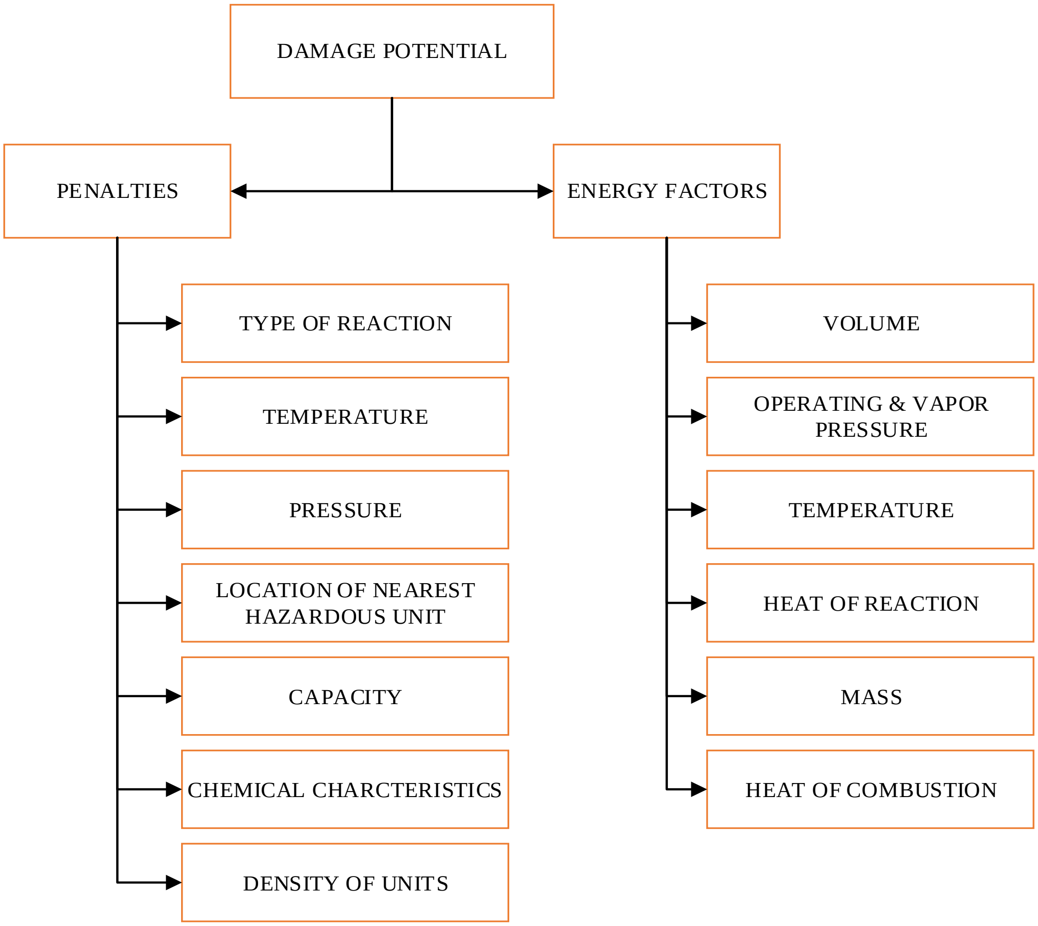


Figure 6: Factors affecting Damage potential.

The toxic damage index methodology is devised to calculate the measure of toxic load that is lethal over an area.(Khan & Abbasi, 1998) It is derived using transport phenomena and empirical models depending on quantity, its toxicity, physical state of chemical, operating conditions and site characteristics.(Khan & Abbasi, 1998) An assumption of slightly stable atmospheric condition is made for dispersion calculations. The calculation of TDI is done by considering a G factor and several other penalties.(Khan & Abbasi, 1998) G factor considers situations such as release of superheated liquid that cause vapor flash and pool of liquid, release of gas leading to dispersion into atmosphere, liquefied gas having two-phase release and pyrophilic solids giving toxic vapors.(Khan & Abbasi, 1998) The formula is given by:(Khan & Abbasi, 1998)

$G = A * m$

In the above formula, A is a function of release conditions and m is the mass released in kg/s. The penalties calculated account for operating pressure, temperature, toxicity of chemical, vapor density and site characteristics.(Khan & Abbasi, 1998) The formula for calculating TDI is given by:(Khan & Abbasi, 1998)

$TDI = 25.35 * (G * \prod \text{penalties})^{0.425}$

The advantage of using the HIRA methodology of hazard identification is that most of the penalties and energy factors calculated are directly from empirical relations and literature studies. This makes it a more reliable quantification and further enables easy interpretation of results. In addition to this, the concept of addressing unit specific hazards based on the different units involved in an industry facilitates accurate calculation of hazard potential. The semi-quantitative ranking enables us to focus on those areas that are extremely hazardous. The disadvantages of this index include the calculation procedure being comprehensive and requirement of detailed design with equipment layout and plot plan. Another drawback of this index is that it does not take into account any credit for control systems or preventive measures taken in the plant thus, giving an overestimated magnitude of impact.(Khan et al., 2001)

Comprehensive tools such as Dow, Mond index are applied in industries extensively after the detailed engineering phase. However, the availability of indices that can accurately measure the amount of inherent safety during the conceptual stage of design are less in number. This is one of the reason why industries do not adopt inherent safety assessment at early stages. From literature review, it is concluded that in this thesis, the hazard identification and ranking system will be adopted for analyzing inherent safety on the ethylene base plants. This is because HIRA index is based on fundamental thermodynamic models which makes the quantification more objective-based. Further, it is flexible in choosing what penalties can be included, depending upon the available amount of information. Since, it does not account for control systems and prevention systems, it is easy to identify the factor that directly impacts the inherent safety of the unit. Otherwise, the general tendency is to add more protection devices than identifying the root cause of the hazard.

Hence, this index is highly suitable for determination of actual inherent safety. In this thesis, penalties accounting for location of nearest hazardous unit and space occupied by the unit will be neglected. This proves to be a valid assumption, since the objective is to compare different units and rank them based on inherent safety. Also, since ethylene is primarily a hydrocarbon compound, only the fire and explosion index will be determined. The scope of this analysis is restricted only to the main process stream and hence other external hazards that impact the unit will not be considered.

II.2. Economic Metrics

Economics of operation plays a crucial role in selecting alternative process routes. Cost of building a plant is influenced by several factors. Some of those factors include process efficiency, process yield, availability of cheap raw material, equipment cost, utility consumption, profit, environmental emissions and safety measures of plant. The main economic metrics that dictate the decision making process are fixed and operating cost. Fixed cost of equipment for two identical well-established technologies having literature data for capacities and capital cost are determined using the correlation:(El-Halwagi, 2012)

$FCI_B = FCI_A * (\text{Capacity of B/ Capacity of A})^{0.6}$

In the above formula, FCI is the Fixed Capital Investment. Another method for calculating the fixed capital investment is based on the cost of delivered equipment. This method includes a factor that incorporates a collective term for cost of installation, piping & instrumentation and other engineering installations.(El-Halwagi, 2012) This method known as Lang method is given by the following formula:(El-Halwagi, 2012)

FCI = FCI Lang factor * Delivered equipment cost

The value of Lang factor depends on the type of material processed. Operating cost or Working Capital Investment (WCI) constitutes of cost of energy, catalysts, raw materials, labor and maintenance.(El-Halwagi, 2012) Utility cost includes cost of steam, power, fuel, cooling water and nitrogen.(El-Halwagi, 2012) Cost of utility depends on the complexity of process and studies show that safety is directly related to the cost of energy. Hence, a safer process tends to have less operating cost thus, leading to greater profits. The sum of FCI and WCI constitutes the total capital investment, which is cost of the entire project.(El-Halwagi, 2012)

Another important parameter that dictates the feasibility of a project is the economic gross potential. This is calculated to assess if the proposed project is feasible considering raw material costing and products costing.(El-Halwagi, 2012)

Economic Gross Potential (EGP) = ∑Annual production rate of products* cost of products - ∑Annual consumption rate of raw material * cost of raw material.

If EGP is greater than one, then project is deemed economically feasible and further studies are carried out to find the actual net profit. If EGP is lesser than one, the project is economically not feasible and shall not be considered for further analysis.(El-Halwagi, 2012)

II.3. Process Metrics

Process technology of manufacturing a product dictates the cost of the project, environmental impact as well as the safety. The chemistry of the process and the separation processes involved to achieve product purity that satisfies customer's requirement is crucial in determining process route. Factors that affect the decision making process are product yield, conversion, specific consumption of the raw material, energy consumption involved in the process, degree of separation processes and process complexity. In this thesis, all of the above mentioned factors are determined to make effective comparison between different process routes by performing a process simulation using Aspen Plus. Aspen Plus is a steady state chemical process simulation software that entails a wide array of rigorous thermodynamic property package specific to each case study. The inputs to the simulation software were given from chemical kinetics and process flow data available from the literature.

CHAPTER III

PROCESS ANALYSIS

In this chapter, a detailed description of the process technology, simulation techniques used, assumptions made and finally the results of steady state simulation are obtained. Only major equipment involved in the main process stream flow were considered for developing the process. ASPEN PLUS version 7.8.2 was used to carry out steady state simulation of the base case plants. A print screen picture of the aspen flow models are attached in the appendix. Peng Robinson was used as the base thermodynamic method for simulation of both the plants. All reactors were simulated using RSTOIC model while all distillation columns, absorption and quench towers were simulated using RADFRAC.

III.1. Ethane Cracking Technology

Steam cracking is the most widely used, established technology for producing ethylene.(Takaoka, 1967) Due to increase in shale gas reserves, ethane supply is found to have increased by 25 % making it a suitable raw material for producing ethylene. (Thomas K. Swift et al., 2011) Over 85 % of ethylene is manufactured from natural gas liquids obtained along with the shale gas. (Thomas K. Swift et al., 2011) Since ethane is not easily transportable, most of the time it is considered as stranded gas and therefore is burnt in flares or used as fuel. But now, ethylene industries are shifting from conventional liquid crackers processing naphtha to gas crackers that process ethane due to cheap raw material cost and higher product yield of ethane. Hence, this process analysis helps in understanding the underlying safety and economic benefits of using ethane as feedstock.

The process chemistry of thermal steam cracking of ethane can be explained by a complex set of reactions that are based on free radical mechanism.(Froment, Van de Steene, Van Damme, Narayanan, & Goossens, 1976) There are number of literature studies done on the thermal cracking of ethane to analyze the product yield patterns and conversion of ethane along the length of reactor.(Froment et al., 1976) On subjecting ethane to high temperatures at low pressures, it undergoes dehydrogenation reaction to primarily form ethylene and hydrogen. Other primary products obtained are methane, acetylene, propylene, propane and butadiene. The products are obtained as result of complex combination of 42 free radical mechanisms.(Sundaram & Froment, 1977) Out of these reactions, only 8 main reactions that adequately define the net effect of the chemistry have been considered for the case study.(Sundaram & Froment, 1977) They are given as follows:

i. $C_2H_6 \longleftarrow\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!-\!\!\longrightarrow C_2H_4 + H_2$

ii. $2C_2H_6$ -----------→ $C_3H_8 + CH_4$

iii. C_3H_8 -----------→ $C_3H_6 + H_2$

iv. C_3H_8 -----------→ $C_2H_4 + CH_4$

v. C_3H_6 ←-----------→ $C_2H_2 + CH_4$

vi. $C_2H_2 + C_2H_4$ -----------→ C_4H_6

vii. $2C_2H_6$ -----------→ $C_2H_4 + 2CH_4$

viii. $C_2H_6 + C_2H_4 \text{-----------}\rightarrow C_3H_6 + CH_4$

Table 3: Reactor yield data of ethane steam cracking.

Components	Reactor yield mass %
Hydrogen	3.8
Methane	2.6
Acetylene	0.08
Ethane	40
Ethylene	52.4
Propylene	1.1
Propane	0.03
Butadiene	1.04

Table 4: Conversions assumed for ethane cracking reactions.

Reaction Number	Conversion %	Conversion of limiting reactant
i	56	Ethane
ii	1.4	Ethane
iii	35	Propane
iv	39.3	Propane
v	65	Propylene
vi	40	Acetylene
vii	35.8	Ethane
viii	2	Ethane

The net effect of these reactions are endothermic hence, in order to increase yield of ethylene, external energy has to be supplied to maintain the temperature of the reactor. This is accomplished by indirect fired heater, where heat release from combustion of fuel is used to heat the reaction mixture that passes through tubes, fixed along the walls of furnace.(Takaoka, 1967) The main dehydrogenation reaction takes place in the temperature range of 750- 850 ^{0}C at low pressures of about 1.5 – 3.5 bar.(Takaoka, 1967) The residence time of the reaction mixture in the cracker coils are about 0.1-0.5 seconds.(Takaoka, 1967) Steam is injected along with ethane, since it reduces the partial pressure of hydrocarbons which in turn reduces the rate of decomposition of hydrocarbon products to coke at high temperatures.(Takaoka, 1967) Steam to hydrocarbon ratio of range 0.3-0.45 is considered for the process.(Sundaram & Froment, 1977) A 60 % single- pass conversion of ethane is assumed, which is in accordance with the literature.(Froment et al., 1976) The cracker yields obtained are shown above in Table 3 and the values are matched with the literature data.(Froment et al., 1976) These values are used for simulating the cracker reactor using RSTOIC. The percentage conversions calculated from reaction kinetic data for the above eight reactions are also shown above in Table 4. Ethane cracker is considered as the heart of the ethylene process plant. Cracker has the maximum energy consumption since endothermicity of the reactions are very high.

The entire process is separated into three major sections: Pyrolysis, Compression and Cooling & Separation. The pyrolysis section comprises of the cracker, where the ethylene product is formed by subjecting ethane feed to high temperature at low pressure. Cooled cracker products exiting the pyrolysis section are compressed in stages to desired pressure in order to effectively separate the ethylene from other compounds. In the compression section, acid gases are removed using caustic scrubbing and any residual moisture is also removed.(Takaoka, 1967) This is done before cooling section to avoid formation of solid CO2 or ice at cryogenic conditions since, they can block equipment and pipelines.(Takaoka, 1967) Following the compression section, the tail gas is cooled in a series of heat exchangers using refrigerants to effectively separate hydrogen from rest of the product gases, which passes to the separation section.(Takaoka, 1967) The separation scheme used in this analysis is Front-end De-Methanizer and Tail-end Acetylene Hydrogenation.(Takaoka, 1967) In this separation scheme, methane and residual hydrogen are removed initially, followed by which heaviers are removed. Acetylene present in residual stream is hydrogenated back to get ethylene following which ethylene is separated as product. The product purity of ethylene obtained is 99.9 wt %.

The process begins with fresh and recycled ethane feed being preheated in the convection section of the cracker by the flue gas up to a temperature of about 775 ^{0}C. The reaction takes place at a low pressure of 1.5 bar and temperature of about 775 ^{0}C in the radiation section of the cracker furnace. Low pressure steam is injected at a steam/ hydrocarbon ratio of 0.35. The reaction products exit the cracker furnace at a temperature of 840 ^{0}C and 1 bar pressure. The reaction products have to be immediately quenched to stop the further formation of acetylene which is an undesired by-product. This is done by rapid cooling of the reaction products to 380 ^{0}C with cooling water in a series of transfer line heat exchangers.(Takaoka, 1967) Following the transfer line exchangers, the products are further quenched in quench towers to about 42 ^{0}C, operating at 1 bar pressure. The cooling medium used in quench towers are cooling water.

The cooled gas is now compressed in three stages of compression. Each stage comprises of a compressor, a cooling water heat exchanger (to cool the compressed gases to 40 ^{0}C) and a flash (to separate the gases from the condensed liquid). In the first compression stage, pressure is increased to 2.4 bar, followed by second stage where pressure is increased to about 6 bar. This is again followed by third stage of compression where the final pressure is around 15 bar. The cooled compressed gases from the third stage of compression is now passed into a caustic scrubber containing 27 trays, where 8 wt % sodium hydroxide is used a solvent to remove any acid gases such as carbon dioxide or sulfur present in the gas.(Hammond & Ham, 2009) The sweet gas exiting the caustic scrubber is compressed again to about 36 bar in a 4th stage of compression subsequently. The cooled product gas at 40 ^{0}C from the 4th stage compressor is further cooled to about 15 ^{0}C using propylene refrigerant. The gas is sent to adsorption tower/dryer to remove any residual moisture in the gas stream, since the stream will be subjected to cryogenic conditions downstream.(Takaoka, 1967) After achieving a dew point of around -73 ^{0}C in the gas stream, the tail end gas from dryer is directed to cooling train. The cooling train consists of 3 stages of cooling, where each stage comprises of three heat exchangers and one flash drum. The heat exchangers in each stage are integrated with two other streams in two exchangers. The remaining heat duty is removed by a propylene refrigerant in parallel exchangers. In the first stage of cooling, the gas is cooled to -29 ^{0}C and flashed in a flash drum. This is followed by second stage of cooling to -74 ^{0}C and third stage where the exit gas from third stage flash drum is at around -124 ^{0}C. The 95 mol % hydrogen gas stream exiting the third flash at -124 ^{0}C is one of the stream that is pinched with three heat exchangers of each stage. After passing through the integrated exchangers, a part of it is regulated back to acetylene hydrogenation reactor while the rest is used as fuel utility.

All the liquids collected from the three flash drums of the cooling train are then regulated into de-methanizer column of 30 trays that operates at 30 bar pressure, top and bottom temperature of -113 ^{0}C and -4 ^{0}C respectively. The vapor distillate from the column containing 61 mole % methane is expanded and used for heat integration in the cooling train. After passing through series of exchangers in cooling train, the gas is used as utility fuel. The bottoms from de-methanizer column is regulated into de-ethanizer column of 45 trays operating at 26 bar, where all C3+ heaviers are removed from the bottom at temperature of 80 ^{0}C. The top of column consisting of C2 and lighter compounds exits the column at -11 ^{0}C. This overhead stream is heated to around 35 ^{0}C and then sent into the acetylene hydrogenation reactor operating at 25 bar.

In the acetylene hydrogenation reactor, the residual acetylene remaining in the gas is reacted with hydrogen and converted back to ethylene using a suitable catalyst. The gas phase hydrogenation reaction is given by following reaction mechanism.(Bond & Wells, 1966)

$C_2H_2 + H_2 \leftarrow\!\!-\!-\!-\!-\!-\!-\!-\!-\!-\!-\!\rightarrow C_2H_4$

The net effect of the reaction is exothermic. The major undesired by-product formed in this reaction is ethane.(Bond & Wells, 1966) Formation of ethane from ethylene will significantly reduce the process yield. Hence, by controlling the rate of hydrogen flowing into the reactor, ethane formation can be reduced. For this case study, acetylene conversion of 100% and 0% ethane formation are assumed. The reactor products now containing only C2 compounds exits at 75 ^{0}C and enters C2 splitter columns. C2 splitter columns contains 100 trays and operates at pressure of 19 bar with top temperature of -31 ^{0}C and bottom temperature of -9 ^{0}C. Ethylene is separated from top with product purity of 99.99 wt % while ethane removed from bottom is recycled back as cracker feed. The reboiler duties of all column in the separation section are given by 6 bar saturated steam while the condenser duties are taken by propylene refrigerant at different temperatures. The block diagram of the ethane cracking process using front-end de-methanizer scheme is shown below in Figure 7.

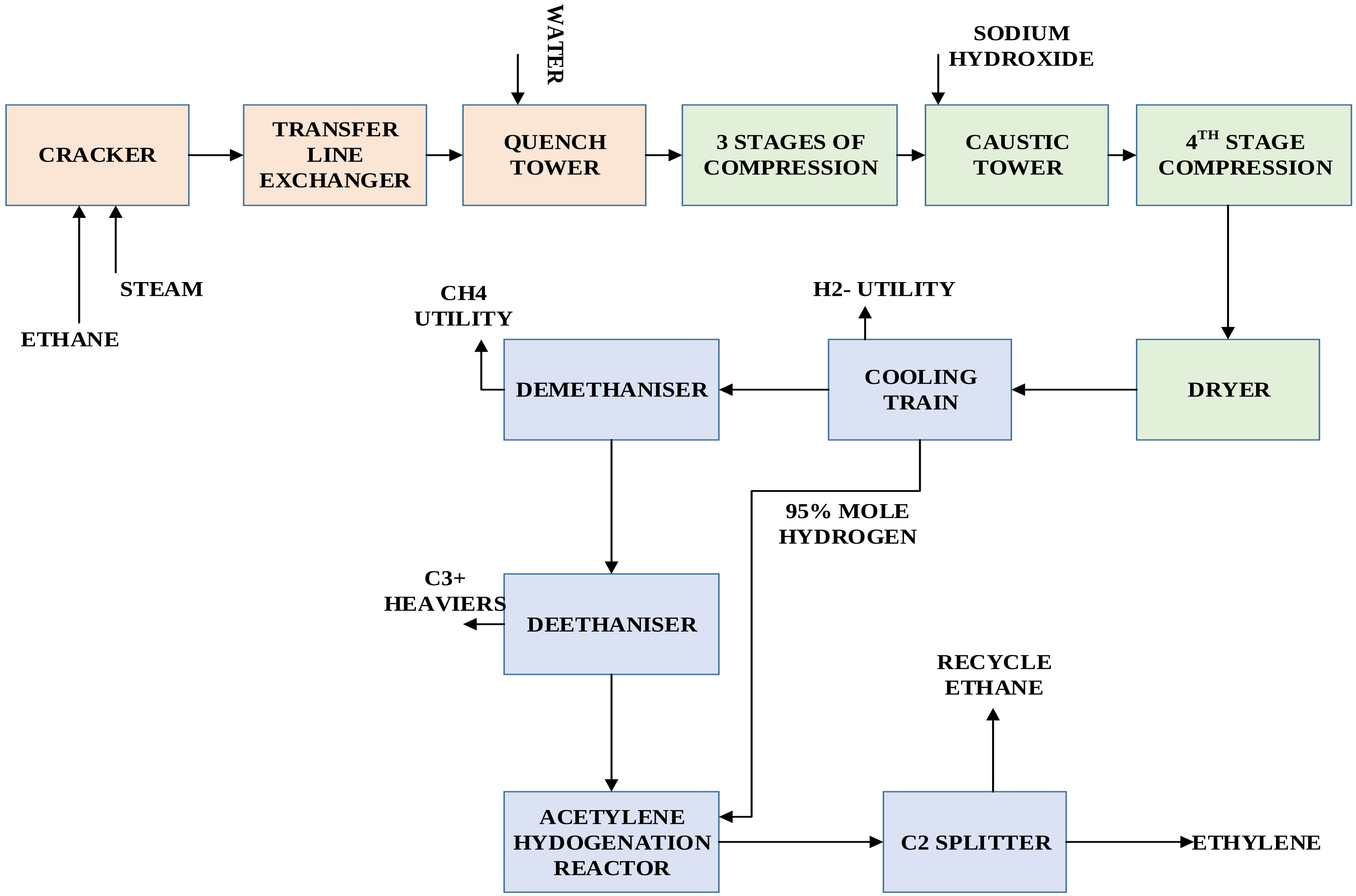


Figure 7: Block diagram of ethane steam cracking process using front end de-methanizer scheme.

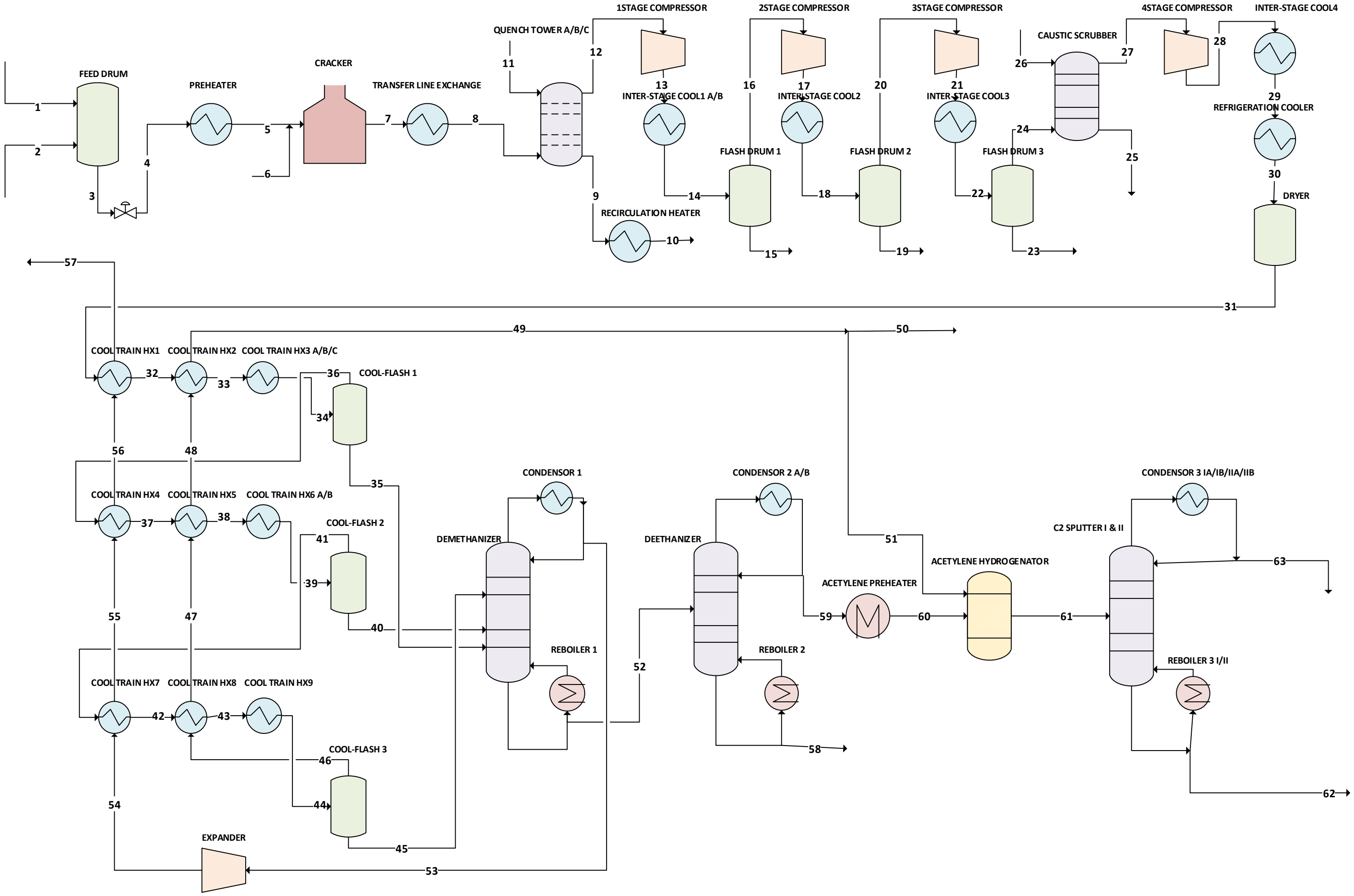


Figure 8: Process flow diagram of ethane steam cracking process.

The process flow diagram of the ethane cracking process obtained after ASPEN simulation is given above in Figure 8. Along with process simulation data, design specifications were also given for each class of equipment. All equipment were simulated and optimized to account for balanced energy consumption, product purity, operation, design and safety considerations. Design of equipment was done using a top level analysis. For columns, compressors and heat exchangers, primary design data were fetched from ASPEN models. The assumptions made for design of certain class of equipment are listed below.

III.1.1. Assumptions

i. A pressure drop of 0.5 bar is assumed for all heat exchangers.

ii. The convection and radiation section of the furnace are shown in separate blocks: preheater for convection and RSTOIC models for reactor.

iii. Ethane fresh feed is assumed to contain only 0.1 wt% of carbon dioxide as impurity and is available at 25 ^{0}C and 19 bar pressure.

iv. The off-gas generated in the process is considered in the form of equivalent amount of natural gas required for heating and is balanced in the final energy of fuel required.

v. Caustic scrubbing was modeled as a RSTOIC reactor where 100 % conversion of carbon dioxide is assumed. Design of caustic scrubber was done based on 27 trays separately in RADFRAC.

vi. All heat exchangers are assumed to be shell and tube type. Heat transfer areas were calculated from ASPEN PLUS. A minimum temperature approach of 5 ^{0}C is assumed for refrigeration operations and 7 ^{0}C for other exchangers. Heat exchanger volume was determined by assuming a surface area density of 100.(Shah & Sekulić, 2003) The formula for calculating volume is given by: (Shah & Sekulić, 2003)

Volume = Heat transfer area / surface area density

vii. The rule of thumb for maximum heat transfer area is 1000 m^2.(Branan, 2012) Any heat exchanger exceeding this value was split accordingly into parallel heat exchangers.

viii. Similarly the maximum allowable column diameter was assumed to be 6. Any column exceeding this value was split accordingly into parallel columns.

ix. Volume of reactors are found using literature value for residence time. Liquid residence time for half full flash vessels is assumed to be 5 min according rule of thumb.(Coker, 2007) Approximate volume of column is calculated using the formula:

Volume = π * (Column diameter) ^{2} * Height of column / 4

Height of column = No of trays * tray spacing + 10 feet

Default tray spacing of 0.6096m was assumed for columns.(Chuang & Nandakumar, 2000)

x. All products recovered from distillation are based on minimum 99% mass recovery.

xi. Compression ratio of compressors was assumed in such a way so as to not exceed compressor outlet temperature greater than 150 ^{0}C, to avoid formation of polymers that plug equipment.(Takaoka, 1967)

xii. Alumina is assumed to be used for adsorption of moisture and a residence time of 5 sec is assumed for dryer. (Olivier Ducreux & Nedez, 2011)

xiii. Heating duties are provided by steam except for preheater and cracker reactor; Cooling duties are provided by cooling water except for cooling & separation section; Propylene refrigerant is used for cooling purposes in cooling and separation section. Natural gas is assumed to be fuel used in furnace. The operating conditions of the utilities are given below in Table 5. The operating efficiencies of utilities are given in Table 6.

xiv. Caustic scrubbing is exothermic reactive absorption, but since the solvent is only 8 wt% of caustic soda, there will be no significant temperature rise, considering only 0.1 wt% of CO2 in the feed.(Hammond & Ham, 2009) Similarly acetylene hydrogenation, which is also exothermic is assumed to be adiabatic, hence the outlet temperature of reactor is high.(Bond & Wells, 1966)

xv. A list of energy consuming equipment in each section and their consumption rates are given below in Table 7.

Table 5: List of utilities and utility operating conditions.

S. No	Utility	Temperature	Pressure
		Deg C	bar
1	Steam	158	6
2	Natural Gas	25	2
3	Propylene refrigerant	-45	-
4	Propylene refrigerant	-101	-
5	Propylene refrigerant	-156	-
6	Cooling water	30	-
7	Chilled water	15	-

Table 6: Process efficiency values of utilities.

Process Efficiency Assumptions	
Natural Gas - Thermal efficiency	**60%**
Cooling water- Cooling efficiency	**100%**
Compressor- shaft efficiency	**45%**
Total compressor efficiency – shaft power from natural gas	**27%**
Refrigeration efficiency	**100%**
Steam- Heating efficiency- Produced from natural gas	**60%**

Table 7: List of energy consuming equipment and their consumption rates- ethane cracking process.

S. NO	SECTION	Units named in PFD	Type of utility used	Actual energy requirements
				MMBtu/hr
1	**PYROLYSIS**	PREHEATER	Natural gas	699
2		CRACKER	Natural gas	697
3		TRANSFER LINE EXCHANGE	cooling water	388
4		RECIRCULATION HEATER	cooling water	272
5		INTERSTAGE COOL1-A	cooling water	32

Table 7: Continued.

S. NO	SECTION	Units named in PFD	Type of utility used	Actual energy require ments
				MMBtu/hr
6	COMPRESSION SECTION	INTERSTAGE COOL1-B	cooling water	32
7		INTERSTAGE COOL2	cooling water	40
8		INTERSTAGE COOL3	cooling water	35
9		INTERSTAGE COOL4	cooling water	36
10		1ST STAGE COMPRESSOR	Power	131
11		2ND STAGE COMPRESSOR	Power	126
12		3RD STAGE COMPRESSOR	Power	124
13		4TH STAGE COMPRESSOR	Power	117
14	SEPARATION SECTION	REFRIGERATION COOLER	Chilled water	14
15		COOL TRAIN HX3-A	refrigerant	10
16		COOL TRAIN HX3-B	refrigerant	10
17		COOL TRAIN HX3-C	refrigerant	10
18		COOL TRAIN HX6-A	refrigerant	24
19		COOL TRAIN HX6-A	refrigerant	24
20		COOL TRAIN HX9	refrigerant	8
21		CONDENSOR 1	refrigerant	5
22		REBOILER 1	Steam	57
23		CONDENSOR 2-A	refrigerant	41
24		CONDENSOR 2-B	refrigerant	41
25		REBOILER 2	Steam	133
26		ACETYLENE PREHEATER	Steam	102
27		CONDENSOR 3-I-A	refrigerant	45
28		CONDENSOR 3-I-B	refrigerant	45
29		CONDENSOR 3-II-A	refrigerant	45
30		CONDENSOR 3-II-B	refrigerant	45
31		REBOILER 3-I	Steam	83
32		REBOILER 3-II	Steam	83
			Total	**3551**

III.1.2. Simulation Results

The results of the process analysis using ASPEN PLUS were found to be in agreement with the literature. The process metrics are summarized below in Table 8. From results, we can see the energy consumption of individual equipment in each section. Depending on this data, it can be concluded that the highest energy consumer is furnace (preheater + cracker), followed by compressors in the second place and then Transfer line exchange. Figure 9 illustrates the contribution of each section to specific energy consumption. The section that has largest specific energy consumption is pyrolysis followed by compression section and then separation. These results are then analyzed with its safety and economics to find areas of concern. But from these results, it is apparent that equipment such as furnace, compressors and transfer line exchanger need more process improvement in terms of energy. At this stage opportunities for heat integration or another less intensive process can be explored. Heat integration enables reduction in energy consumption as well reduces the number of equipment required thus indirectly enhancing safety. Off gas generated from the process is accounted in the cost analysis. The energy reduction achieved by utilizing off gas as utility fuel is considered to be 100%. The major energy contributors along with consumption rates are illustrated in Figure 10.

Table 8: Simulation results- ethane cracking process.

Parameter	Value	UOM
Annual Production rate of ethylene	830,132	Tonnes/yr
Product purity	99.90	wt %
Annual Ethane Feed rate	978,492	Tonnes/yr

Table 8: Continued.

Parameter	Value	UOM
Process yield of ethylene	85	%
Cracker single-pass conversion	60	%
Cracker yield of ethylene	51	wt %
Minimum energy requirements	2,446	MMBtu/hr
Minimum Specific Energy Consumption	26	MMBtu/tonne of ethylene
Specific consumption of raw material	1.2	Tonne of ethylene/ tonne of ethane

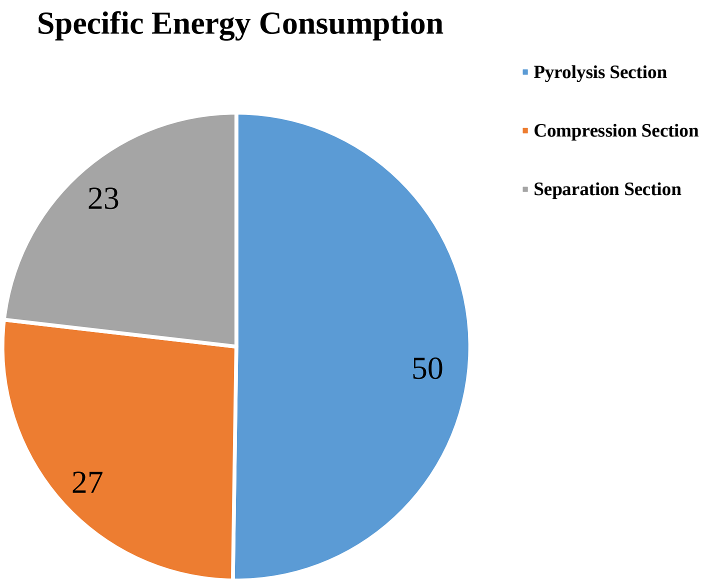


Figure 9: Specific energy consumption of major sections- ethane cracking process.

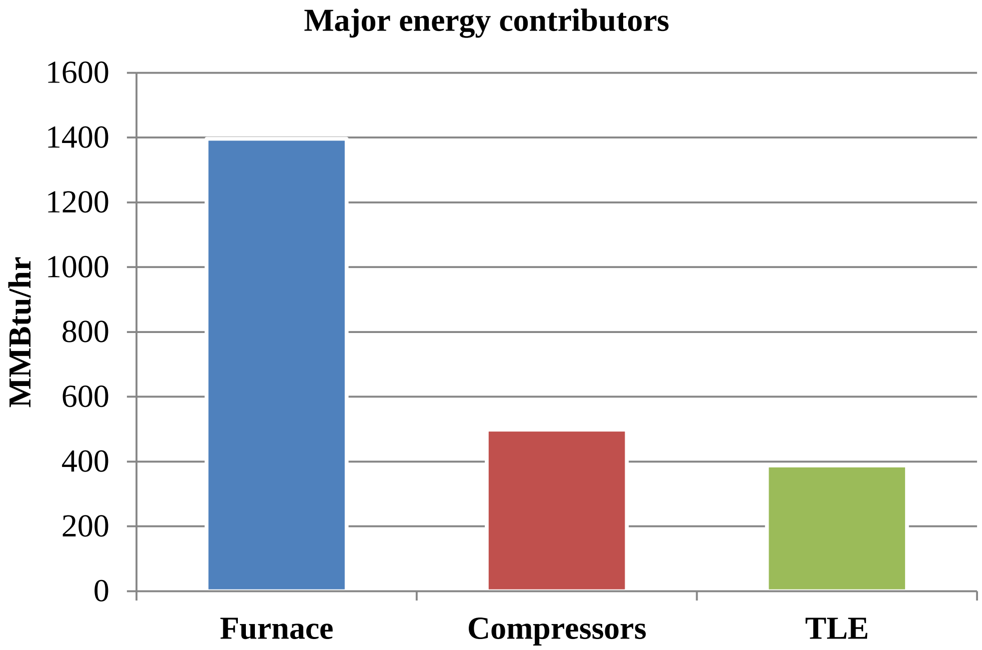


Figure 10: Major energy contributors- ethane cracking process.

III.2. Pyrolysis of Methane

Natural gas is a clean source of energy and is available in abundance. The increase in reserves and low cost of natural gas have paved way for exploration of new methods of converting methane to valuable chemicals rather than using it as fuel.(Cantrell, Bullin, McIntyre, Butts, & Cheatham, 2013) Also, transportation of natural gas by liquefaction is expensive and tougher. Hence, opportunities that directly convert gas to petrochemicals are gaining more focus. One such new technology of that kind is the Gas to Ethylene Technology or ECLAIRS (Ethylene from concentrated liquid phase acetylene- Integrated rapid and safe).(Hall, 2005) This new technology utilizes natural gas to convert it into acetylene, a stable petrochemical intermediate and converting the same into ethylene through liquid phase hydrogenation.(Hall, 2005) The technology is still not commercialized and it is in pilot plant scale. This process claims to be economical for low gas feed rates as low as 30 kSCMD up to any further larger scale when compared to traditional GTL processes (Fischer Tropsch), that require larger gas feed rates of the order of 300 MMSCFD to be economical.(Hall, 2005) Application of safety and economic evaluation techniques on such a novel process can render useful in justifying the replacement of one technology over the other. The intermediate acetylene is produced primarily by subjecting methane to high temperatures at low pressures. The process called as pyrolysis of methane is a widely used technology adopted in the manufacture of acetylene and syngas.(Holmen, Olsvik, & Rokstad, 1995) Since the methane pyrolysis reaction is highly endothermic, and in order to maintain high reaction temperature heat is supplied to cracker in many different ways such as partial oxidation of methane, indirect heating in furnace, electric arc furnace and Wullf pyrolysis process.(Holmen et al., 1995) For our case study, partial oxidation of methane to acetylene is considered. Partial oxidation method was chosen since it is a practically feasible, well established process and detailed literature data on chemical kinetics are available.

The process chemistry of natural gas pyrolysis is explained by the below mentioned reactions. At high temperatures in the range of 2500 K and low pressures of about 1 bar, methane undergoes dehydrogenation consequently to form acetylene, a much stable compound than ethylene at those temperature.(Holmen et al., 1995) The residence time required for the reaction is as low as 0.01 seconds since, decomposition of acetylene to carbon has to be stopped. Hence, the hot product gases are immediately quenched using cooling water or quench oil.(Holmen, 2009) Partial oxidation of methane employs a direct medium of heat transfer by burning part of natural gas feed with oxygen to produce enough heat to crack the rest of the feed.(Holmen et al., 1995) A methane to oxygen ratio of 1.65 moles is usually selected, by which approximately 60% of methane is burned to produce combustion products while 30% is converted to acetylene. (Wolf, 1992)

i. $2CH_4 \leftarrow\text{---------}\rightarrow C_2H_4 + 2\ H_2$
ii. $2CH_4 \leftarrow\text{---------}\rightarrow C_2H_2 + 3\ H_2$
iii. $CH_4 + O_2$ $\text{--------}\rightarrow CO + H_2 + H_2O$ (incomplete combustion)
iv. $CO + H_2O \leftarrow\text{-------}\rightarrow CO_2 + H_2$
v. $C_2H_2 + CH_4 \leftarrow\text{------}\rightarrow C_3H_4 + H_2$
vi. $CH_4 + 2O_2$ $\text{--------}\rightarrow CO_2 + 2\ H_2O$

The main products formed in the partial oxidation method are hydrogen, acetylene, carbon dioxide, carbon monoxide, ethylene, methane and heaviers.(Pässler et al., 2012) The products formed are immediately quenched in order of 0.02 milliseconds to prevent formation of carbon.(Ries, 1966) The reactor yield and feed conversion values were assumed based on the values given in literatures. (Pässler et al., 2012) The cracker was simulated using RSTOIC by taking conversion values from chemical reaction kinetic data and literature studies. The dry gas composition of pyrolysis reactor outlet is given in Table 9. The conversion values assumed for the above mentioned reactions are listed in Table 10.

Table 9: Reactor yield mole composition- methane pyrolysis.

Components	Reactor yield mol %
Hydrogen	54.7
Methane	4.9
Acetylene	8.4
Carbon dioxide	4.8
Ethylene	0.4
Carbon monoxide	26.4
Propadiene	0.4

Table 10: Conversions of methane pyrolysis reaction using partial oxidation method.

Reaction Number	Conversion %	Conversion of limiting reactant
i	1.3	Methane
ii	32	Methane
iii	56	Methane
iv	1.8	Carbon monoxide
v	4	Acetylene
vi.	9	Methane

The entire process is divided into 4 main sections namely; pyrolysis, compression, solvent separation and product separation. In the pyrolysis section, preheated natural gas and oxygen undergoes partial oxidation at high temperature in the cracker to form acetylene and combustion products, which are immediately quenched using quench water. The quenched gas is further cooled and consequently compressed in stages to pressures of about 12 bar. Carbon dioxide present in the cooled gas is removed in an amine sweetening unit between two compressor stages. The sweet gas exiting the compression section is sent into an absorption column where N methyl 2- Pyrrolidine is used as solvent for absorbing acetylene.(Tabe-Mohammadi, Villaluenga, Kim, Chan, & Rauw, 2001) The solvent laden acetylene enters into hydrogenation reactor where acetylene is converted to ethylene. The tail gas from NMP absorption tower is partially regulated into a pressure swing adsorption to extract pure hydrogen for using in hydrogenation reactor.(Peramanu, Cox, & Pruden, 1999) The rest of tail gas is used as utility fuel. The solvent containing ethylene is now regulated into a series of flash network for separating solvent from hydrocarbon product mixture and solvent is recycled back into absorption tower.(Abedi, 2007) The remaining hydrocarbon gas is compressed again in two stages and sent to two distillation columns, where lighters and heavier are separated and ethylene product is obtained with 99.99wt% purity.

The block diagram of methane pyrolysis of natural gas using partial oxidation method is shown in Figure 11. The process flow diagram obtained from Aspen simulation is illustrated below in Figure 12.

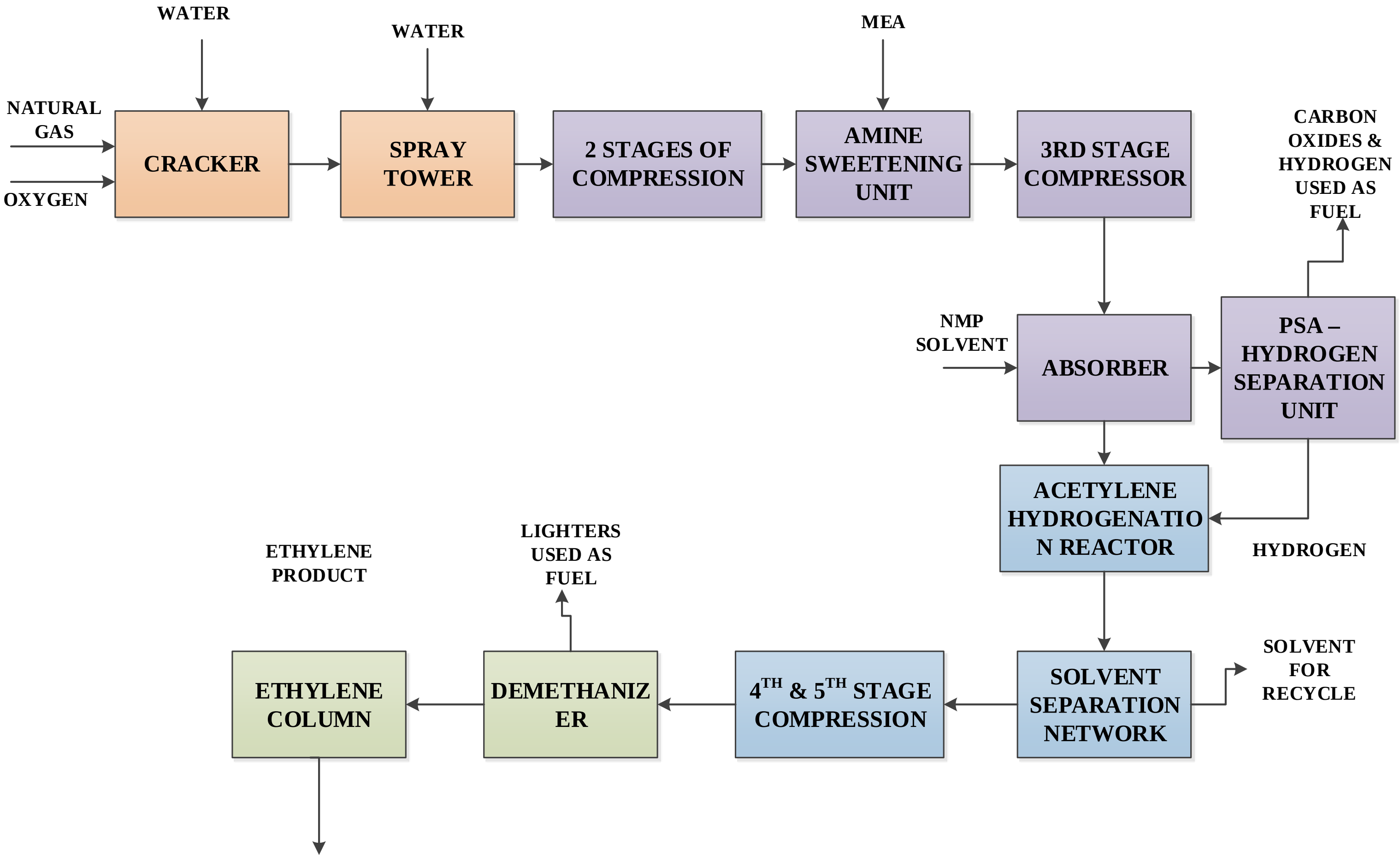


Figure 11: Block diagram of methane pyrolysis using partial oxidation method of heat transfer.

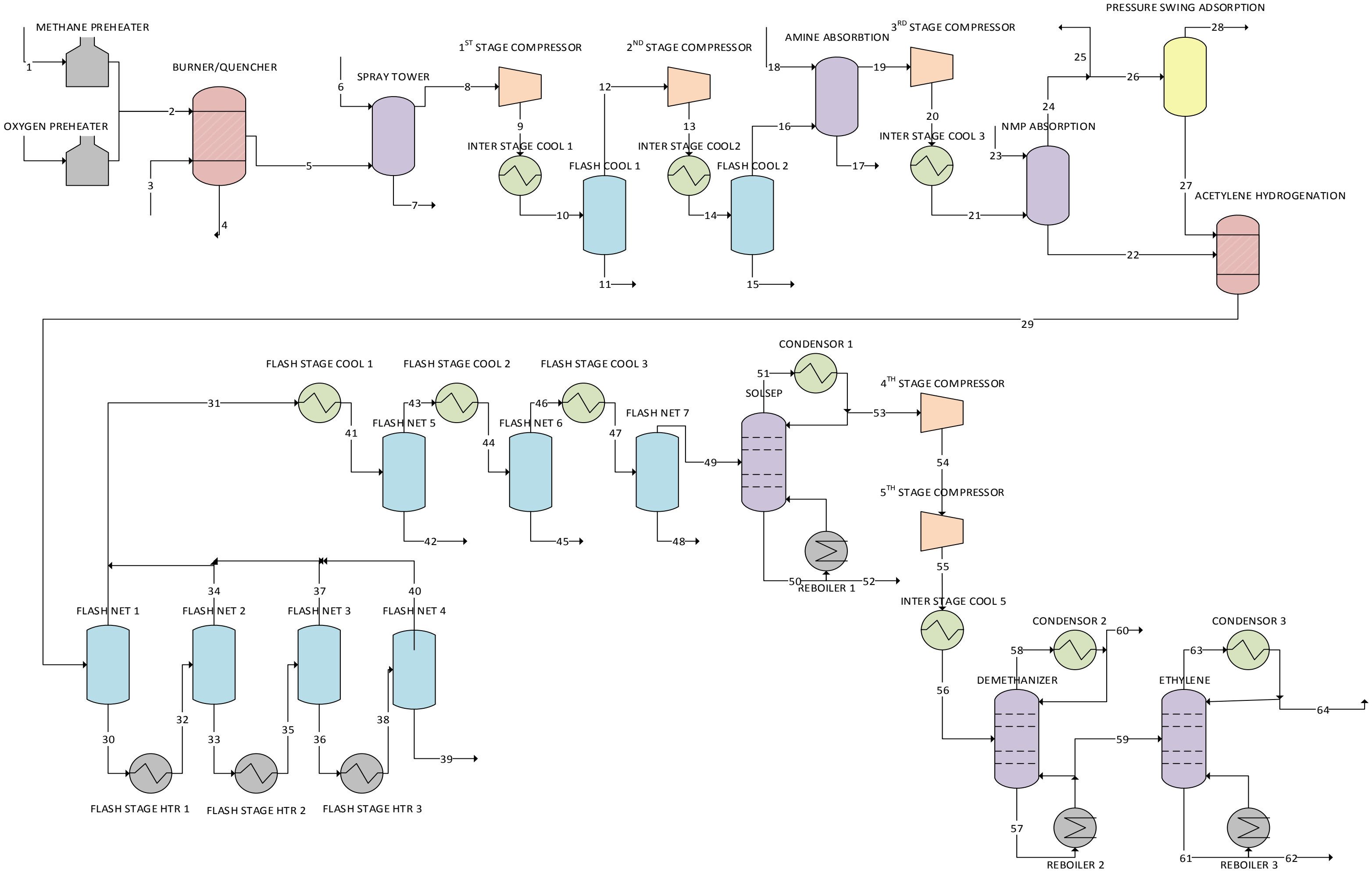


Figure 12: Process flow diagram of methane pyrolysis process.

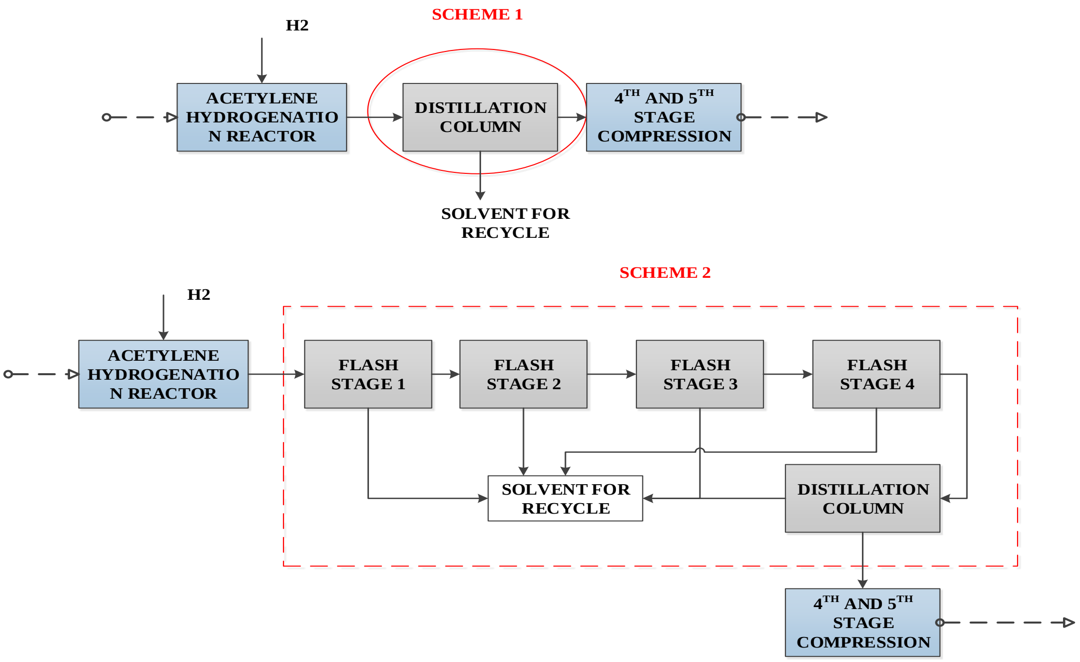


Figure 13: Scheme 1 and scheme 2 for solvent separation.

In the solvent separation section, three solvent separation schemes were proposed and analyzed for feasibility. Scheme 1 and 2 for solvent separation is depicted by Figure 13. The 1st scheme involves using distillation column to separate hydrocarbons from solvent. Though a complete separation is effected with minimal loss of solvent and product, the energy duties and capital cost required for the columns were very high, making it an infeasible solution. The scheme 2 involves using a series of 4 flash vessels where pressure is reduced subsequently along with intermediate heating, to remove majority of the solvent. The vapors from all flash vessels were fed into distillation column to study separation. This scheme also had the disadvantage of utilizing high energies in reboilers and condensers and also required huge capital investment and hence, this scheme was not selected.

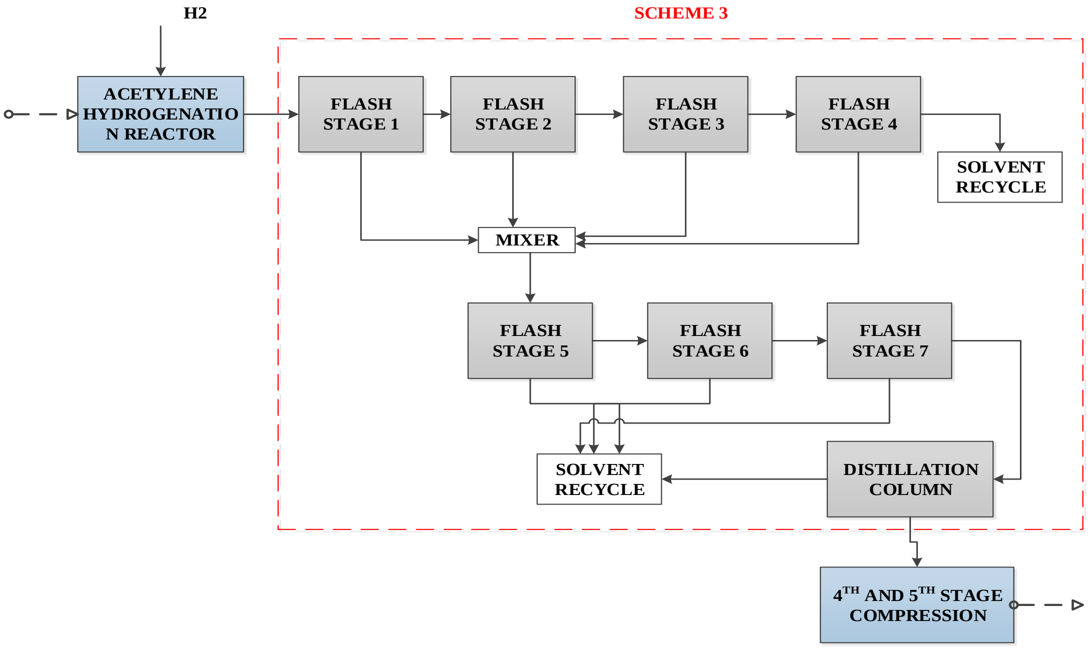


Figure 14: Scheme 3 proposed for solvent separation.

Scheme 3 of solvent separation is shown in Figure 14. Scheme 3 is a continuation of scheme 2, where the vapors collected from 4 flash vessels are cooled in 3 stages of flash vessels and finally when the hydrocarbon to solvent composition is about 50 mole %, a distillation column is used to separate the same. This scheme proved to be energy efficient and also reduced the capital cost. Hence, this scheme is selected for developing process flow diagram. A comparison chart of 3 schemes are shown below in Table 11.

Table 11: Comparison of different schemes proposed for solvent separation.

PARAMETERS	SCHEME 1	SCHEME 2	SCHEME 3
No of flash vessels	0	4	7
Distillation column condenser duty, MMBtu/hr	1084	96.04	68
Distillation column reboiler duty, MMBtu/hr	915	712.99	17

The process flow starts with methane and oxygen being preheated separately to 600 ^{0}C, followed by which they are mixed in ratio of 1: 1.65 moles of methane to oxygen and fed into burners.(Ries, 1966) About 56% of methane is burned at 1 bar pressure, producing large amounts of heat required to crack the remaining methane into various products. The cracked gas at around 1500 ^{0}C is immediately quenched in burners using quench water to 80 ^{0}C to prevent decomposition to coke. The quenched gas is further cooled in a spray tower to 30 ^{0}C. The cooled gas is consequently sent to two stage of compression where in each stage, the gas is compressed, cooled and then flashed again to compress the vapors. The product gas is compressed to 2 bar in 1st stage and then to 5 bar in second stage. The compression ratios were chosen in such a way not to exceed acetylene partial pressure of 1.4 MPa for safety considerations.(Ries, 1966) The gas exiting the second stage is passed into a amine sweetening unit where 31 wt% solution of MEA(Mono EthanolAmine) is used a solvent for absorbing carbon dioxide.(Burr & Lyddon, 2008) A 100% percent removal of carbon dioxide is assumed. The sweet gas exiting the amine sweetening unit is then sent to third stage of compression where it is compressed further to 12 bar. The compressed gas now enters into absorption tower where chilled solvent, N methyl 2- Pyrrolidine at -50 ^{0}C is used for absorbing acetylene.(Gattis et al., 2004) A 95% mass recovery of acetylene is assumed to optimize the capital cost and operating cost of the tower. The tail gas devoid of acetylene is separated into two streams where one stream is sent to utility for fuel use while other stream is sent to pressure swing adsorption for extracting 99.9% pure hydrogen. The pure hydrogen stream is regulated back into acetylene hydrogenation reactor while the remaining off gas is sent as utility fuel.

The solvent laden acetylene enters the acetylene hydrogenation reactor, where acetylene is converted into ethylene in the presence of catalyst at liquid phase.(Gattis et al., 2004) The reaction chemistry is same as gas phase hydrogenation. The product exiting the reactor is at 88 ^{0}C and 11 bar pressure and this is regulated into solvent separation section. The solvent laden product is a mixed phase and hence is flashed in 4 flash columns with a pressure reduction of 2 bar for each flash vessels along with intermediate heating. The stream had to be heated due to the presence of large amount of solvent. Flash vessels 1,2,3 and 4 are operated at a temperature of 88 ^{0}C, 100 ^{0}C, 110 ^{0}C and 120 ^{0}C, and pressures of 10 bar, 8 bar, 6 bar and 4 bar respectively. The liquid from each flash were regulated to subsequent flash drums and finally the liquid collected from the 4th flash vessel that contain approximately 99.5 wt% solvent are assumed to be directly recycled. The vapors from all 4 flash drums are mixed, cooled and flashed in three stages. These vapors are cooled in these stages because the solvent concentration has reduced significantly. Flash vessel 5, 6 and 7 are operated at temperatures 102 ^{0}C, 95 ^{0}C and 85 ^{0}C with no significant pressure reduction.

The vapors from each flash drum is regulated to subsequent flash drums and the final vapor exiting flash 7 is sent into distillation column, SOLSEP operating at 3 bar with top temperature of -72 ^{0}C and bottom temperature of 19 ^{0}C. The liquids collected from all the three flash drums 5, 6 and 7 contain 99.5wt% of solvent and are recycled. The vapor distillate from SOLSEP column is regulated into two 4th and 5th stage of compression in order to prepare for effective separation in product separation section. Meanwhile the bottoms of SOLSEP containing 99.99wt% of solvent is again recycled back to NMP absorption tower. The product gas is compressed to 12 bar in 4th stage and 30 bar in 5th stage. The hot gas exiting 5th stage compressor is then cooled in a cooling water heat exchanger and sent into de-methanizer column.

The de-methanizer column operates at 30 bar, with top temperature at -116 ^{0}C and bottom temperature of -12 ^{0}C. The vapor distillate containing predominantly methane, carbon monoxide and hydrogen are used as utility fuel. The bottoms of de-methanizer column are then regulated into ethylene column where ethylene is removed as liquid distillate, while heaviers are removed at bottom. The column operates at 25 bar pressure with top temperature of -20 ^{0}C and bottom temperature of 77 ^{0}C. A product purity of 99.99 wt% is obtained. The heating utilities for the columns and heat exchangers are supplied by saturated steam at 6 bar pressure. The cooling utilities for inter-stage cooling exchangers are supplied by cooling water, while propylene refrigerant is used for condensers in columns. The process efficiencies and utilities used are same as those used for ethane cracking technology. All equipment were simulated to give optimized values of energy consumption. The general assumptions considered for this process are given below.

III.2.1. Assumptions

1. The natural gas feed is assumed to be sweet and contain 100 % methane.
2. 100 % pure oxygen is assumed to be available as feed.
3. Heat duties of methane and oxygen preheaters are rendered by indirect heating furnaces using natural gas as utility fuel.
4. Amine sweetening tower was modeled by using RSTOIC and 100 % conversion of CO2 is assumed. The design of amine absorber was done separately by assuming 20 trays in RADFRAC.
5. Acetylene conversion to ethylene in acetylene hydrogenation reactor was assumed to be 100%. The reactor is considered adiabatic and owing to exothermic reaction of acetylene hydrogenation, the reactor outlet temperature increases.
6. All distillation columns were simulated for more than 99% mass recovery of products.
7. Residence time of 200 seconds is assumed for pressure swing adsorption cycle.(Jain, Moharir, Li, & Wozny, 2003)
8. Residence time of both gas phase and liquid phase acetylene hydrogenation reaction is assumed to be 20 seconds. (Anderson, 1967)

ix. Only the main stream process equipment were considered hence, the recovery units and utility treatment units were not considered for evaluation of energy consumption.

x. A list of energy consuming equipment in each section and their consumption rates are given below in Table 12.

Table 12: List of energy consuming equipment and rate of energy consumptions- methane pyrolysis process.

S. NO	SECTION	Units named in PFD	Type of utility used	Actual heat requirements
				MMBtu/hr
1	PYROLYSIS	METHANE PREHEATER	Natural gas	1105
2		OXYGEN PREHEATER	Natural gas	445
3		REACTOR QUENCHER	cooling water	2239
4		SPRAY TOWER COOLER	cooling water	1441
5	COMPRESSION	INTERCOOL STAGE 1-A	cooling water	51
6		INTERCOOL STAGE 1-B	cooling water	50
7		INTERCOOL STAGE 1-C	cooling water	50
8		INTERCOOL STAGE 1-D	cooling water	50
9		INTERCOOL STAGE 2-A	cooling water	55
10		INTERCOOL STAGE 2-B	cooling water	55
11		INTERCOOL STAGE 2-C	cooling water	57
12		INTERCOOL STAGE 3-A	cooling water	72
13		INTERCOOL STAGE 3-B	cooling water	72
14		1ST STAGE COMPRESSOR	Power	550
15		2ND STAGE COMPRESSOR	Power	536
16		3RD STAGE COMPRESSOR	Power	531
17		4TH STAGE COMPRESSOR	Power	50
18		5TH STAGE COMPRESSOR	Power	45
19		FLASH STAGE 1 HTR	Steam	130

Table 12: Continued.

S. NO	SECTION	Units named in PFD	Type of utility used	Actual heat requirements
				MMBtu/hr
20	**SOLVENT SEPARATION**	FLASH STAGE 2 HTR	Steam	116
21		FLASH STAGE 3 HTR	Steam	132
22		FLASH STAGE 4 COOL	cooling water	36
23		FLASH STAGE 5 COOL	cooling water	47
24		FLASH STAGE 6 COOL	cooling water	47
25		SOLSEP REBOILER	steam	30
26		SOLSEP CONDENSOR-A	refrigerant	34
27		SOLSEP CONDENSOR-B	refrigerant	34
28		SOLSEP CONDENSOR-C	refrigerant	33
29		INTERCOOL STAGE 5	cooling water	14
30	**PRODUCT SEPARATION**	DEMETHANIZER REBOILER	steam	36
31		DEMETHANIZER CONDENSOR-A	refrigerant	29
32		DEMETHANIZER CONDENSOR-B	refrigerant	29
33		ETHYLENE REBOILER	steam	80
34		ETHYLENE CONDENSOR-A	refrigerant	25
35		ETHYLENE CONDENSOR-B	refrigerant	25
			Total	**8332**

III.2.2. Simulation Results

The simulation results calculated from ASPEN were used for calculating the energy requirements. From the simulation results, it can be seen that pyrolysis section is the largest energy consumer of the entire process. This is mainly attributed to the abundant supply of quench water required to quench the coke formation reaction. The energy consumption was calculated on basis of energy required to cool the exit quench water from reactor. It can also be seen that solvent and product separation energy consumptions are considerable low. Literature studies show different methods of heat recovery in acetylene cracker quench part by using different quench fluid such as oil or hydrocarbon such that effective utilization of the energy removed can be done.(Ries, 1966) In this case study water without heat recovery is analyzed. The process metrics that define the process technology are also shown below in Table 13. Following the reactor, compressors also contribute to large energy consumption, which is again followed by spray tower. Heat integration opportunities can be widely explored to reduce the minimum energy consumption in pyrolysis and compression section. One of the major limitations of using direct heat integration in pyrolysis section is the short residence time required for quench water. A total ethylene recovery of 95% is calculated based on the acetylene and ethylene available at reactor outlet compared to ethylene column product flow rate. The recovery is low because much of potential acetylene is lost in NMP absorption section. A large amount of off gas is generated in this process primarily constituting of hydrogen and carbon monoxide. This has been accounted in the cost analysis. Specific consumption is based on natural gas that is used for partial oxidation also. If methane that is utilized only for pyrolysis is considered, specific consumption will go down to 1.5 tonnes of methane/tonne of ethylene. Figure 15 shows the contribution of each section to specific energy consumption. Figure 16 shows the list of highest energy contributors along with their consumption rates.

Table 13: Simulation results - methane pyrolysis process.

Parameter	Value	UOM
Production rate of ethylene	827,820	Tonnes/yr
Product purity	99.99	wt%
Feed rate of fresh methane	3,320,040	Tonnes/yr
Feed rate used only for pyrolysis reaction	1,238,401	Tonnes/hr
Process yield of ethylene-entire methane	25	% (mass basis)
Process yield of ethylene-partial methane	67	% (mass basis)
Pyrolysis single-pass conversion	33	%
Ethylene recovery -total	96	%(mass basis)
Minimum energy requirements	6253	MMBtu/hr
Minimum Specific Energy Consumption	66	MMBtu/tonne of ethylene
Specific consumption of raw material	**4**	**Tonnes of methane/tonne of ethylene**

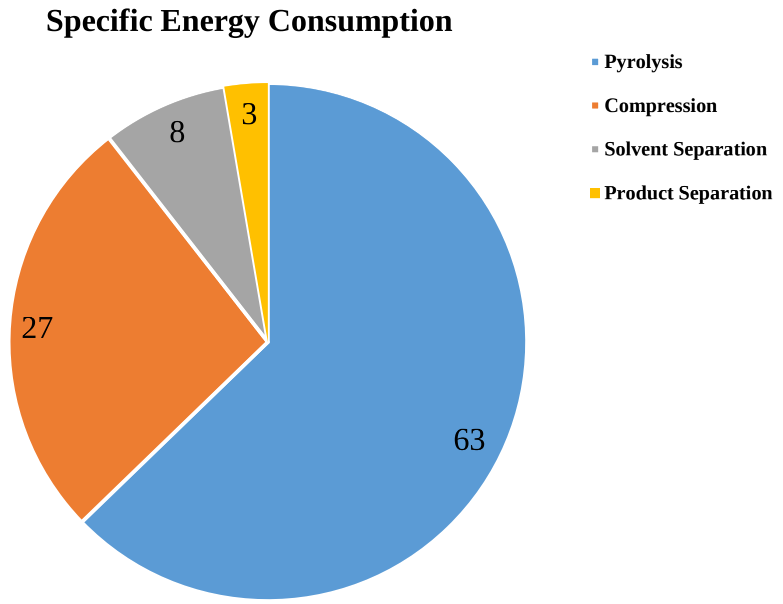


Figure 15: Specific energy consumption of major sections- methane pyrolysis.

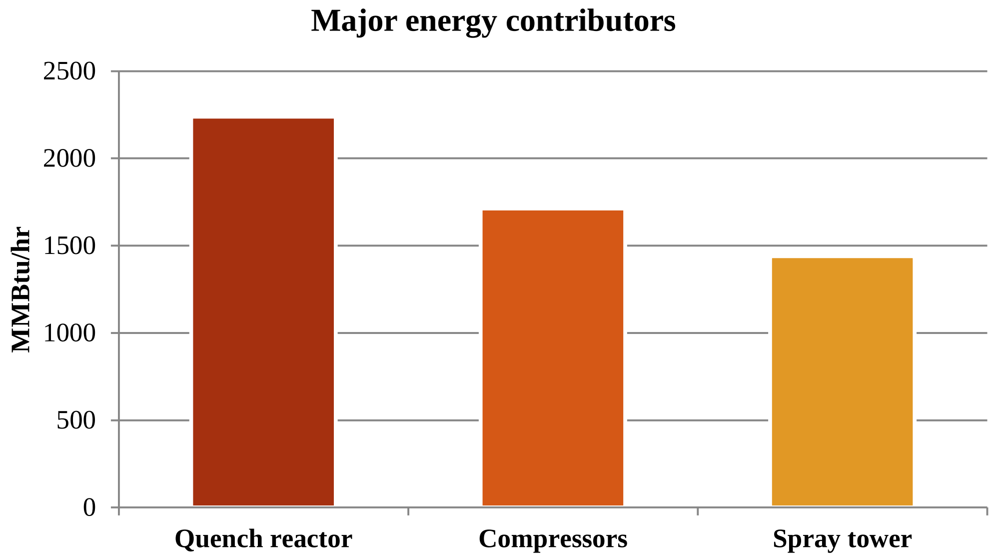


Figure 16: Major contributors to energy consumption- methane pyrolysis.

CHAPTER IV

ECONOMIC ANALYSIS

In this chapter, a top level economic analysis using shortcut tools are used to evaluate the economics of operation of both the plants. Fixed and operating costs of the plants are calculated based on the production capacity of each plant, energy consumption and cost of raw material and utility. The cost of maintenance or labor will not be included as a part of the operating cost in this study. The utility assumptions made are in accordance to the general range of prices as given in the literature (El-Halwagi, 2012). The price of raw material is taken from energy information administration (EIA) and ICIS website.

IV.1. Ethane Cracking

In the ethane cracking process, the major raw material used is cracker feed ethane. The cost of ethane is found by taking an average of NGL- ethane trend from energy information association website. Table 14 shows the estimation of raw material cost. A comparison of price between naphtha and ethane is made to justify the use of ethane as feedstock. From the results, it can be found that the cost of ethane is 5 times higher than Naphtha price and hence, ethane is highly favorable than naphtha as feedstock for producing ethylene. The prices were taken as average value of predicted trend in EIA website. Table 15 shows the consolidated cost metrics obtained for the plant. Table 16 shows the operating cost of each equipment that was calculated according to the actual consumption in the plant.

Table 14: Estimation of raw material cost - Ethane steam cracking.

Parameter	**Value**	**UOM**
Specific gravity of Naptha	0.75	
Density of Naphtha	46.8	lb/ft3
Average Price of Gasoline	3.5	$/gal
Average Price of Crude Oil (barrell)	100	$/bbl
Average Price of Crude Oil (Gallon)	2.3	$/gal
Assuming price of Naphtha price	**3**	**$/gal**
Average Price of Naphtha (cubic foot)	22	$/ft3
Average Price of Naphtha (Pound basis)	0.48	$/lb
Average Price of Naphtha (kg)	**1.1**	**$/kg naphtha**
Specific Consumption of Naphtha to ethylene	2.86	kg/kg ethylene
Amount of Naphtha required	272	Tonnes/hr
Price of Naphtha	288334	$/hr
Gross heating Value of ethane	1783	Btu/SCF
Average Price of NGL - Ethane	4	$/MMBtu
Basis of 1 MMBtu (SCF)	560.9	SCF ethane
Basis of 1 MMBtu (kg)	20.2	kg of ethane
Average Price of NGL - Ethane (kg)	**0.2**	**$/kg ethane**
Amount of ethane required	112	Tonnes/hr
Price of ethane	22171	$/hr

Table 15: Consolidated cost data- Ethane cracking process.

Parameter	**Value**	**UOM**
Cost of Energy	526.6	Million $/yr
Cost of Raw material	195.2	Million $/yr
Total Operating Cost	**721.8**	**Million $/yr**
Fixed Capital Cost	**870.8**	**Million $/yr**
Annual sales of product	1336.2	Million $/yr
Economic Gross Potential	1141	Million $/yr

Table 16: Operating cost of equipment- ethane cracking.

SECTION	Units named in PFD	Total cost of utility
		$/hr
PYROLYSIS	PREHEATER	2797
	CRACKER	2788
	TRANSFER LINE EXCHANGE	775
COMPRESSION SECTION	RECIRCULATION HEATER	544
	INTERSTAGE COOL1-A	64
	INTERSTAGE COOL1-B	64
	INTERSTAGE COOL2	80
	INTERSTAGE COOL3	70
	INTERSTAGE COOL4	72
	1ST STAGE COMPRESSOR	523
	2ND STAGE COMPRESSOR	505
	3RD STAGE COMPRESSOR	495
	4TH STAGE COMPRESSOR	469
SEPARATION SECTION	REFRIGERATION COOLER	283
	COOL TRAIN HX3-A	192
	COOL TRAIN HX3-B	192
	COOL TRAIN HX3-C	198
	COOL TRAIN HX6-A	471
	COOL TRAIN HX6-A	471
	COOL TRAIN HX9	164
	CONDENSOR 1	97
	REBOILER 1	9702
	CONDENSOR 2-A	826
	CONDENSOR 2-B	826
	REBOILER 2	17640
	ACETYLENE PREHEATER	8820
	CONDENSOR 3-I-A	898
	CONDENSOR 3-I-B	898
	CONDENSOR 3-II-A	898
	CONDENSOR 3-II-B	898
	REBOILER 3-I	11907
	REBOILER 3-II	11907
	TOTAL OFF-GAS GENERATION	**-4757**

Table 16: Continued.

SECTION	Units named in PFD	Total cost of utility
		$/hr
	DILUTION STEAM	245
	Total	60113

Table 17: Cost of utilities. (El-Halwagi, 2012)

Type of utility	Parameter	Value	UOM
Heating utility	Steam	**4.41**	$/tonne
	Natural gas	**4**	$/MMBtu
Cooling Utility	Refrigeration	**20**	$/MMBtu
	Cooling water	**2**	$/MMBtu

The assumptions made for utility prices are given in Table 17. The total operating cost is sum of energy cost and raw material cost. The raw material cost includes the cost of ethane and cost of caustic since, caustic regeneration is not considered here. The price of caustic taken from ICIS website is found to be $545/ tonne. In this analysis, the cost of utility is assumed in terms of energy except for steam. The amount of steam consumed in each exchanger is calculated using ASPEN PLUS such that only latent heat is utilized by the process stream. It can also be seen that the credit for utilizing off gas generated in the plant as fuel for cracker can be reflected in terms of negative cost of natural gas saved in the furnace. The total off gas generated constitutes of 12,259 Kg/hr of light gases, whose composition is given by 54.79 mol % of hydrogen, 6.8 mol % of ethylene, 37 mol % of methane and 1 mol % of ethane. It produces a combined heat duty of around 1189 MMBtu/hr, which when multiplied with natural gas thermal efficiency and the cost of natural gas gives the credit for off gas to energy cost. The cost of injecting dilution steam in the cracker for prevention of coke formation is also added in the operating costs. It can be seen from cost analysis table, that cost of energy is approximately 73% of the total operating cost.(Ren et al., 2006) Hence this proves that this process is highly energy intensive. The fixed cost is calculated using the formula:(El-Halwagi, 2012)

$FCI_B = FCI_A * (\text{Capacity of B/ Capacity of A})^{0.6}$

Where FCI_A is found to be 691 $MM for 568,000 annual rate of production of ethylene (Capacity).(El-Halwagi, 2012) Here, capacity of B is 832000 Tonnes per year (present case study).

IV.2. Pyrolysis of Methane

The basic raw materials involved in methane pyrolysis are natural gas and oxygen. To get pure oxygen, an air separation unit needs to be installed at the same process facility in order to be cost effective. In this case study, a cost of 0.021$/kg of oxygen is assumed as raw material price.(Noureldin, Elbashir, & El-Halwagi, 2013) Similarly the amine absorber involving the usage of MEA requires installation of recovery system to recover MEA and recycle it back to the tower.(Chapel, Mariz, & Ernest, 1999) In this case, capital and operating cost of MEA recovery units are included and shown separately in order to make reasonable comparison with ethane cracking process where no recovery system has been accounted. N methyl 2-pyrrolidine is considered to be almost fully recovered and recycled directly. The NMP make up to be added to the system according to simulation results is 549 kg/hr. The detailed cost estimation of raw materials is given below in table. It is assumed that MEA is fully recovered in the amine recovery unit hence, no makeup is accounted. The cost of utility is assumed to be same as that of ethane cracking technology. The raw material estimation is given below in Table 18.

Table 18: Estimation of raw material cost- methane pyrolysis.

Parameter	Value	UOM
Average Price of Natural Gas	4	$/MMBtu
Basis of 1 MMBtu (SCF)	1000	SCF methane
Basis of 1 MMBtu (kg)	19.2	kg of methane
Average Price of methane (kg)	0.21	$/kg methane
Amount of methane required	379	Tonnes/hr
Price of methane	**692975349**	**$/year**
NMP make up rate	549	kg/hr
Value of NMP	1.85	$/lb
Annual cost of NMP makeup	**19771320**	**$/year**
Cost of oxygen	0.021	$/kg oxygen
Amount of oxygen consumed	491370	kg/hr
Annual cost of oxygen	**90392425**	**$/year**
Total raw material cost	803.1	$M/year

The cost of energy consumption on an annual basis is calculated using results derived from simulation. The cost of utilities namely steam, power, natural gas, refrigeration and cooling water are assumed to be same as that of ethane cracking plant. It can be seen from process simulation results that the maximum energy consumed was in the quench and spray tower where cooling water is the cooling medium. Though amount of cooling water required is high, the cost of cooling water is low per energy basis and hence, the energy cost is comparatively lesser than the previous process. From the raw material analysis, it can clearly be seen that cost of natural gas is very high when compared to other materials and this is due to high consumption of gas in the reactor. It is to be noted that only 33% of methane is converted to valuable intermediate, acetylene and hence, the economic gross potential is also low compared to previous process. The capital and operating cost of amine sweetening unit were calculated according to literature data. The consolidated cost metrics is shown below in Table 19.

Table 19: Consolidated cost data- methane pyrolysis process.

Parameter	Value	UOM
Cost of Energy	598.5	Million $/yr
Cost of Raw material	803.1	Million $/yr
Total Operating Cost(without amine recovery)	1401.6	Million $/yr
Operating cost of amine recovery unit	20.1	Million $/yr
Total Operating Cost(including amine recovery)	**1421.7**	**Million$/year**
Fixed Capital Cost (including amine recovery units)	**385.1**	**Million $/yr**
Annual sales of product	1336.2	Million $/yr
Economic Gross Potential	533.1	Million $/yr

The energy cost of each equipment is shown below in Table 20. The total operating cost is addition of raw material cost and utility cost. The amount of steam utilized in heat exchangers are obtained using ASPEN simulation. The total off gas generated from NMP absorption, Pressure swing adsorption and de-methanizer lighters accrue to a mass flow rate of 401.2 tonnes /hr. The composition of off gas is given by 60 mol% of hydrogen, 33.5 mole % of carbon monoxide, 6.2 mole % of methane and other hydrocarbons contribute to about 1 mole%. The off gas generated is equivalent to 10676 MMBtu/hr of energy and this when multiplied with cost of natural gas gives the credit for energy. It can be seen from the energy cost table that 38% of the actual energy cost has been balanced by accounting for the energy consumed by off gas. It can also be seen that raw material accounts for 57% of the total operating cost.

Table 20: Operating cost of equipment- methane pyrolysis.

SECTION	Units named in PFD	Total cost of utility
		$/hr
PYROLYSIS	METHANE PREHEATER	4419
	OXYGEN PREHEATER	1778
	REACTOR QUENCHER	4477
	SPRAY TOWER COOLER	2881
COMPRESSION	INTERCOOL STAGE 1-A	101
	INTERCOOL STAGE 1-B	101
	INTERCOOL STAGE 1-C	101
	INTERCOOL STAGE 1-D	101
	INTERCOOL STAGE 2-A	110
	INTERCOOL STAGE 2-B	110
	INTERCOOL STAGE 2-C	114
	INTERCOOL STAGE 3-A	144
	INTERCOOL STAGE 3-B	144
	1ST STAGE COMPRESSOR	2201
	2ND STAGE COMPRESSOR	2143
	3RD STAGE COMPRESSOR	2123
	4TH STAGE COMPRESSOR	200
	5TH STAGE COMPRESSOR	179
	FLASH STAGE 1 HTR	22051
	FLASH STAGE 2 HTR	22051

Table 20: Continued.

SECTION	Units named in PFD	Total cost of utility
		$/hr
SOLVENT SEPARATION	FLASH STAGE 3 HTR	22051
	FLASH STAGE 4 COOL	73
	FLASH STAGE 5 COOL	95
	FLASH STAGE 6 COOL	94
	SOLSEP REBOILER	3087
	SOLSEP CONDENSOR-A	680
	SOLSEP CONDENSOR-B	680
	SOLSEP CONDENSOR-C	660
	INTERCOOL STAGE 5	28
PRODUCT SEPARATION	DEMETHANIZER REBOILER	4851
	DEMETHANIZER CONDENSOR-A	586
	DEMETHANIZER CONDENSOR-B	586
	ETHYLENE REBOILER	11025
	ETHYLENE CONDENSOR-A	496
	ETHYLENE CONDENSOR-B	496
	OFF GAS GENERATION	-42704
	Total	**68318**

The fixed capital cost of this plant is calculated by extracting equipment cost values obtained from ASPEN plus economic analyzer. For equipment namely methane and oxygen preheaters, cracker reactor, pressure swing absorption unit and amine sweetening unit, the capital cost was calculated based on literature values using six tenth factor rule. (Ries, 1966) (Peramanu et al., 1999) (Chapel et al., 1999) The equipment costs obtained from economic analyzer were then multiplied with a Lang factor of 5 to obtain the fixed capital cost.(El-Halwagi, 2012) For those values obtained from literature, six by tenth rule was applied to calculate the equipment cost at given capacity. The formula for scale factor of equipment cost is given by:

$$\text{Equipment Cost}_B = \text{Equipment Cost}_A * (\text{Capacity of B/ Capacity of A})^x$$

The value of x is determined depending on the type of equipment. For furnaces an exponent of 0.78 was used while for rest of the equipment a general value of 0.6 was used for calculation purposes. (El-Halwagi, 2012) Table 21 lists the fixed capital investment calculated for each equipment.

Table 21: Capital investment of equipment- Methane pyrolysis.

S.No	Physical Units	FCI in USD
1	Methane preheater	83553047
2	Oxygen preheater	
3	Cracker reactor	13806232.21
4	Spray tower (10 nos.)	22660000
5	1st stage compressor	45440000
6	Intercool stage 1 (4 nos.)	3239000
7	Cool flash 1	1285000
8	2nd stage compressor	44712814
9	Intercool stage 2 (3 nos.)	2197000
10	Cool flash 2	1219000
11	Amine sweetening unit (including recovery)	21876470
12	3rd stage compressor	65093500
13	Intercool stage 3 (2 nos.)	1490000
14	NMP absorption (3 nos.)	8026500
15	Pressure swing absorption unit	8512069
16	Acetylene hydrogenation	7160000
17	Flash net 1	2821500
18	Flash stage 1 heater	468000
19	Flash net 2	2428000
20	Flash stage 2 heater	492500

Table 21: Continued.

S.No	Physical Units	FCI in USD
21	Flash net 3	2292500
22	Flash stage 3 heater	749500
23	Flash net 4	1698500
24	Flash stage cool 4	213500
25	Flash net 5	574000
26	Flash stage cool 5	295500
27	Flash net 6	374000
28	Flash stage cool 6	328500
29	Flash net 7	330500
30	Solsep column	1958500
31	Solsep reboiler	268500
32	Solsep condensor (3 nos.)+ reflux pump	1798500
33	4th stage compressor	12373000
34	5th stage compressor	8341500
35	Interstage cool 5	241000
36	De-methanizer column	3949500
37	De-methanizer reboiler	177500
38	De-methanizer condenser (2 nos.)+reflux pump	5022000
39	Ethylene column	2351500
40	Ethylene reboiler	452500
41	Ethylene condenser (2 nos.)	4825500
	Total	385096632
	Total in Million USD	**385.1**

CHAPTER V

SAFETY ANALYSIS

In this chapter, the details of safety analysis will be outlined for both the processes. The index chosen to measure safety is Hazard Identification and RAnking system (HIRA). After carrying out a through literature study, it can be understood that one of main reasons why companies do not measure inherent safety in the conceptual stage is because almost all available safety indices require comprehensive data. At the conceptual stage there is not much information on the process except for process flow diagram and approximate economic analysis. The advantage of using HIRA is that this index offers flexibility in neglecting those parameters that are not available, for example, location, spacing and congestion. Another advantage is that this index, though not completely qualitative, most of the operating conditions are estimated through thermodynamic and empirical models. Hence, this index will prove to be a reliable tool for safety analysis.

Further, most of the indices are based on quantification safety index, depending on possible abnormal situations that can be encountered and this requires expertise and experience to choose credible scenarios. But in this approach, the capacities of plant as such will be used for estimating the value of index. This is because the purpose of the analysis is not to calculate accurate value of risks in order to design layers of protection. Instead a rough approximate estimate of safety levels is to be determined in order to rank the equipment in terms of safety and then focus on each section to identify opportunities for application of ISD approaches. Hence, this top level approach requires less time for calculation and can be easily applied at early stage of design.

V.1.General Assumptions

a. For this analysis, only gas phase and vapor phase conditions and compositions will be used for the purpose of calculation. The vapor phase is more dangerous than liquid and hence has more damage potential than liquid. Hence vapor phase conditions are used to represent the extent of damage of each equipment.
b. Effects due to location of the nearest hazardous units and density of units are neglected.
c. In all unit operations, only the composition of hydrocarbons is taken into consideration.
d. For heat exchangers, the design shortcut method used yields the volume of entire equipment. But for safety calculations, instead of counting the volume occupied by hydrocarbon, the value for entire equipment volume will be considered. This is due to the lack of detailed design data available for calculation. This will slightly overestimate the measure of damage potential in heat exchangers.
e. For distillation columns and absorption towers, the conditions at the top of column will be considered for safety calculations. This is because top of column contains maximum amount of lighters in comparison with to

bottom and most of them are in vapor phase. Only vapor load at top of column will be assumed for calculation.

f. Invariably for all equipment, the conditions at the inlet or outlet that has maximum temperature will be considered for safety analysis except for reactors.

g. Since the volumes of compressors are variable and small, the volume term in calculation of compressors and expanders are neglected.

V.1.1 Units with Chemical Reactions and Physical Operations

The procedure for calculation of Fire and explosion damage index using HIRA is different for each equipment class. Since all the equipment considered for analysis of both the plants fall under the category of either physical operations or reactors, calculation algorithm for only these two equipment class is shown. In this sub division, step by step procedure for calculating units involving chemical reaction and physical operation will be listed. The fire and explosion damage index is given by:(Khan & Abbasi, 1998)

$\text{FEDI} = 4.76^* (\text{Damage potential})^{0.333}$

Damage potential (Reactions) = (F1*pn1 +F *pn2+ F4*pn7 *pn8) * pn3*pn4* pn5* pn6

Damage Potential (Physical operations) = (F1*pn1 +F *pn2) * pn3*pn4* pn5* pn6

F1, F and F4 are energy factors and pn1-8 are penalties assigned to each operating condition. F1 is the energy factor that takes account for chemical energy. F is summation of F2 and F3, where both these sub factors account for physical energy based on certain physical conditions.(Khan & Abbasi, 1998) F4 accounts for energy released due to chemical reactions.(Khan & Abbasi, 1998) Penalties pn1 is assigned for temperature, pn2 for pressure, pn3 for quantity of chemical handled in the unit, pn4 for effect of chemical characteristics namely flammability and reactivity, pn5 for effect of location of nearest hazardous unit, pn6 for density of units, pn7 for type of reaction and pn8 for probability of side reaction.(Khan & Abbasi, 1998) The formulas for calculating energy factors and penalties are given as follows:(Khan & Abbasi, 1998)

i. F1 = 0.1* M * (Heat of combustion) / K

ii. F2 = 1.304* 10^{-3} * Operating pressure * Volume

iii. F3 = $1*10^{-3}$ / (T +273)* (Operating pressure- vapor pressure) ^{2} * Volume

iv. F4 = M * Heat of reaction /K

v. Pn1 = f1 (flash, fire, auto ignition, operating temperature)

   Where f1 is given by the algorithm:

   If (Temperature> Flash point<Fire point)

   f1= 1.45

   Else if (Temperature>Fire point<0.75 Auto-ignition temperature)

   f1= 1.75

   Else if (Temperature> 0.75 Auto-ignition temperature)

   f1= 1.95

   Else

   f1= 1.1

vi. Pn2 is calculated using the following algorithm:

If (Vapor pressure>Atmospheric pressure and operating pressure>vapor pressure)

Pn2 = 1+ (1- (vapor pressure/operating pressure))*0.6

F = F2 +F3

Else

Pn2 = 1+ (1- (vapor pressure/operating pressure))*0.4

F= F2

If (Atmospheric pressure > vapor pressure and operating pressure > Atmospheric pressure)

Pn2 = 1+ (1- (vapor pressure/operating pressure))*0.2

F=F3

Otherwise

Pn2 = 1.1

F=F3

vii. Pn3 is calculated based on weightage for chemical handled in the unit. This is based on the chemical characteristics namely flammability and reactivity. Since, both the process are steady state, flow rates are with respect to time. Hence quantity cannot be defined properly. Hence a limiting value of 1.1 is assumed for all operations.

viii. Pn4 describes the effect of chemical characteristics. It is given by the following equation:

Pn4 = 1+0.25* (NFPA flammability score+ NFPA reactivity score)

ix. Pn5 is the effect due to location of nearest hazardous unit. Since this has been neglected for this case study, a minimum value of 1.2 is taken as value.

x. Pn6 is the penalty due to density of units. Since this is neglected for this case study a minimum value of 1 is assumed. The formula is given by the equation below:

Pn6 = (1 + % space occupied by unit in an area of 30 m in radius from the unit/100)

xi. Pn7 is the penalty used for units involving chemical reactions, where the score is assigned based on the type of reaction.

xii. Pn8 is the penalty assigned to account for probability of undesired side reactions in units involving reactions.

M is mass flow rate with units in kg/sec, Heat of combustion in J/mol, Operating pressure in kPa, Volume in m^3, Temperature (T) in ^{0}C and Heat of reaction in kJ/kg. K is a constant with value of 3.148. The damage potential and the final fire and explosion index are measured as radius of impact in meters. In units where temperature varies as a function of length, temperature of decision was chosen to be the one that was maximum at any part of the length. The heat of combustion was calculated based on mole fraction of vapor phase in each equipment. NFPA rankings for flammability and reactivity were also calculated based on mole fractions. For equipment processing only gas, conditions at the end where the temperature is maximum is considered for calculation.

V.2. Ethane Cracking

For safety analysis of ethane cracking technology, only the 8 main hydrocarbon compounds in the plant are considered. The detailed calculation sheet is attached in appendix. The base data on heat of combustion, flash point, auto ignition temperature and NFPA rankings are obtained from National Institute of Standards and Technology (NIST) handbook. The heat of reaction of reactors were calculated using values obtained from ASPEN simulation. Since reactors have change in composition with respect to length, the conditions at the state where maximum FEDI value is encountered is taken into consideration for calculation. After all the necessary design data were collected for calculating the safety index, the following results were obtained and are ranked in the descending order in Table 22.

Table 22: Equipment ranking based on FEDI values- Ethane cracking process.

S. No	Equipment Class	Physical Units	Fire and Explosion Damage index
1	Distillation Column	C2splitter-I	1456
2	Distillation Column	C2splitter-II	1456
3	Distillation Column	De-ethanizer	1430
4	Heat Exchanger	Reboiler 2	1384
5	Heat Exchanger	Reboiler 1	1241
6	Heat Exchanger	Preheater	1049
7	Heat Exchanger	Reboiler 3	1029
8	Heat Exchanger	Acetylene preheater	1006
9	Heat Exchanger	Condenser 2-A	976
10	Heat Exchanger	Condenser 2-B	976
11	Tower	Caustic scrubber	950
12	Reactor	Cracker	945

Table 22: Continued.

S. No	Equipment Class	Physical Units	Fire and Explosion Damage index
13	Reactor	Acetylene hydrogenation	944
14	Distillation Column	De-methanizer	932
15	Vessel	Dryer	918
16	Heat Exchanger	Inter-stage cool4	912
17	Heat Exchanger	Inter-stage cool3	911
18	Heat Exchanger	Cool train hx2	911
19	Heat Exchanger	Refrigeration cooler	911
20	Heat Exchanger	Cool train hx1	910
21	Vessel	Flash drum 2	909
22	Compressor	3rdstage compressor	909
23	Compressor	4th stage compressor	908
24	Heat Exchanger	Inter-stage cool2	908
25	Vessel	Flash drum 1	907
26	Compressor	2nd stage compressor	907
27	Compressor	1stage compressor	897
28	Heat Exchanger	Transfer Line exchange	896
29	Vessel	Cool-flash 1	804
30	Heat Exchanger	Cool train hx5	792
31	Heat Exchanger	Cool train hx4	791
32	Heat Exchanger	Condenser 3-I-A	774
33	Heat Exchanger	Condenser 3-I-B	774
34	Heat Exchanger	Condenser 3-II-A	774
35	Heat Exchanger	Condenser 3-II-B	774
36	Heat Exchanger	Inter-stage cool 1 A	713
37	Heat Exchanger	Inter-stage cool 1 B	713
38	Heat Exchanger	Cool train hx3-C	647
39	Heat Exchanger	Cool train hx3-A	646
40	Heat Exchanger	Cool train hx3-B	646
41	Heat Exchanger	Cool train hx6-A	639
42	Heat Exchanger	Cool train hx6- B	639
43	Column	Quench tower-1	635
44	Column	Quench tower-2	635

Table 22: Continued.

S. No	Equipment Class	Physical Units	Fire and Explosion Damage index
45	Column	Quench tower-3	635
46	Vessel	Cool-flash 2	446
47	Heat Exchanger	Condenser 1	371
48	Heat Exchanger	Cool train hx9	362
49	Heat Exchanger	Cool train hx8	357
50	Heat Exchanger	Cool train hx7	354
51	Vessel	Cool-flash 3	255
52		Expander	186

From the results it can be seen that the C2 splitter columns are the more dangerous with highest impact radius, followed by de-ethanizer column and de-ethanizer reboiler. The preheater and cracker are essentially in the same unit, but since the index distinguishes different classes of equipment, they have been separated as convection section (preheater), where the feed is preheated and radiation section (cracker) where ethane dehydrogenation takes place respectively. Figure 17 shown below gives approximately the number of equipment that falls under each range of fire and explosion damage index. It can be seen that 17 out of 52 equipment fall under the category of 900< FEDI< 1000, while 8 equipment fall under the range that has FEDI>1000. This chart gives us an approximate idea on which equipment we need to concentrate to improve safety. Effort should be taken at this stage to apply Inherent safety guidewords to modify the process and the procedure should be repeated to achieve lower impact radius. It should be noted that the value of index is a highly overestimated figure, since the units were not evaluated for any abnormal conditions. Hence, the magnitude does not literally imply the exact damage radius, but on a comparative basis, it indicates where each unit stands with respect to other equipment on inherent safety. Similarly those 7 equipment falling under the category of 400< FEDI <200 does not require much attention in terms of safety.

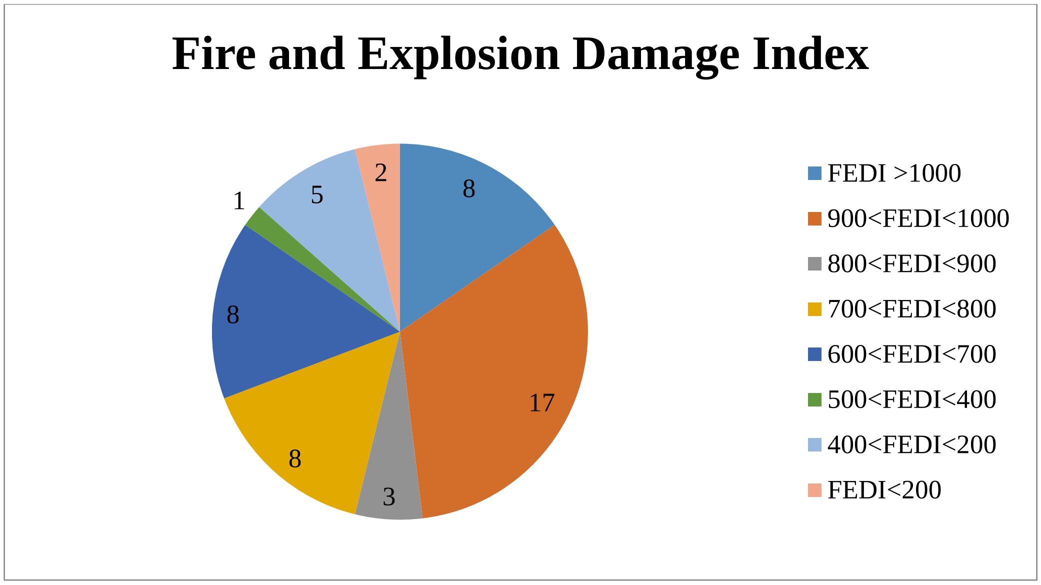


Figure 17: Distribution of equipment under various ranges of damage radius-Ethane Cracking.

Figure 18 shows the semi-quantitative ranking of equipment. By using the semi-quantitative chart of HIRA for deducing the final results, it can be seen that almost 83% of equipment are highly hazardous. This chart merely shows an analysis of how many equipment are highly hazardous and hence gives an overview of safety present in the process technology. The qualitative ranking will not be used for comparative study since it does not identify the areas of improvement accurately.

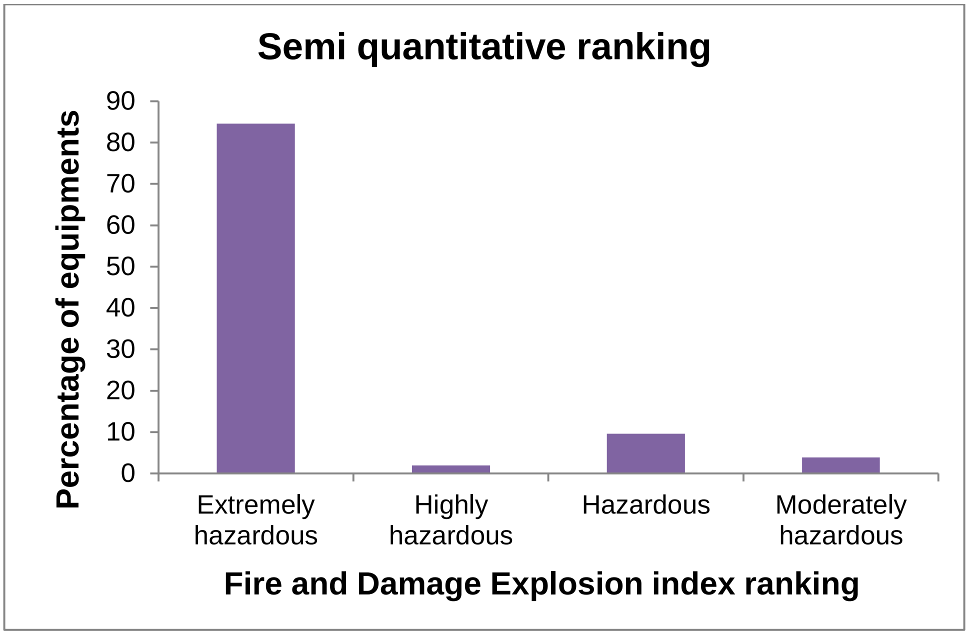


Figure 18: Semi-quantitative ranking based on HIRA method- Ethane Cracking.

Figure 19 shows the section wise ranking of top 5 most hazardous equipment of the process and this gives a detailed overview of areas of improvement in terms of safety. It can be seen that since cooling and separation has maximum number of equipment (32 nos.), this section is more hazardous because it consists of large number of dangerous equipment. The reason for large value of indices infer to be due to chemical composition, mass flow rate handled and chemical characteristics such as flammability, reactivity and heat of combustion. The general safety data sheet shows that heat of combustion values are high for ethylene, ethane, propylene, propane, butadiene and acetylene. It can be seen that since most of the products are purified in the separation section, the presence of the above mentioned chemicals in high quantities and in pure state, increases the impact of damage in the event of abnormal release. It can be seen within each section except for the compression section, there is difference in damage radius between units in same section. It can also be seen that magnitude of impact of C2 splitter column in separation section is approximately 1.5 times higher than caustic scrubber in compression section and preheater in pyrolysis section. This shows that C2 splitter column has be investigated first to identify the root cause of damage radius. One of the observation is that the effect of temperature and pressure difference between different units does not have a stark impact on the damage potential and this is a limitation of the index. Figure 20 showing the overall block diagram displays highest radius of impact of each unit and depicts how the damage radius varies along the process flow.

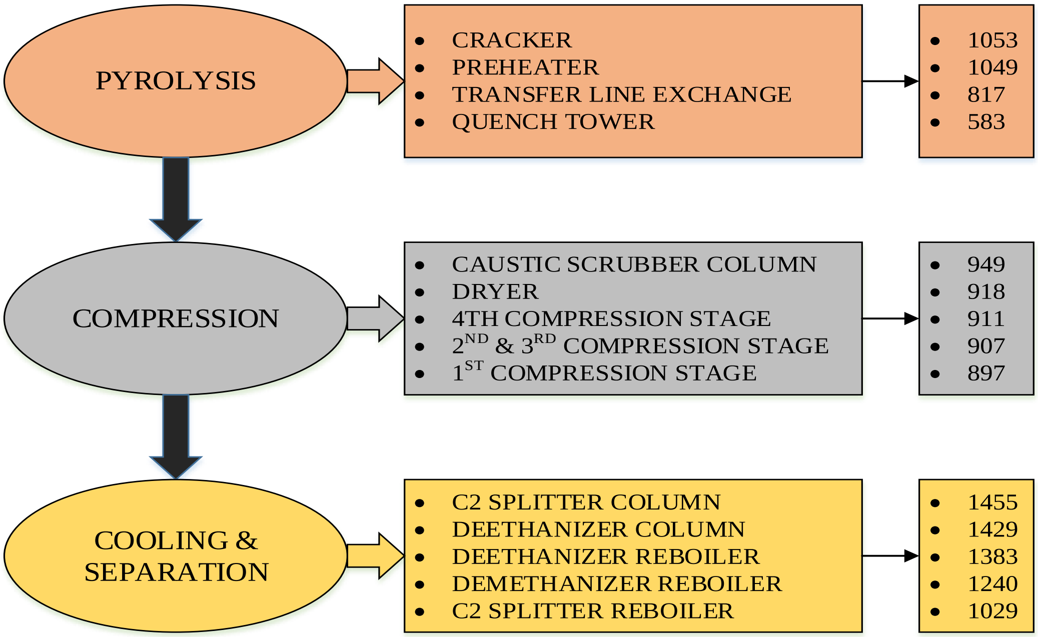


Figure 19: Section wise ranking of FEDI- Ethane Cracking.

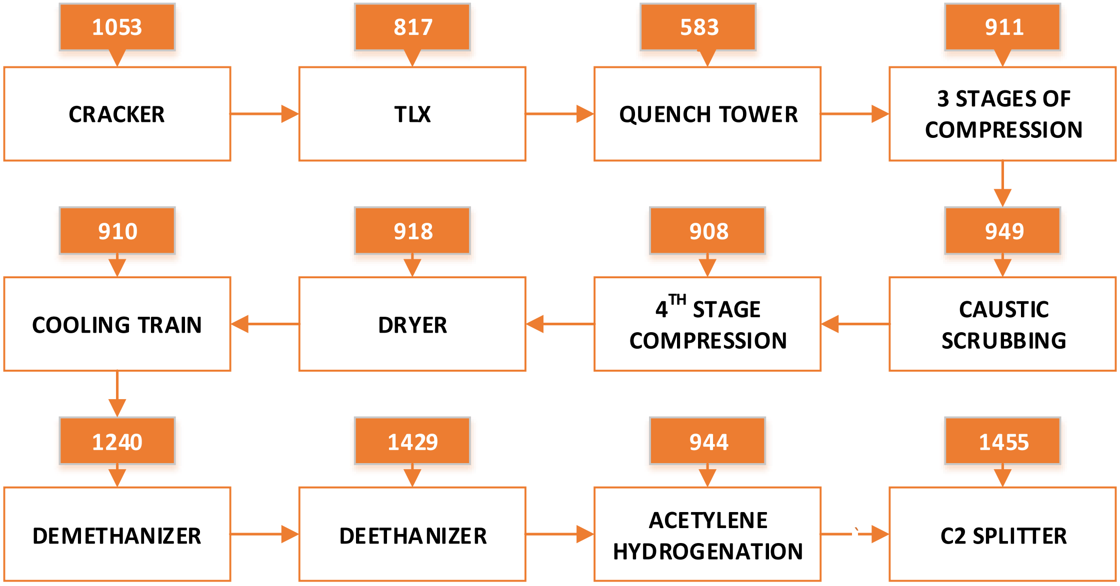


Figure 20: Overall block diagram of inherent safety levels- Ethane cracking.

V.3. Pyrolysis of Methane

Safety analysis of GTE technology is carried out in a similar way as ethane cracking technology. The main compounds considered for calculation of safety index are methane, hydrogen, ethylene, acetylene, propadiene and carbon monoxide. Carbon monoxide is non-environmental friendly, toxic and also highly flammable. In this case study index will be calculated to account only for flammability and hence, only the flammable characteristics of carbon monoxide will be considered. The cracker is evaluated in the same way as ethane cracker. Since composition varies along the length, conditions at that state where calculated FEDI is higher is considered for analysis. Also mass release rate accounts only for hydrocarbons assumed for the safety analysis. The detailed calculation sheet is shown in appendix. Table 23 shows the equipment wise ranking in descending order. There are a total of 62 equipment in this process and the ranking table shows only the representative equipment for those that are in network of parallel equipments.

Table 23: Equipment ranking based on FEDI values- Methane Pyrolysis.

S.No	Equipment Class	Physical Units	Fire and Explosion Damage index
1	Cracker	Reactor	1147
2	Furnace	Methane preheater	1107
3	Heat Exchanger	Ethylene reboiler	1104
4	Column	Ethylene column	1104
5	Column	De-methanizer column	1093
6	Heat Exchanger	De-methanizer reboiler	1061
7	Compressor	3rd stage compressor	943

Table 23: Continued.

S.No	Equipment Class	Physical Units	Fire and Explosion Damage index
8	Vessel	Cool flash 2	915
9	Vessel	Cool flash 1	910
10	Compressor	2nd stage compressor	910
11	Compressor	1st stage compressor	897
12	Heat Exchanger	Interstage cool 5	863
13	Compressor	4th stage compressor	861
14	Compressor	5th stage compressor	861
15	Column	Solsep column	857
16	Heat Exchanger	Ethylene condenser (2 nos.)	836
17	Column	Amine absorber (2 nos.)	812
18	Heat Exchanger	De-methanizer condenser (2 nos.)	773
19	Vessel	Pressure swing absorption	766
20	Heat Exchanger	Intercool stage 3 (2 nos.)	752
21	Vessel	Flash net 1	752
22	Column	NMP absorption (3 nos.)	748
23	Vessel	Flash net 7	658
24	Vessel	Flash net 2	647
25	Heat Exchanger	Intercool stage 2 (3 nos.)	633
26	Vessel	Flash net 6	601
27	Heat Exchanger	Flash stage cool 6	599
28	Heat Exchanger	Solsep condenser (3 nos.)	586
29	Heat Exchanger	Intercool stage 1 (4 nos.)	567
30	Heat Exchanger	Flash stage 1 heater	562
31	Vessel	Flash net 3	560
32	Vessel	Flash net 5	556
33	Heat Exchanger	Flash stage cool 5	554
34	Heat Exchanger	Flash stage cool 4	532
35	Heat Exchanger	Flash stage 2 heater	443
36	Heat Exchanger	Flash stage 3 heater	388
37	Vessel	Flash net 4	356
38	Column	Spray tower (10 nos.)	349
39	Acetylene hydrogenation	Reactor	210
40	Heat Exchanger	Solsep reboiler	33
41	Furnace	Oxygen preheater	17

From the safety analysis results, we can see that Cracker/ reactor is most hazardous unit operation in the process. This is followed by methane preheater and then ethylene reboiler. Though the residence time of cracker is small leading to a small volume equipment, the amount of gas processed and operating temperature are high. Pyrolysis, Compression, Solvent Separation and Product separation section consists of 4, 12, 19 and 6 equipment respectively. Though the pyrolysis section consists of only 4 equipment, the magnitude of damage for 2 equipment, is very high. Hence, pyrolysis section may be considered more hazardous.

The number of equipment for different range of FEDI values were plotted. This is shown in Figure 21. It can be seen that 6 out of 62 equipment (around 9.5%) have damage radius more than 1000 meters. More number of equipment fall under the category of 500- 600 and 200-400 range of FEDI values. Necessary area of focus needs to be given to those equipment in the higher range for safety improvement. It should be noted that cracker reactor is also highly energy intensive and most hazardous. A semi quantitative ranking based on HIRA ranking methodology is plotted to gain insight into the whole process. This is shown in Figure 22. It can be seen that almost 75% of equipment in the process are extremely hazardous. Proper ISD approaches should be applied to these equipment to find out opportunities for enhancing safety. Since GTE technology is a relatively new technology, there exists huge benefits of analyzing the process at this stage to make it inherently safer and process efficient.

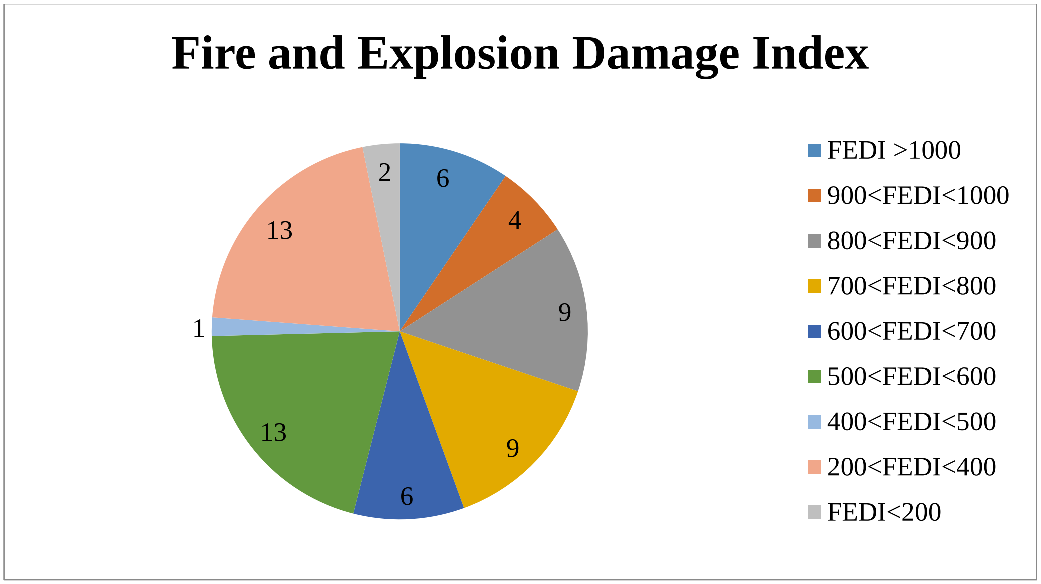


Figure 21: Distribution of equipment under various ranges of danage radius- Methane pyrolysis.

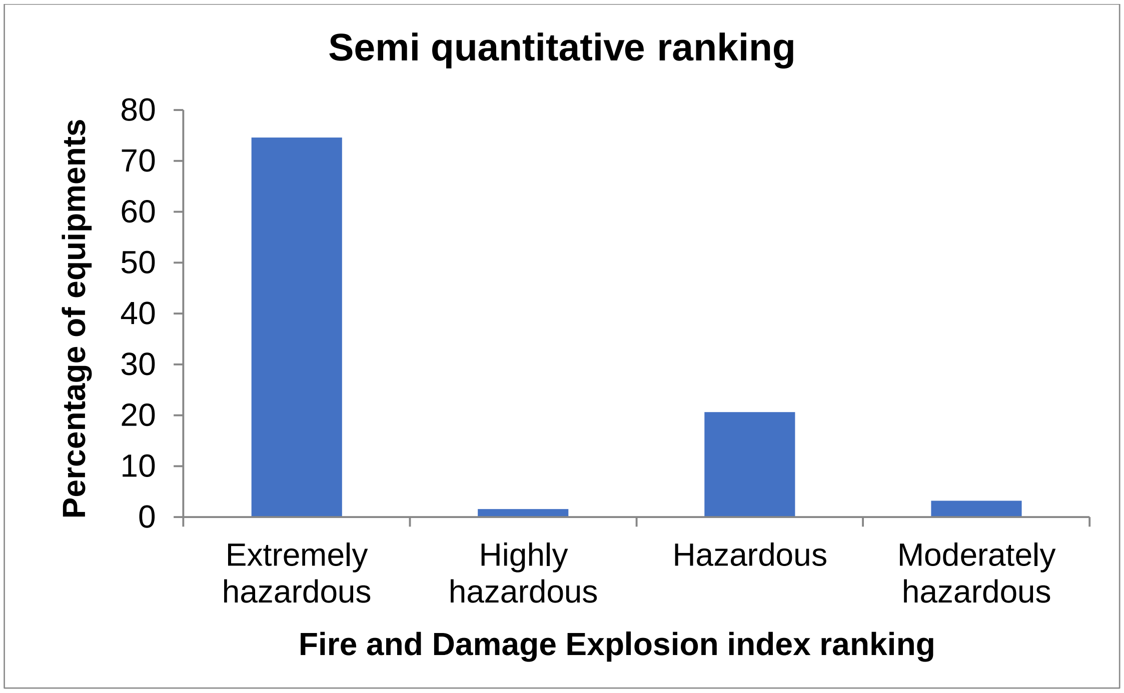


Figure 22: Semi-quantitative ranking based on HIRA method- Methane pyrolysis.

The section wise ranking of equipment is illustrated by Figure 23. It can be seen that in the pyrolysis section, cracker has highest damage potential followed by methane preheater. The remaining equipment in the pyrolysis section are safer. Analysis of compression section shows that all the compressors have an impact radius around 900 m. The 3rd compressor is highest because of increase in acetylene concentration and other lighters. In the solvent separation section, the SOLSEP column has highest damage potential, followed by flash stages that have higher mole percent of hydrocarbon in their vapor streams. Similarly, in product separation section ethylene column and reboiler are more hazardous than de-methanizer column.

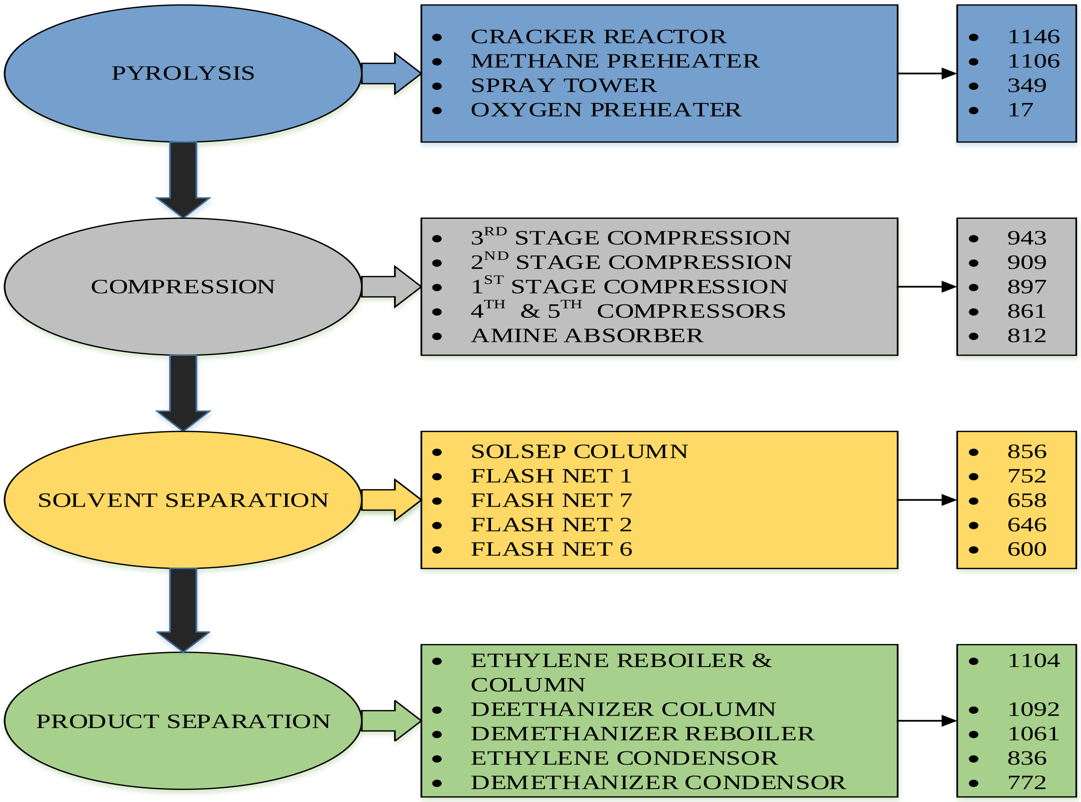


Figure 23: Section wise ranking of FEDI- Methane Pyrolysis.

From the figure, it can be inferred that almost all the high ranked equipment in each section have same radius of impact. Once again, the magnitude does not reflect the exact damage index but instead sheds some knowledge about the parameters that affect the impact radius. The main parameters that affect the impact radius are flammability, heat of combustion, gas composition, mass flow rate and penalties for temperature and pressure.

The block diagram displayed in Figure 24 shows how the impact radius varies along the process flow. It can be seen that starting from cracker, the FEDI value decreases at Spray tower and the increases. This is because Spray tower section consists of 10 parallel networks of equipment due to design considerations. This once again proves that reduction in size increases safety. It can be well noted that the safety index of acetylene hydrogenation is very low in the range of 200. This is because the hydrogenation reaction is carried out in liquid phase and only the vapor phase containing hydrogen is considered for analysis. Starting from solvent separation the FEDI values increase due to increase in concentration of pure hydrocarbons.

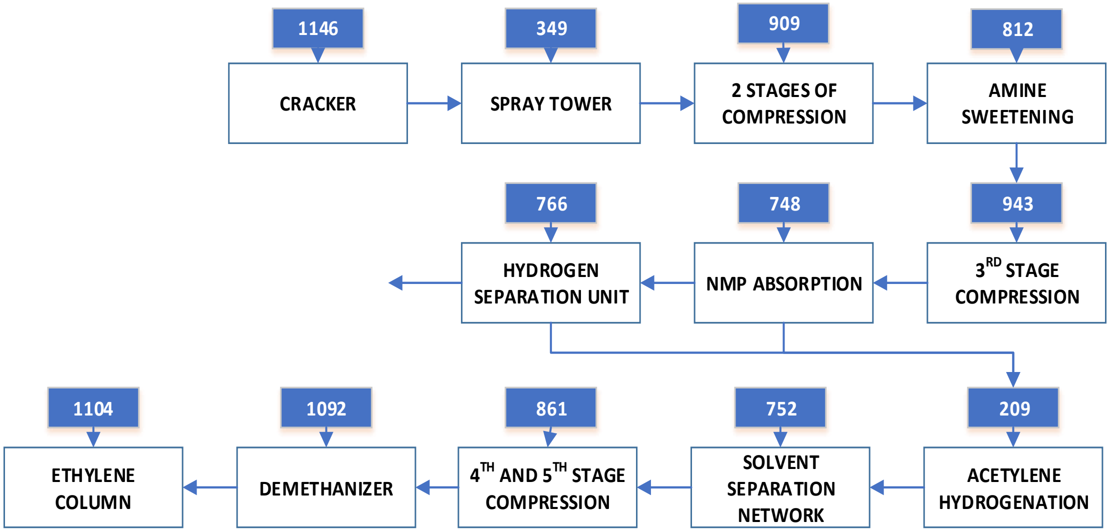


Figure 24: Overall block diagram of inherent safety levels- Methane pyrolysis.

CHAPTER VI

RESULTS AND DISCUSSION

From the previous chapters, results of techno-economic and safety analysis were discussed separately for each base case. In this chapter, the overall objective of this research is achieved by comparing both the processes to identify the superior process that balances process performance, economics of operation and inherent safety. Each analysis was performed by applying same techniques and assumptions so that a reasonable comparison can be made. For the same reason, ethylene production rate of 830,000 Tonnes/annum is considered as the basis of process simulation for both the plants. The final results are obtained by comparing the key performance indicators of each metrics.

VI.1. Process Metrics

The key process metrics that are compared are process yield, specific consumption of raw material, conversion, minimum energy requirements and specific energy consumption. Both the plants are optimized and simulated to produce 99.9wt% pure ethylene. The results of the analysis are shown below in Table 24. From the comparative table, it can be clearly seen that process performance of ethane cracking technology is better than the methane pyrolysis. The process yield of methane pyrolysis is considerably low because of the requirement of part of the natural gas to be used as fuel in order to generate enough heat required to crack methane. Hence, this also increases the specific consumption of raw material of natural gas to produce ethylene. Another reason for the specific consumption of methane to be very high is because the methane crackers are once through reactors. Since most of the methane is burned, recovery of methane in the final product purification level is relatively insignificant and hence, there is no feed recycle unlike ethane cracking process, where unconverted ethane is recovered and recycled back to the reactor. It can also be seen that the product recovery in ethane cracking technology is higher than methane pyrolysis. This is dictated by optimized use of external solvent and energy required for separation.

Table 24: Comparison of process performance metrics.

S.No	Parameters	Ethane Cracking	Methane Pyrolysis	UOM
1	Process yield of ethylene	85	25	%(mass basis)
2	Specific consumption of raw material	1.2	4	Tonne of raw material/tonne of product
3	Conversion of raw material	60	33	%(mass basis)
4	Product recovery	99	96	%(mass basis)
5	Minimum energy requirements	2446	6252	MMBtu/hr
6	Minimum heating requirements	1112	1244	MMBtu/hr
7	Minimum cooling requirements	1200	4546	MMBtu/hr
8	Specific energy consumption	26	66	MMBtu/tonne of ethylene

In terms of energy requirements, it is clear that ethane cracking requires less energy than methane pyrolysis. The underlying fact is that majority of the energy requirements in methane pyrolysis is contributed by quench water in the reactor, which is used for bringing down the temperature of the reactor immediately to stop carbon decomposition reaction. Since this requires very less residence time, large amounts of cooling water needs to be used and this increases cooling requirements of quench water. The reasons can be attributed mainly due to process chemistry requiring high temperatures for producing acetylene and insufficient heat recovery systems. This paves way for modification in the process chemistry such that acetylene is produced at less intensive operating conditions or heat recovery systems be introduced such that a proper heat integration network is formed that will significantly reduce external energy consumption.

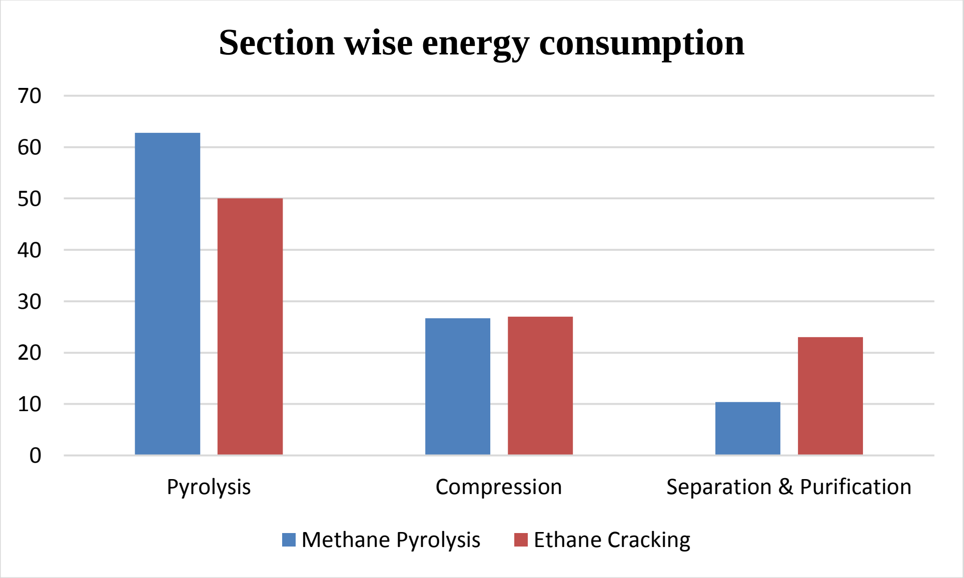


Figure 25: Comparison of section-wise energy consumption.

A section wise comparison of specific energy consumption is illustrated by Figure 25. In the pyrolysis section, Methane pyrolysis has contribution to specific energy consumption when compared to ethane cracking process. This is attributed to high reactor temperature and cooling requirements. Input to specific energy consumptions of compression section are almost same for both the plants. It can be seen that percentage of specific energy consumed is higher for ethane cracking process when compared to methane pyrolysis. The reason can be attributed due to cryogenic operations required for separation of purification of products in ethane cracking technology. It is to be noted that solvent separation and product purification sections in methane pyrolysis plant have been clubbed into separation and purification section.

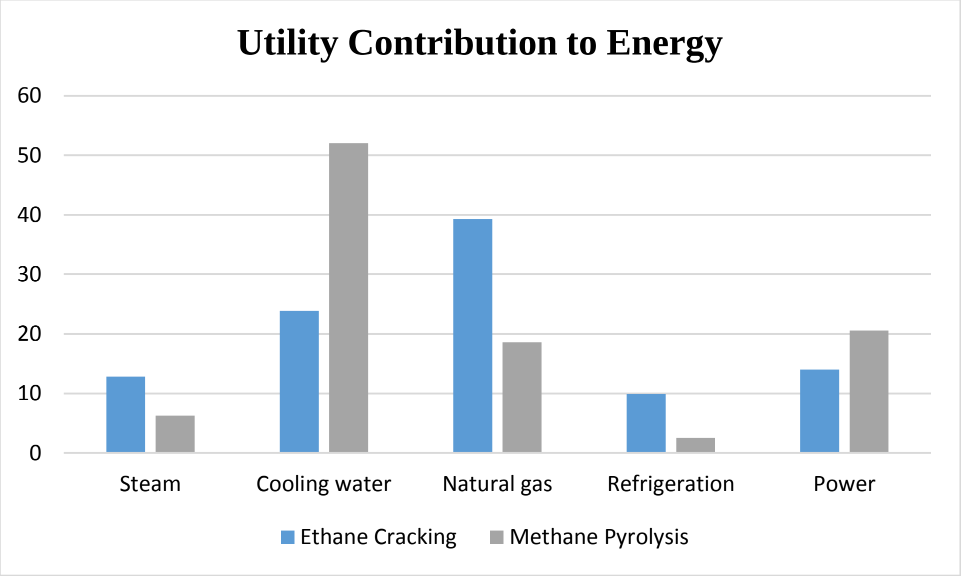


Figure 26: Comparison of utility consumption.

Figure 26 shows individual contribution of each utility to the total energy requirements is shown below. Methane pyrolysis utilizes almost 50% of energy requirements from cooling water, followed by power required for compression. Ethane cracking technology utilizes more natural gas for energy requirements, followed by steam and power. It can be clearly seen that refrigeration demands in ethane cracking process is higher than methane pyrolysis, leading to higher energy cost.

VI.2. Economic Metrics

The main cost metrics that decide which process is more economically viable are cost of energy, raw material cost, total operating cost and fixed capital cost. In order to justify comparison of both the processes, same cost of utility have been chosen. The prices of raw material are taken as an average value of natural gas and natural gas liquids trends in the EIA website. The results of the economic comparison are shown below in Table 25.

Table 25: Comparison of economic metrics.

S.No	Parameters	Ethane Cracking	Methane Pyrolysis	UOM
1	Energy Cost	526.6	598.5	Million $/year
2	Raw material cost	195.2	803.1	Million $/year
3	Total operating cost	721.8	1421.7	Million $/year
4	Fixed Capital Cost	870.8	385.1	Million $/year
5	EGP	1141.1	533.1	Million $/year

From the table, it can be seen that Ethane cracking process has more economic advantage over methane pyrolysis process. The total operating cost of methane pyrolysis is almost twice that of ethane cracking process. This is because of the high rates of natural gas consumption and external solvent makeup involved in the process. Also, the study does not include cost of a separate air separation unit, but instead accounts for cost of oxygen as a raw material. Addition of air separation unit will increase the fixed cost but there will be no significant reduction in the total operating cost. It can be seen that the fixed capital cost of Methane pyrolysis is much lower than ethane cracking. This is because, the reaction chemistry involved is not much complex and does not involve much hydrocarbons that require rigorous separation processes. The use of selective absorption of acetylene and conversion of acetylene to ethylene in liquid phase, has decreased the fixed cost considerably due to ease of separation of product from the solvent. Also the fixed capital cost of methane pyrolysis may be an underestimation of the actual cost since other minor unit operations such as pumps, blowers, and other utility unit operations have not been accounted in the calculation. Nevertheless, the huge difference in fixed capital cost of both plants emphasize that this error of underestimation can be neglected thus, proving that fixed capital cost of methane pyrolysis is lower than ethane cracking process.

Another important analysis that can be inferred from cost of energy is that though the minimum energy requirements of methane pyrolysis plant were very high, the operating cost of both the plants are almost same. This is because the utility price of cooling water is cheaper and even though requirement of cooling water is very high in this plant, the low price offsets the energy cost. Whereas in the ethane cracking technology, refrigeration demands are very high leading to increase in energy cost because the cost of refrigeration is \$20/ MMBtu when compared to cooling water cost of \$2/ MMBtu. Moreover off- gas generation in GTE process is very high thus, reducing external fuel consumption required for furnaces and boilers. Also, it can be understood that Economic gross potential of ethylene from ethane cracking is much higher than from methane pyrolysis, once again showing that raw material consumption of methane is very high in the second process.

VI.3. Safety Metrics

The individual plant safety metrics for each equipment were evaluated and analyzed. The comparative study was done based on highest ranking of equipment that are more hazardous, section wise ranking of equipment and proportion of hazardous equipment in the entire process. All the safety assumptions made were applied equally to both the plants. Design data required for safety analysis were also evaluated in the similar way for both the processes. Table 26 given below shows top 5 equipment with highest FEDI rankings in each plant.

Table 26: Comparison of inherent safety levels.

Ranking	**Ethane Cracking**		**Methane Pyrolysis**	
	Equipment	FEDI	Equipment	FEDI
1	**C2splitter**	**1454**	**Cracker reactor**	**1147**
2	De-ethanizer	1430	Methane preheater	1107

Table 26: Continued.

Ranking	Ethane Cracking		Methane Pyrolysis	
	Equipment	FEDI	Equipment	FEDI
3	De-ethanizer reboiler	1384	Ethylene reboiler	1104
4	De-methanizer reboiler	1241	Ethylene column	1104
5	Cracker reactor	1053	De-methanizer column	1093

From the results, it is evident that Methane pyrolysis process is relatively inherently safer than the ethane cracking process, since the magnitude of impact of 1st ranked equipment of methane pyrolysis is lower than the one in ethane cracking process. The main parameters that attribute to this difference in impact are mass of flammable chemical handled, chemical characteristics of chemicals, temperature, heat of combustion of each chemical and gas composition. It is to be noted that C2splitter in ethane cracking operates at 19 bar pressure and -31 ^{0}C top temperature, while reactor in methane pyrolysis operates at 1500 ^{0}C and 1 bar pressure. Effects of temperature, partial pressure, chemical composition and mass flow rate have a pronounced effect on above mentioned equipment.

Similarly due to above mentioned parameters, it can be seen that Ethane cracker has less damage radius than methane pyrolysis. The acetylene hydrogenation reactor in ethane cracking process has an FEDI value of 944 meters while the one in methane pyrolysis has a value of 209 meters. This stark difference can be contributed to the consideration of only vapor phase since acetylene hydrogenation in ethane cracking is gas phase reaction whereas in methane pyrolysis, it is governed by liquid phase reaction.

This shows an example of reduction in process intensification thus proving that inherent safety approach of design is effective.

The section wise ranking of both the plants are shown below in Table 27. From the results, it is evident that pyrolysis section of ethane cracking is less hazardous than methane pyrolysis plant. Transfer line exchange and Spray tower have similar purpose of operation in both the processes. The huge difference in the value of FEDI for both the equipment can be attributed mainly to the operating temperature. The compression section of both the plants have almost same impact radius. Compressors in methane pyrolysis plant rank higher than the ones in ethane cracking plant.

In the separation and purification section, it can be observed that the most hazardous equipment in both the technologies have similar operating conditions and are involved in separation of product. The difference in damage radius of ethylene column in methane pyrolysis and C2splitter column in ethane cracking is due to large vapor load rate present in C2splitter. C2splitter separates ethylene from ethane while ethylene column separates ethylene from Propadiene. Since ethane and ethylene are close boiling points, separation requires large number of trays and reflux ratios and hence, the vapor load of the column is high. The separation of ethylene from Propadiene is relatively easy and this leads to less vapor load. Another factor to be considered is the quantity of feed mixture handled.

The above analysis in the section wise ranking gives insight into the process and this enables easy interpretation of process with safety. This aids in selecting a suitable separation method and also allocation of units in the process flow.

Table 27: Section-wise comparison of FEDI values.

Section	Ethane Cracking		Methane Pyrolysis	
	Equipment	**FEDI**	**Equipment**	**FEDI**
Pyrolysis	Cracker reactor	1053	Cracker Reactor	1147
	Preheater	1049	Methane Preheater	1106
	Transfer Line exchange	817	Spray Tower	349
Compression	Caustic scrubber	949	3rd stage compression	943
	Dryer	918	2nd stage compression	909
	4th stage compression	911	1st stage compression	897
Separation and Purification	C2 splitter column	1455	Ethylene column & reboiler	1106
	De-ethanizer column	1429	De-methanizer column	1092
	De-methanizer reboiler	1383	De-methanizer reboiler	1061

From the semi quantitative charts shown in previous chapters, it can be observed that approximately 86% of equipment in ethane cracking process are extremely hazardous while 76% of equipment in methane pyrolysis are extremely hazardous. This again proves that methane pyrolysis is inherently safer than ethane cracking process. Moreover, the number of equipment in the higher range of FEDI (>800 meters) is higher in ethane cracking process than in methane pyrolysis process. This analysis can be helpful in providing focus on those areas where process improvement needs to be achieved. From the above discussed safety analysis it can also be inferred that splitting equipment for design considerations caused significant reduction in damage radius. This proves effectiveness of inherent safety design principles.

From the above comparative study it can be understood that a top level comparative study of process, economics and safety can provide significant insights into the process for improvement in all of the above mentioned areas. The approach used for this research has proved to be effective in identifying grey areas and has also enabled easy interpretation of the results thereby, clearly revealing the root causes of discrepancies in metrics. The analysis shows that ethane cracking process is better in terms of process performance and economics while methane pyrolysis is better in terms of inherent safety. This proves the current trends of new projects proposed for installation of ethane crackers to produce ethylene. Ethane cracking technology is a well-established, saturated technology and the opportunities for process improvement are very less. Meanwhile, gas to ethylene process is a relatively new technology where there exists huge opportunities for improvement. Though process performance and economics parameters of this technology are poor when compared to ethane cracking process, appropriate process modifications and material and heat integration can be applied to improve the process such that safety of the process is improved.

CHAPTER VII

CONCLUSION AND RECOMMENDATIONS

In this research, a top level techno-economic and safety analysis of two technologies producing ethylene, namely the ethane steam cracking and gas to ethylene processes (Methane pyrolysis) was carried out. The results obtained from this analysis show that the ethane cracking process is more process efficient and economically superior while the gas to ethylene is more inherently safer. The approach adopted for carrying out the analysis was aimed at identifying areas of process improvement and key safety parameters at a preliminary stage of design while weighing the economic advantages. The results clearly prove that ethane to ethylene cracking technology is more widely adapted due to process and economic benefits. At the same time it is inferred that the new gas to ethylene technology has more scope of process improvement and requires detail analysis on the process to improve operating efficiency. The early stage approach used in this thesis has served to reason out different options available for producing a chemical utilizing minimum process information and this can help take better future decisions that accounts for technology, cost as well as inherent safety.

From the general methodology of evaluation and results obtained from the study, it is evident that safety has a direct impact on energy consumption and operating cost. This enables easy interpretation of process modifications if safety is measured along with other parameters in the preliminary stages. The limitations of this approach will be availability of suitable indices that can measure inherent safety and huge amount of time and resource spent on evaluation methods at preliminary stage. The study can be expanded to identify different safety indices that measure inherent safety needing minimum process information and the results can be compared to support the decision making process. Finally, time and resources invested at the initial stage can prove to be worthy by choosing inherently safer and economically superior process.

Based on the results obtained, the following observations and recommendations are made that would address the methods of measurement of different metrics, identification of key performance variables and root causes of hazards.

i. The safety index, HIRA chosen is identified to be flexible in eliminating those factors that are not essential at the early stage and hence can serve as a suitable index for measuring inherent safety.

ii. Inclusion of safety analysis in the traditional techno-economic comparison of two processes provides more insight into the technology and sparks novel ideas for improving or integrating technologies to achieve better decision making. Though the gas to ethylene process does not have a good process or economic potential, low inherent safety levels of the process creates more necessity to improve the process in terms of cost and technology.

iii. The assumptions made for safety calculations namely accounting only for vapor phase, can be modified to suit different application of process based on solid or fluid handling capability.

iv. It is observed that the index has a subtle impact to changes in temperature and pressure, unless the operating conditions are variable with respect to flash point and auto ignition temperature. This does not give vital information about weak areas since most of chemicals in hydrocarbon industry are operated above flash points and the magnitude of temperature modification will not be properly reflected in safety index.

v. Similarly, since assumption of vapor phase is made for all unit operations, the role of pressure deviations will not be effected unless operating pressure is lesser than atmospheric pressure. This can be overcome by assuming mixed phase but it can prove to be difficult for evaluating complex operations such as absorption and distillation columns.

vi. The magnitude of damage potential does not merely point out the direct damage radius but it indicates the ranking of each equipment with other. This kind of analysis will help in identifying those equipment which require more attention in terms of safety and energy consumption.

vii. The above observations indicate that there is a need for invention of new safety indices that quantitatively measure process parameters while requiring less process information.

viii. The areas identified for process improvement should be analyzed further by applying four main design principles of inherent safety design, namely minimize, moderate, simplify and substitute.

ix. The cooling and separation section of ethane cracking process needs to be studied further for possible alterations in process flow to reduce the damage radius of distillation columns. It is found that C2splitter is the most hazardous equipment hence, substitution of another separation process or splitting of parallel streams should be analyzed for reducing energy consumption as well as improving safety.

x. Ethane cracking technology has other separation schemes such as front end de-propanizer, front end de-ethanizer and front end acetylene hydrogenation.(Takaoka, 1967) The scheme used for this study was front end de-methanizer. This study can be expanded to analyze all different schemes for inherent safety and choose that separation scheme that is inherently safer.

xi. The advantage of using methane pyrolysis technology is that it is a simple process and has an energy efficient and inherently safer product separation process when compared to ethane cracking process. The front end part of the process involving production of acetylene is the portion that needs focus on safety and process improvement. Studies show that different types of heat transfer methods can be used for pyrolysis of methane. All of these methods also have high energy demands due to large requirements of reaction temperatures, but a study can be done to compare different processes that can yield less impact on safety and energy consumption.

xii. Since majority of the operating cost of methane pyrolysis plant is due to large consumption of natural gas, this technology can prove to be cost efficient in places where natural gas is stranded thus, reducing much of raw material cost.

xiii. Alternatively, methane pyrolysis technology can prove to be feasible on being coupled with plants that produce either of raw materials (oxygen or methane) or utilize the off gas generated in the process to produce some other value added chemical. This either offsets the cost of raw material or increases the product value thus, causing an increase in economic gross potential.

xiv. Since off-gas generated in methane pyrolysis process has large amounts of hydrogen and carbon monoxide, a feasibility study of integrating syngas to gasoline or Fischer Tropsch process can be studied. Hence, methane pyrolysis might have an economic potential on a plants-coupled basis than as a stand-alone plant.

xv. Heat integration and material integration techniques can be applied to identify areas that can be pinched for reducing the minimum requirements of heating and cooling duties thereby reducing energy consumption and also the number of equipments.

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APPENDIX

Table 28: Safety data of chemicals

Chemicals	Fire point	Autoignition Temperature	Flash Point	NFPA - F	NFPA - R	Heat of Combustion
		Deg C	Deg C			KJ/mol
Hydrogen	-190	570	-200	4	0	-286
Ethane	-125	515	-135	4	0	-1561
Methane	-177.9	580	-187.9	4	0	-891.1
Propane	-94	470	-104	4	0	-2219.7
Ethylene	-126	490	-136	4	2	-1410.9
Propylene	-98	458	-108	4	1	-2057.8
Butadiene	-75	415	-85	4	2	-2540.4
Acetylene	-8	300	-18	4	3	-1299.6
Propadiene	-86	453.85	-96	4	1	-1913.4
Carbon monoxide	-181	609	-191	4	2	-284

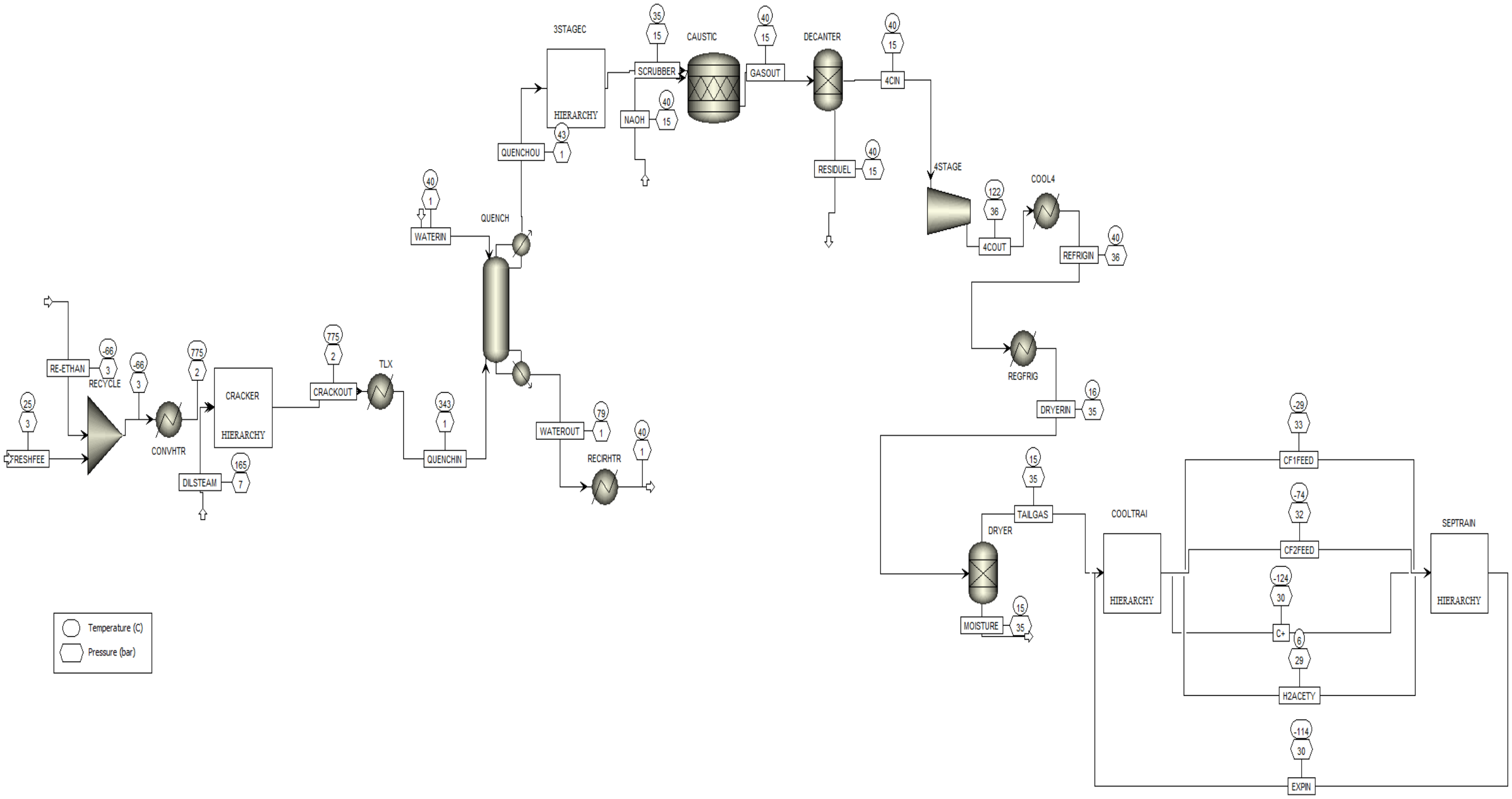

Figure 27: ASPEN Flowsheet- Ethane Cracking - Overall Process

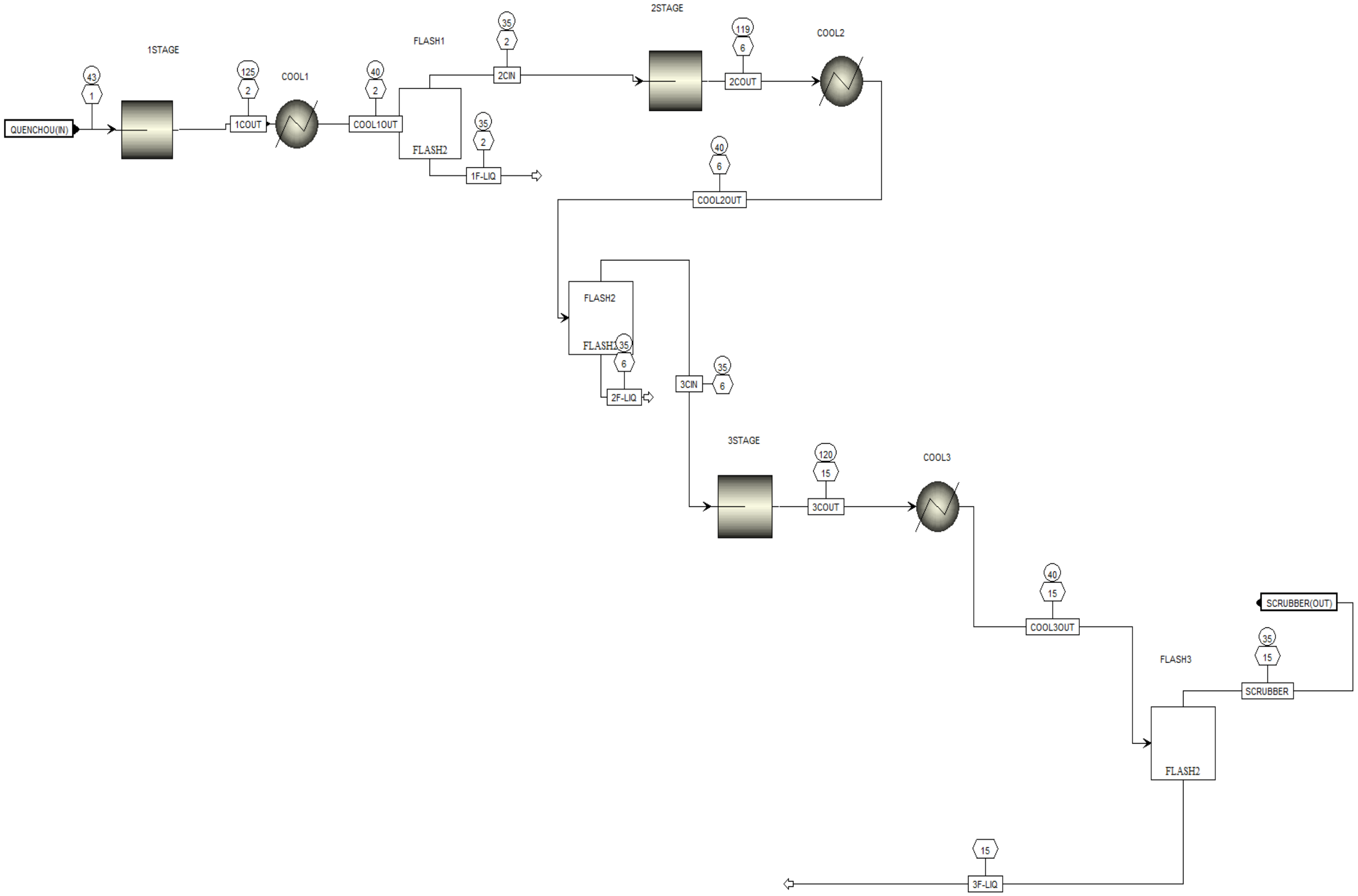

Figure 28: ASPEN Flowsheet: Ethane Cracking- Compression Section

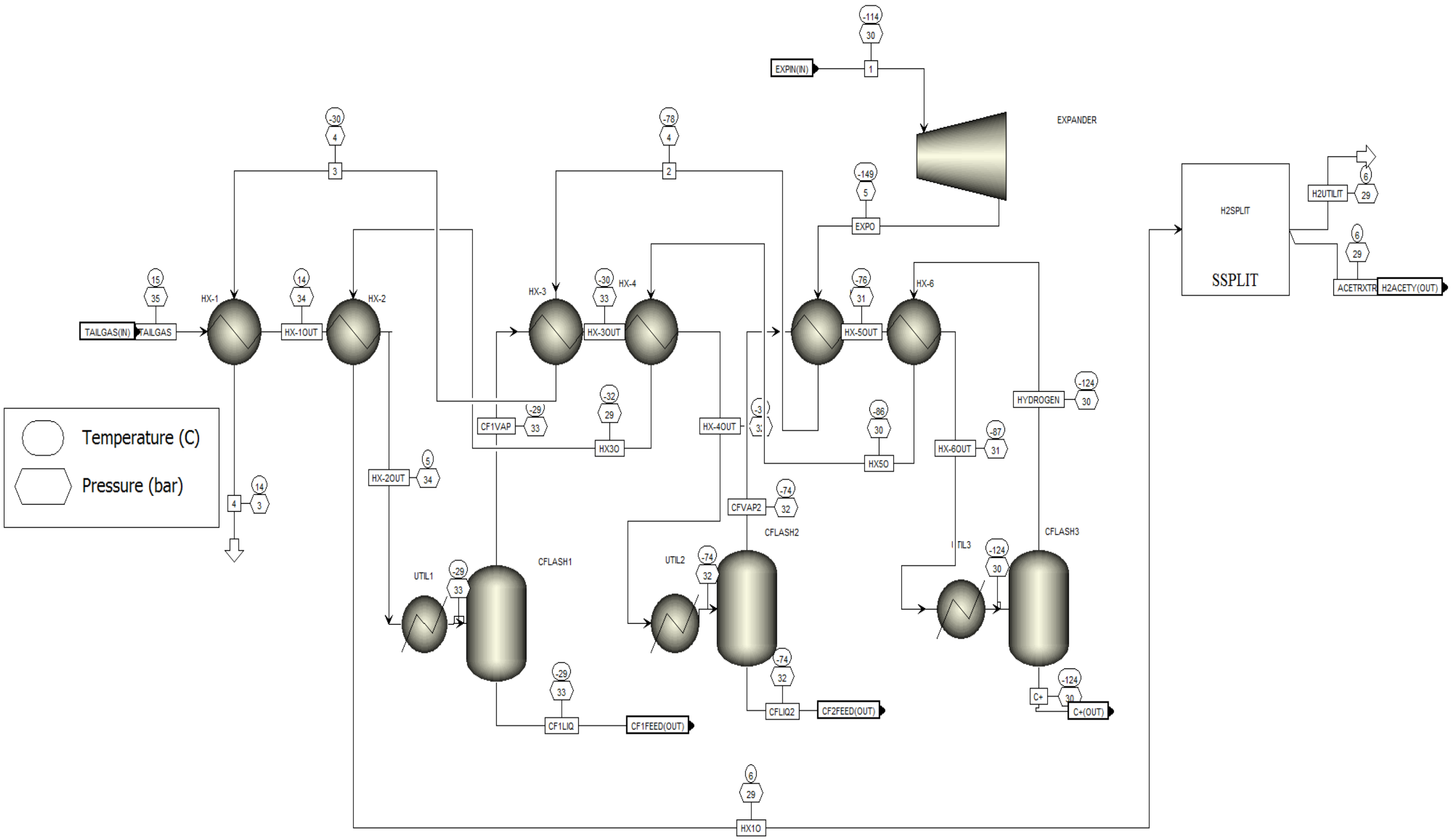

Figure 29: ASPEN Flowsheet- Ethane Cracking- Cooling train

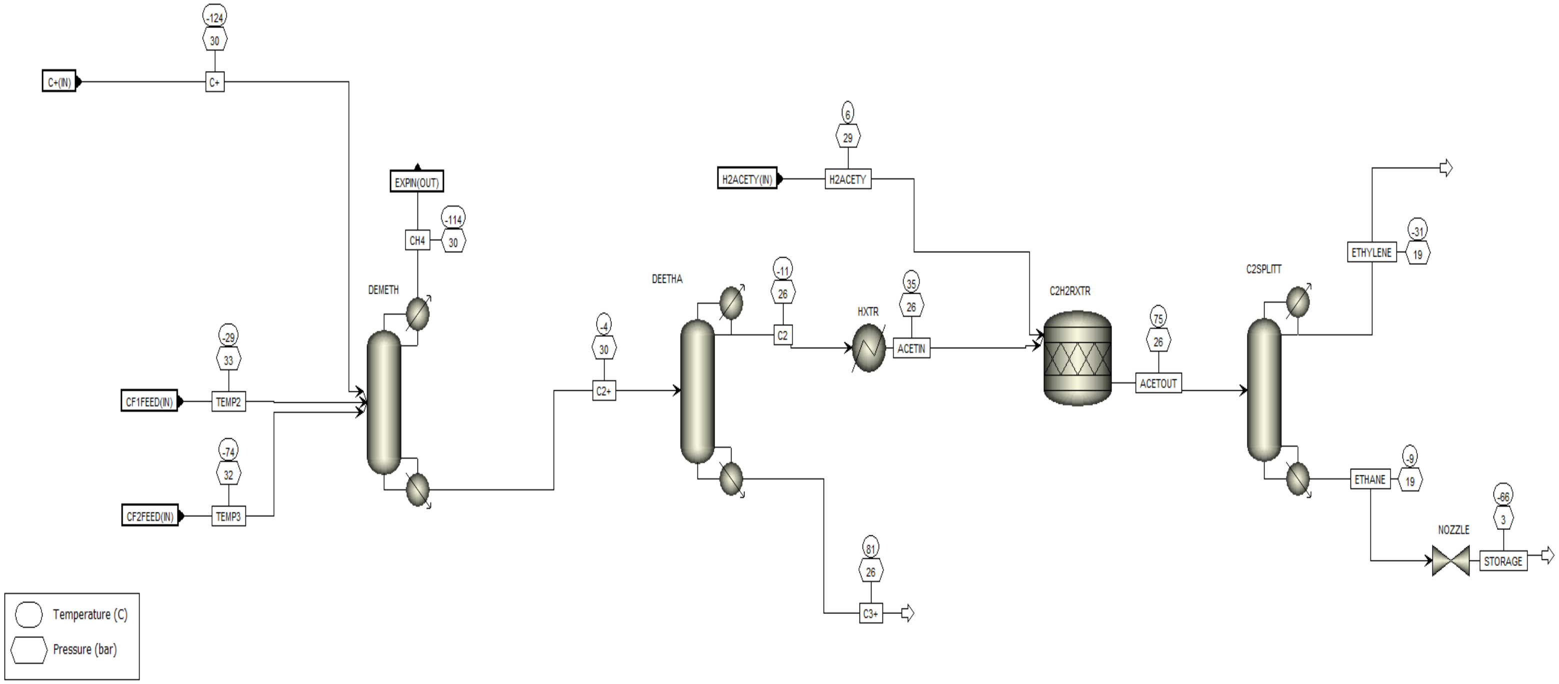

Figure 30: ASPEN Flowsheet- Ethane Cracking- Separation Section

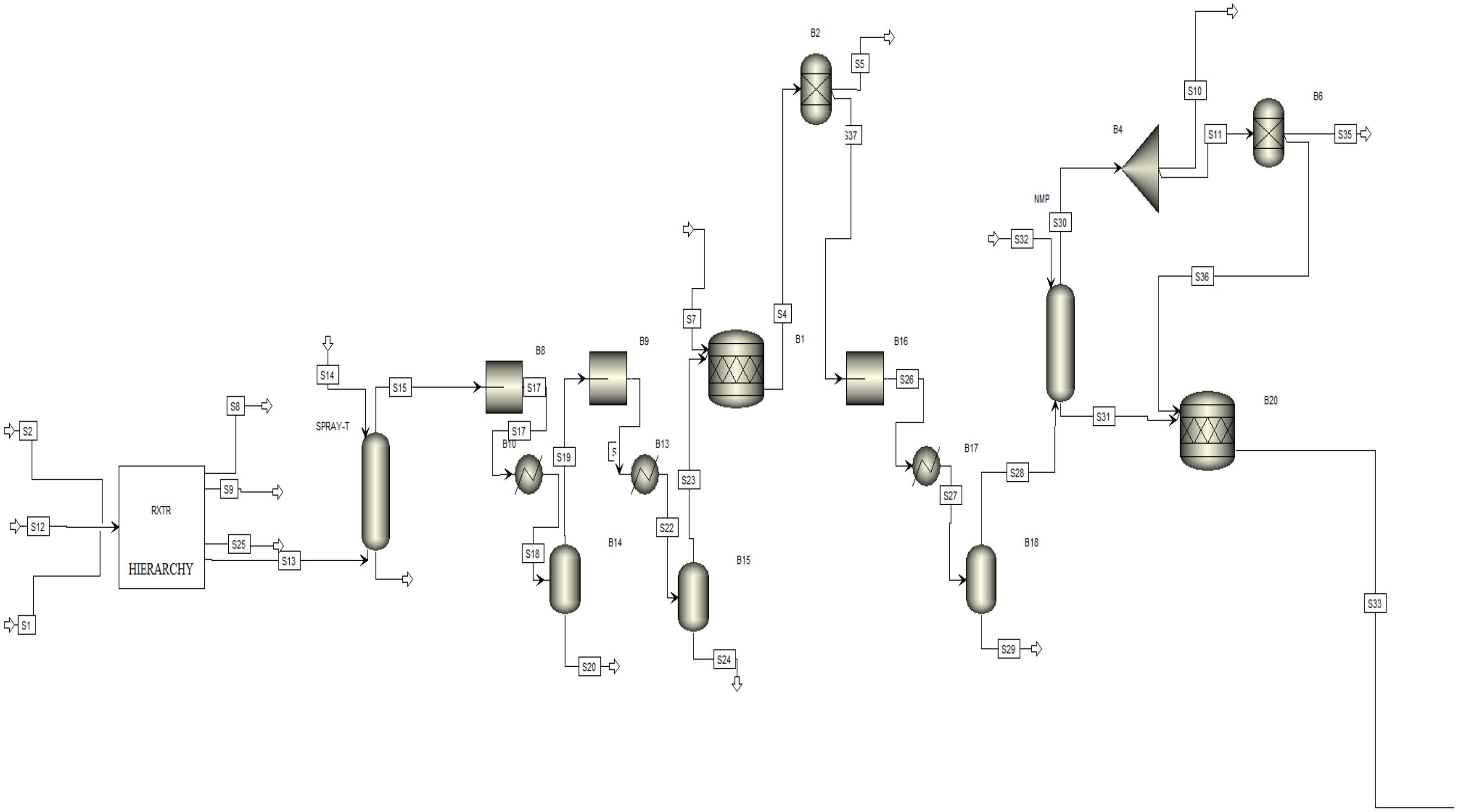

Figure 31: ASPEN Flowsheet- Gas to Ethylene - Pyrolysis and Compression Section

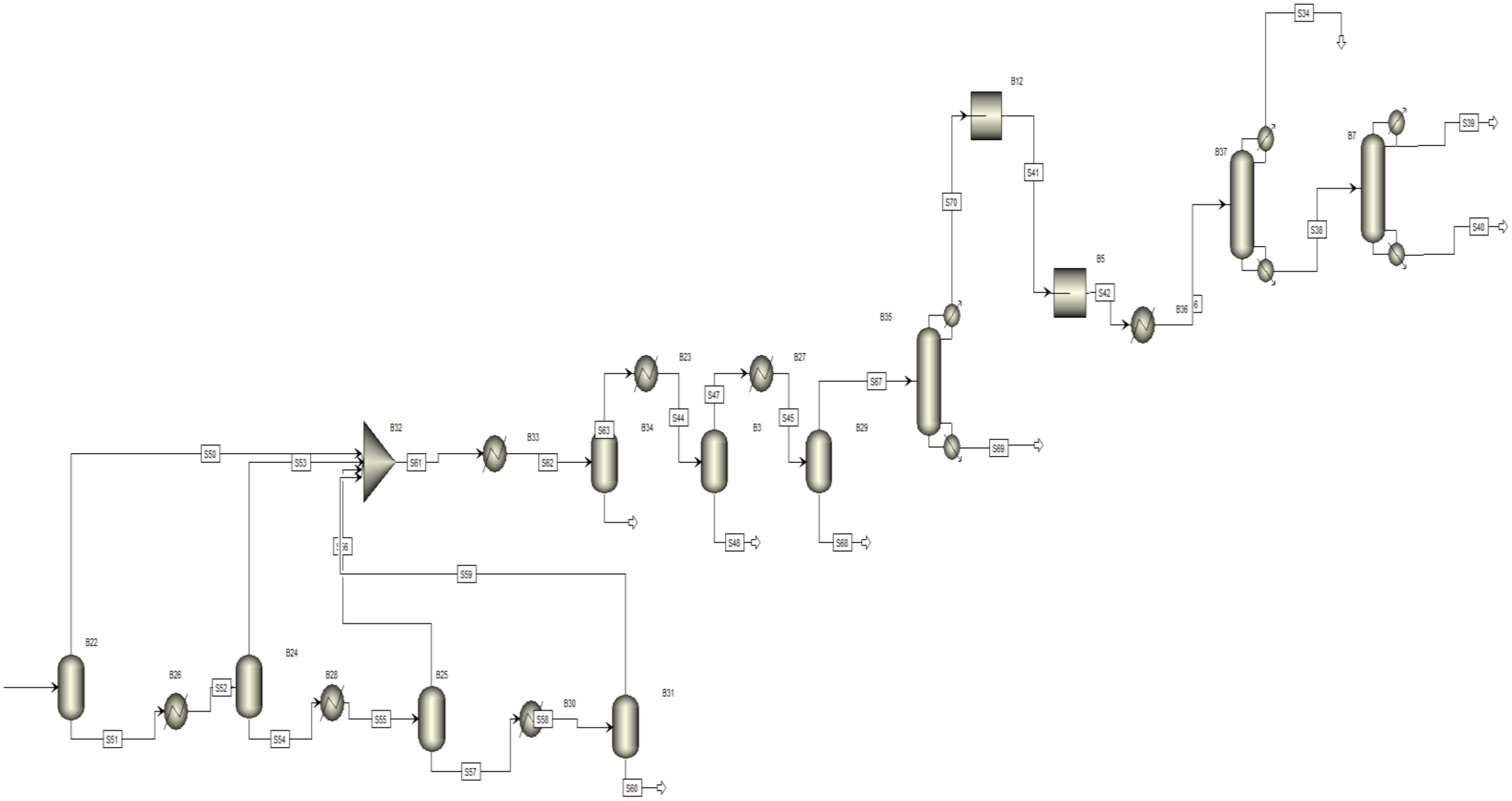

Figure 32: ASPEN Flowsheet - Gas to Ethylene- Solvent Separation and Product Separation Section

Table 29: Safety calculation sheet of physical units- Ethane Cracking

S.No	Physical Units	Mass flow rate (kg/s)	Heat of combustion (J/mol)	Processing Pressure (kPa)	Volume (m3)	Temperature (degC)	NFPA ranking Reactivity	NFPA ranking flammability	F1	F2	Hydrogen mol frac	Ethylene mol frac	Methane mol frac	Propane mol frac	Acetylene mol frac	Butadiene mol frac	Ethane mol frac	Propylene mol frac	pn1	pn2	pn3	pn4	pn5	pn6	Damage Potential	FEDI
1	Preheater	51	1552152	300	0.2	775	0.0	4.0	2530355	118	0	2.01E-02	3.84E-26	2.82E-08	0	1.05E-12	0.9762	6.12E-06	1.95	1.4	1.1	2.0	1	1	10889697	1049
2	Transfer Line exchange	51	788187	160	2.6	840	0.6	3.0	1265206	796	0.2668	0.2653	2.26E-02	8.45E-04	4.14E-03	2.76E-03	0.1893	3.71E-03	1.95	1.4	1.1	1.9	1	1	5141118	817
3	Quench tower-1	17	788187	110	247.5	343	0.6	3.0	421735.3	51884	0.2668	0.2653	2.26E-02	8.45E-04	4.14E-03	2.76E-03	0.1893	3.71E-03	1.95	1.4	1.1	1.9	1	1	1864230	583
4	Quench tower-2	17	788187	110	247.5	343	0.6	3.0	421735.3	51884	0.2668	0.2653	2.26E-02	8.45E-04	4.14E-03	2.76E-03	0.1893	3.71E-03	1.95	1.4	1.1	1.9	1	1	1864230	583
5	Quench tower-3	17	788187	110	247.5	343	0.6	3.0	421735.3	51884	0.2668	0.2653	2.26E-02	8.45E-04	4.14E-03	2.76E-03	0.1893	3.71E-03	1.95	1.4	1.1	1.9	1	1	1864230	583
6	1stage compressor	55	963468	240		125.2	0.7	3.7	1688840	0	0.3261	0.3243	2.77E-02	1.03E-03	5.06E-03	3.37E-03	0.2314	4.54E-03	1.75	1.4	1.1	2.1	1	1	6801830	897
7	Inter-stage cool 1 A	28	963468	240	5.3	125.2	0.7	3.7	844420	2437	0.3261	0.3243	2.77E-02	1.03E-03	5.06E-03	3.37E-03	0.2314	4.54E-03	1.75	1.4	1.1	2.1	1	1	3408766	713
8	Inter-stage cool 1 B	28	963468	240	5.3	125.2	0.7	3.7	844420	2437	0.3261	0.3243	2.77E-02	1.03E-03	5.06E-03	3.37E-03	0.2314	4.54E-03	1.75	1.4	1.1	2.1	1	1	3408766	713
9	Flash drum 1	52	1019824	240	0.9	35	0.7	3.9	1694487	401	0.3452	0.3433	2.93E-02	1.09E-03	5.35E-03	3.57E-03	0.2449	4.80E-03	1.75	1.4	1.1	2.2	1	1	7034283	907
10	2nd stage compressor	52	1019824	600		119	0.7	3.9	1694487	0	0.3452	0.3433	2.93E-02	1.09E-03	5.35E-03	3.57E-03	0.2449	4.80E-03	1.75	1.4	1.1	2.2	1	1	7033096	907
11	Inter-stage cool2	52	1019824	600	5.7	119	0.7	3.9	1694487	6462	0.3452	0.3433	2.93E-02	1.09E-03	5.35E-03	3.57E-03	0.2449	4.80E-03	1.75	1.4	1.1	2.2	1	1	7054551	908
12	Flash drum 2	52	1032146	600	0.2	35	0.7	4.0	1695926	203	0.3494	0.3474	2.96E-02	1.11E-03	5.42E-03	3.61E-03	0.2479	4.86E-03	1.75	1.4	1.1	2.2	1	1	7085283	909
13	3rdstage compressor	52	1032146	1500		120	0.7	4.0	1695926	0	0.3494	0.3474	2.96E-02	1.11E-03	5.42E-03	3.61E-03	0.2479	4.86E-03	1.75	1.4	1.1	2.2	1	1	7084654	909
14	Inter-stage cool3	52	1032146	1500	4.2	77	0.7	4.0	1695926	12021	0.3494	0.3474	2.96E-02	1.11E-03	5.42E-03	3.61E-03	0.2479	4.86E-03	1.75	1.4	1.1	2.2	1	1	7124827	911
	Flash drum 3			NO		LIQUID																1.0	1	1		
15	Caustic scrubber	52	1032146	1500	105.4	40	0.7	4.0	1690552	301400	0.3494	0.3474	2.96E-02	1.11E-03	5.42E-03	3.61E-03	0.2479	4.86E-03	1.75	1.4	1.1	2.2	1	1	8069473	950
16	4th stage compressor	52	1032146	3600		122	0.7	4.0	1690552	0	0.3494	0.3474	2.96E-02	1.11E-03	5.42E-03	3.61E-03	0.2479	4.86E-03	1.75	1.4	1.1	2.2	1	1	7062206	908
17	Inter-stage cool4	52	1032146	3600	3.4	122	0.7	4.0	1690552	23203	0.3494	0.3474	2.96E-02	1.11E-03	5.42E-03	3.61E-03	0.2479	4.86E-03	1.75	1.4	1.1	2.2	1	1	7139749	912
18	Refrigeration cooler	52	1032146	3550	2.3	40	0.7	4.0	1690552	15558	0.3494	0.3474	2.96E-02	1.11E-03	5.42E-03	3.61E-03	0.2479	4.86E-03	1.75	1.4	1.1	2.2	1	1	7114201	911
19	Dryer	51	1043266	3500	8.2	15	0.7	4.0	1691460	54646	0.3532	0.3511	2.99E-02	1.12E-03	5.48E-03	3.65E-03	0.2506	4.91E-03	1.75	1.4	1.1	2.2	1	1	7290748	918
20	Cool train hx1	51	1043266	3450	0.1	15	0.7	4.0	1691460	654	0.3532	0.3511	2.99E-02	1.12E-03	5.48E-03	3.65E-03	0.2506	4.91E-03	1.75	1.4	1.1	2.2	1	1	7109261	910
21	Cool train hx2	51	1043266	3400	0.7	14	0.7	4.0	1691460	4253	0.3532	0.3511	2.99E-02	1.12E-03	5.48E-03	3.65E-03	0.2506	4.91E-03	1.75	1.4	1.1	2.2	1	1	7121360	911
22	Cool train hx3-A	17	1043266	3350	8.0	5	0.7	4.0	563820	51253	0.3532	0.3511	2.99E-02	1.12E-03	5.48E-03	3.65E-03	0.2506	4.91E-03	1.75	1.4	1.1	2.2	1	1	2541302	646
23	Cool train hx3-B	17	1043266	3350	8.0	5	0.7	4.0	563820	51253	0.3532	0.3511	2.99E-02	1.12E-03	5.48E-03	3.65E-03	0.2506	4.91E-03	1.75	1.4	1.1	2.2	1	1	2541302	646
24	Cool train hx3-C	17	1043266	3350	8.3	5	0.7	4.0	563820	52806	0.3532	0.3511	2.99E-02	1.12E-03	5.48E-03	3.65E-03	0.2506	4.91E-03	1.75	1.4	1.1	2.2	1	1	2546523	647
25	Cool train hx4	37	946011	3300	0.1	-29	0.7	4.0	1115733	544	0.4268	0.3254	3.40E-02	4.56E-04	4.78E-03	5.74E-04	0.2057	2.32E-03	1.75	1.4	1.1	2.2	1	1	4656384	791
26	Cool train hx5	37	946011	3250	1.1	-29.7	0.7	4.0	1115733	6733	0.4268	0.3254	3.40E-02	4.56E-04	4.78E-03	5.74E-04	0.2057	2.32E-03	1.75	1.4	1.1	2.2	1	1	4677039	792
27	Cool train hx6-A	19	946011	3200	6.1	-33	0.7	4.0	557866.6	37062	0.4268	0.3254	3.40E-02	4.56E-04	4.78E-03	5.74E-04	0.2057	2.32E-03	1.75	1.4	1.1	2.2	1	1	2450974	639
28	Cool train hx6- B	19	946011	3200	6.1	-33	0.7	4.0	557866.6	37062	0.4268	0.3254	3.40E-02	4.56E-04	4.78E-03	5.74E-04	0.2057	2.32E-03	1.75	1.4	1.1	2.2	1	1	2450974	639
29	Cool train hx7	7	472554	3150	0.1	-74	0.2	4.0	105337.2	535	0.819	0.1005	4.30E-02	9.93E-06	1.06E-03	1.86E-06	3.63E-02	7.05E-05	1.75	1.4	1.1	2.1	1	1	417582	354
30	Cool train hx8	7	472554	3100	0.6	-76	0.2	4.0	105337.2	3616	0.819	0.1005	4.30E-02	9.93E-06	1.06E-03	1.86E-06	3.63E-02	7.05E-05	1.75	1.4	1.1	2.1	1	1	427313	357
31	Cool train hx9	7	472554	3050	1.7	-87	0.2	4.0	105337.2	9775	0.819	0.1005	4.30E-02	9.93E-06	1.06E-03	1.86E-06	3.63E-02	7.05E-05	1.75	1.4	1.1	2.1	1	1	446768	362

Table 29: Continued

S.No	Physical Units	Mass flow rate (kg/s)	Heat of combustion (J/mol)	Processing Pressure (kPa)	Volume (m3)	Temperature (degC)	NFPA ranking Reactivity	NFPA ranking flammability	F1	F2	Hydrogen mol frac	Ethylene mol frac	Methane mol frac	Propane mol frac	Acetylene mol frac	Butadiene mol frac	Ethane mol frac	Propylene mol frac	pn1	pn2	pn3	pn4	pn5	pn6	Damage Potential	FEDI
32	Cool-flash 1	37	946011	3300	9.3	-29	0.7	4.0	1115733	58229	0.4268	0.3254	3.40E-02	4.56E-04	4.78E-03	5.74E-04	0.2057	2.32E-03	1.75	1.4	1.1	2.2	1	1	4848899	802
33	Cool-flash 2	7	472554	3150	17.6	-74	0.2	4.0	105337.2	105511	0.819	0.1005	4.30E-02	9.93E-06	1.06E-03	1.86E-06	3.63E-02	7.05E-05	1.75	1.4	1.1	2.1	1	1	749152	430
34	Cool-flash 3	3	320385	3000	2.3	-124	0.0	4.0	27415.64	12912	0.9522	8.74E-03	3.77E-02	1.30E-08	4.91E-05	1.17E-10	1.30E-03	1.52E-07	1.75	1.4	1.1	2.0	1	1	145642	249
35	Expander	1	657733	3000		-113	0.0	4.0	15763.93	0	0.3868	1.31E-03	0.6119	1.43E-20	1.33E-06	8.62E-30	3.83E-07	5.21E-18	1.75	1.4	1.1	2.0	1	1	60711	186
36	De-methanizer	5	834438	3000	404.8	-113.9	0.0	4.0	121299.7	2314537	0.10499	1.32E-02	0.8818	2.68E-18	2.91E-05	1.29E-26	9.16E-06	5.42E-16	1.75	1.4	1.1	2.0	1	1	7620879	932
37	Condenser 1	5	834438	3000	0.5	-113.9	0.0	4.0	121299.7	3140	0.10499	1.32E-02	0.8818	2.68E-18	2.91E-05	1.29E-26	9.16E-06	5.42E-16	1.75	1.4	1.1	2.0	1	1	478250	371
38	Reboiler 1	86	1465095	3000	0.7	-4.3	1.3	4.0	4016716	4142	1.65E-14	0.64074	2.37E-04	5.93E-04	9.06E-03	8.65E-04	0.34547	3.04E-03	1.75	1.4	1.1	2.3	1	1	18018124	1241
39	De-ethanizer	83	1472028	2600	590.2	-9.4	1.2	4.0	3900781	2924862	1.29E-15	0.57697	8.14E-05	2.81E-08	9.05E-03	6.15E-17	0.4139	6.14E-06	1.75	1.4	1.1	2.3	1	1	27573827	1430
40	Condenser 2-A	42	1472028	2600	8.3	-9.4	1.2	4.0	1950391	40948	1.29E-15	0.57697	8.14E-05	2.81E-08	9.05E-03	6.15E-17	0.4139	6.14E-06	1.75	1.4	1.1	2.3	1	1	8762361	976
41	Condenser 2-B	42	1472028	2600	8.3	-9.4	1.2	4.0	1950391	40948	1.29E-15	0.57697	8.14E-05	2.81E-08	9.05E-03	6.15E-17	0.4139	6.14E-06	1.75	1.4	1.1	2.3	1	1	8762361	976
42	Reboiler 2	85	2126055	2600	3.3	75.5	1.0	4.0	5764275	16382	5.46E-41	2.25E-04	1.05E-16	0.11867	2.93E-04	0.21078	0.10529	0.56474	1.75	1.4	1.1	2.2	1	1	24988861	1384
43	Acetylene preheater	46	1472752	2600	1.3	75	1.2	4.0	2170246	6545	4.84E-05	0.5858	4.42E-04	2.82E-08	0	1.12E-12	0.4137	6.14E-06	1.75	1.4	1.1	2.3	1	1	9602201	1006
44	C2splitter-I	79	1411128	1900	851.5	-30.7	2.0	4.0	3561307	3083449	8.23E-05	0.99491	7.51E-04	4.77E-46	0.00E+00	1.46E-80	4.26E-03	4.34E-38	1.75	1.4	1.1	2.5	1	1	28980557	1454
45	C2splitter-II	79	1411128	1900	851.5	-30.7	2.0	4.0	3561307	3083449	8.23E-05	0.99491	7.51E-04	4.77E-46	0.00E+00	1.46E-80	4.26E-03	4.34E-38	1.75	1.4	1.1	2.5	1	1	28980557	1454
46	Condenser 3-I-A	20	1411128	1900	6.2	-30.7	2.0	4.0	890326.5	22352	8.23E-05	0.99491	7.51E-04	4.77E-46	0.00E+00	1.46E-80	4.26E-03	4.34E-38	1.75	1.4	1.1	2.5	1	1	4366304	774
47	Condenser 3-I-B	20	1411128	1900	6.2	-30.7	2.0	4.0	890326.5	22352	8.23E-05	0.99491	7.51E-04	4.77E-46	0.00E+00	1.46E-80	4.26E-03	4.34E-38	1.75	1.4	1.1	2.5	1	1	4366304	774
48	Condenser 3-II-A	20	1411128	1900	6.2	-30.7	2.0	4.0	890326.5	22352	8.23E-05	0.99491	7.51E-04	4.77E-46	0.00E+00	1.46E-80	4.26E-03	4.34E-38	1.75	1.4	1.1	2.5	1	1	4366304	774
49	Condenser 3-II-B	20	1411128	1900	6.2	-30.7	2.0	4.0	890326.5	22352	8.23E-05	0.99491	7.51E-04	4.77E-46	0.00E+00	1.46E-80	4.26E-03	4.34E-38	1.75	1.4	1.1	2.5	1	1	4366304	774
50	Reboiler 3	54	1560443	1900	1.0	-9.4	0.0	4.0	2664780	3739	4.36E-58	3.68E-03	5.65E-26	2.11E-08	0.00E+00	3.02E-13	0.99631	5.74E-06	1.75	1.4	1.1	2.0	1	1	10280349	1029

Table 30: Safety calculation sheet of physical units- Methane Pyrolysis

S.No	Physical Units	Mass flow rate (kg/s)	Heat of combustion (J/mol)	Processing Pressure (kPa)	Volume (m3)	Temperature (degC)	NFPA ranking Reactivity	NFPA ranking flammability	F1	F2	Methane mole frac	CO mol frac	CO2 mol frac	Acetylene mol frac	Hydrogen mol frac	Oxygen mol frac	water mole frac	ethylene mol frac	propadiene mol frac	pn1	pn2	pn3	pn4	pn5	pn6	Damage Potential	FEDI
1	Methane preheater	105	891100	150	0.26	600	0.00	4.0	2980083	74.3	1	0	0	0	0	0	0	0	0	1.95	1.4	1.1	2	1	1	12784786	1107
2	Oxygen preheater	136	0	150	0.11	600	0.00	0.0	0	29.9	0	0	0	0	0	1	0	0	0	1.1	1.4	1.1	1	1	1	46	17
3	Spray tower (10 nos.)	14	224876	100	167.2	80	0.5	2.2	100431.5	31869.4	2.8E-02	0.15	2.7E-02	4.8E-02	0.3106	0	0.4326	2.0E-03	1.9E-03	1.75	1.4	1.1	1.7	1	1	400562	349
4	1st stage compressor	140	377470	230		143	0.8	3.6	1685558	0	4.7E-02	0.2518	4.6E-02	8.0E-02	0.5214	0	4.8E-02	3.4E-03	3.3E-03	1.75	1.4	1.1	2.1	1	1	6798200	897
5	Intercool stage 1 (4 nos.)	35	377470	230	8.1	143	0.8	3.6	421389.5	3582.1	4.7E-02	0.2518	4.6E-02	8.0E-02	0.5214	0	4.8E-02	3.4E-03	3.3E-03	1.75	1.4	1.1	2.1	1	1	1711107	566
6	Cool flash 1	140	388056	230	1.9	35	0.8	3.7	1732820	824.2	4.8E-02	0.2589	4.7E-02	8.2E-02	0.536	0	2.1E-02	3.5E-03	3.4E-03	1.75	1.4	1.1	2.1	1	1	7094064	909

Table 30: Continued

S.No	Physical Units	Mass flow rate (kg/s)	Heat of combustion (J/mol)	Processing Pressure (kPa)	Volume (m3)	Temperature (degC)	NFPA ranking Reactivity	NFPA ranking flammability	F1	F2	Methane mole frac	CO mol frac	CO2 mol frac	Acetylene mol frac	Hydrogen mol frac	Oxygen mol frac	water mole frac	ethylene mol frac	propadiene mol frac	pn1	pn2	pn3	pn4	pn5	pn6	Damage Potential	FEDI
7	2nd stage compressor	140	388056	529		143	0.8	3.7	1732820	0	4.8E-02	0.2589	4.7E-02	8.2E-02	0.536	0	2.1E-02	3.5E-03	3.4E-03	1.75	1.4	1.1	2.1	1	1	7091365	909
8	Intercool stage 2 (3 nos.)	46	388056	529	7.2	143	0.8	3.7	577606.8	7275	4.8E-02	0.2589	4.7E-02	8.2E-02	0.536	0	2.1E-02	3.5E-03	3.4E-03	1.75	1.4	1.1	2.1	1	1	2387606	633
9	Cool flash 2	140	392616	529	0.8	35	0.8	3.8	1753189	792.3	4.9E-02	0.2619	4.8E-02	8.3E-02	0.5423	0	9.2E-03	3.5E-03	3.5E-03	1.75	1.4	1.1	2.1	1	1	7221822	915
10	Amine absorber (2 nos.)	70	416291	500	339	35	0.8	4.0	929463.9	323383	5.1E-02	0.2777	0	8.8E-02	0.575	0	0	3.7E-03	3.7E-03	1.75	1.4	1.1	2.2	1	1	5049725	812
11	3rd stage compressor	140	416291	1250		152	0.8	4.0	1858928	0	5.1E-02	0.2777	0	8.8E-02	0.575	0	0	3.7E-03	3.7E-03	1.75	1.4	1.1	2.2	1	1	7900445	943
12	Intercool stage 3 (2 nos.)	70	416291	1250	6.94	152	0.8	4.0	929463.9	16529.6	5.1E-02	0.2777	0	8.8E-02	0.575	0	0	3.7E-03	3.7E-03	1.75	1.4	1.1	2.2	1	1	4006423	752
13	NMP absorption (3 nos.)	46	416291	1200	168.2	35	0.8	4.0	619642.6	384649.6	5.1E-02	0.2777	0	8.8E-02	0.575	0	0	3.7E-03	3.7E-03	1.75	1.4	1.1	2.2	1	1	3941291	748
14	Pressure swing absorption	16	325480	1200	466.7	-47	0.6	4.0	167241.8	1067344	5.4E-02	0.3034	0	4.9E-03	0.6354	0	0	2.4E-03	6E-17	1.75	1.4	1.1	2.2	1	1	4238637	766
15	Flash net 1	11	1078719	1000	359.4	88	1.6	3.4	382322.5	684920.6	4.5E-02	7.6E-02	0	0	6.3E-03	0	0	0.7068	9.4E-03	1.75	1.4	1.1	2.2	1	1	4005965	752
16	Flash stage 1 heater	11	1078719	950	4.3	100	1.6	3.4	382322.5	7856.5	4.5E-02	7.6E-02	0	0	6.3E-03	0	0	0.7068	9.4E-03	1.75	1.4	1.1	2.2	1	1	1673458	562
17	Flash net 2	6	999952	800	358.3	100	1.4	2.9	197991.1	546266.8	2.6E-02	2.4E-02	0	0	9.9E-04	0	0	0.6699	1.3E-02	1.75	1.4	1.1	2.1	1	1	2546776	646
18	Flash stage 2 heater	6	999952	750	4.7	110	1.4	2.9	197991.1	6650.6	2.6E-02	2.4E-02	0	0	9.9E-04	0	0	0.6699	1.3E-02	1.75	1.4	1.1	2.1	1	1	815410	442
19	Flash net 3	6	766989	600	352.4	110	1.1	2.2	151519	403004.4	1.1E-02	4.9E-03	0	0	1.0E-04	0	0	0.5138	1.6E-02	1.75	1.4	1.1	1.8	1	1	1650622	559
20	Flash stage 3 heater	6	766989	550	6.6	120	1.1	2.2	151519	6934.6	1.1E-02	4.9E-03	0	0	1.0E-04	0	0	0.5138	1.6E-02	1.75	1.4	1.1	1.8	1	1	547046	387
21	Flash net 4	0.62	183850	400	299	120	0.2	0.5	3646.905	227996.2	1.1E-03	2E-04	0	0	2E-06	0	0	0.115	1.1E-02	1.75	1.4	1.1	1.2	1	1	425215	356
22	Flash stage cool 4	29	501474	400	1.72	113	0.7	1.5	475509	1311.7	1.3E-02	1.6E-02	0	0	1.2E-03	0	0	0.3285	1.2E-02	1.75	1.4	1.1	1.5	1	1	1417108	532
23	Flash net 5	29	549390	384	9.21	102	0.8	1.6	519441.3	6742.6	1.4E-02	1.8E-02	0	0	1.3E-03	0	0	0.36	1.3E-02	1.75	1.4	1.1	1.6	1	1	1613398	555
24	Flash stage cool 5	29	549390	368	2.5	102	0.8	1.6	519441.3	1737.0	1.4E-02	1.8E-02	0	0	1.3E-03	0	0	0.36	1.3E-02	1.75	1.4	1.1	1.6	1	1	1601088	554
25	Flash net 6	29	651214	368	14.8	95	0.9	1.9	612093.4	10405.3	1.6E-02	2.1E-02	0	0	1.5E-03	0	0	0.427	1.5E-02	1.75	1.4	1.1	1.7	1	1	2039761	600
26	Flash stage cool 6	29	651214	350	2.8	95	0.9	1.9	612093.4	1891.2	1.6E-02	2.1E-02	0	0	1.5E-03	0	0	0.427	1.5E-02	1.75	1.4	1.1	1.7	1	1	2017367	598
27	Flash net 7	29	793451	350	14	85	1.1	2.3	740535.3	9377.0	2E-02	2.6E-02	0	0	1.9E-03	0	0	0.5207	1.7E-02	1.75	1.4	1.1	1.9	1	1	2682732	658
28	Solsep column	78	759707	300	200	-15.36	0.5	1.7	1906080	114608.1	2.7E-04	8.2E-05	0	0	1.4E-06	0	0	7.6E-02	0.3410	1.75	1.4	1.1	1.5	1	1	5923762	856
29	Solsep reboiler	0.10	805	30	3.8	119	0	0.0	2.693631	217.9	6.5E-10	3.9E-12	0	0	3.0E-15	0	0	4.8E-06	4.2E-04	1.75	1.4	1.1	1.0	1	1	340	33
30	Solsep condenser (3 nos.)	26	759707	300	7.5	-15.36	0.5	1.7	635360	4294.2	2.7E-04	8.2E-05	0	0	1.4E-06	0	0	7.6E-02	0.3410	1.75	1.4	1.1	1.5	1	1	1894151	586
31	4th stage compressor	29	1354873	1200		33	1.9	4.0	1264037	0	3.4E-02	4.4E-02	0	0	3.2E-03	0	0	0.8895	2.9E-02	1.75	1.4	1.1	2.5	1	1	6019808	861
32	5th stage compressor	29	1354873	3000		112	1.9	4.0	1264037	0	3.4E-02	4.4E-02	0	0	3.2E-03	0	0	0.8895	2.9E-02	1.75	1.4	1.1	2.5	1	1	6019808	861
33	Interstage cool 5	29	1354873	3000	1.4	112	1.9	4.0	1264037	8209.9	3.4E-02	4.4E-02	0	0	3.2E-03	0	0	0.8895	2.9E-02	1.75	1.4	1.1	2.5	1	1	6051087	862
34	De-methanizer column	54	1120406	3000	190	-88	1.1	4.0	1928348	1091145	0.44	5.5E-02	0	0	1.7E-04	0	0	0.5053	1.9E-05	1.75	1.4	1.1	2.3	1	1	12295381	1092
35	De-methanizer reboiler	51	1426951	3000	0.45	-12	2	4.0	2346824	2560.9	7.4E-05	3.3E-09	0	0	5.4E-16	0	0	0.9680	3.2E-02	1.75	1.4	1.1	2.5	1	1	11267742	1061
36	De-methanizer condenser (2 nos.)	27	1120406	3000	5.8	-88	1.1	4.0	964174.2	33160.6	0.44	5.5E-02	0	0	1.7E-04	0	0	0.50533	1.9E-05	1.75	1.4	1.1	2.3	1	1	4348417	772

Table 30: Continued

S.No	Physical Units	Mass flow rate (kg/s)	Heat of combustion (J/mol)	Processing Pressure (kPa)	Volume (m3)	Temperature (degC)	NFPA ranking Reactivity	NFPA ranking flammability	F1	F2	Methane mole frac	CO mol frac	CO2 mol frac	Acetylene mol frac	Hydrogen mol frac	Oxygen mol frac	water mole frac	ethylene mol frac	propadiene mol frac	pn1	pn2	pn3	pn4	pn5	pn6	Damage Potential	FEDI
37	Ethylene column	49	1410968	2500	105	-20.59	2	4.0	2234360	501533	2.3E-05	4.7E-10	0	0	0	0	0	0.9999	2.6E-05	1.75	1.4	1.1	2.5	1	1	12683657	1104
38	Ethylene reboiler	48	1911795	2500	2	77	1	4.0	2920917	9799.7	1.2E-12	9.3E-21	0	0	0	0	0	3.0E-03	0.9969	1.75	1.4	1.1	2.3	1	1	12689282	1104
39	Ethylene condenser (2 nos.)	24	1410968	2500	7	-20.69	2	4.0	1117180	33319.5	2.3E-05	4.7E-10	0	0	0	0	0	0.9999	2.6E-05	1.75	1.4	1.1	2.5	1	1	5504664	836

Table 31: Safety calculation of reactors- Ethane Cracking

S.No	Reactors	Mass flow rate (kg/s)	Heat of combustion (J/mol)	Processing Pressure (kPa)	Volume (m3)	Temperature (degC)	NFPA ranking Reactivity	NFPA ranking flammability	F1	F2	F4	Hx rxn, kj/kg	Hydrogen mol frac	Ethylene mol frac	Methane mol frac	Propane mol frac	Butadiene mol frac	Ethane mol frac	Propylene mol frac	pn1	pn2	pn3	pn4	pn5	pn6	pn7	pn8	Damage Potential	FEDI
1	Cracker	51	1561000	150	140	775	0	4	2520674	27	43922	2720	0	0	0.0	0.0	0.0	1	0.0	2	1.4	1.1	2	1	1	1.5	1.5	11016939	1053
2	Acetylene hydrogenation	46	1472752	2550	32	75	1.2	4	2170245	106	-1871	-127	4.8E-05	0.5858	4.4E-04	2.8E-08	1.1E-12	0.4137	6.1E-06	1.5	1.4	1.1	2.2	1	1	1.4	1.5	7928100	944

Table 32: Safety calculation of reactors- Methane Pyrolysis

S.No	Reactors	Mass flow rate (kg/s)	Heat of combustion (J/mol)	Processing Pressure (kPa)	Volume (m3)	Temperature (degC)	NFPA ranking Reactivity	NFPA ranking flammability	F1	F2	F4	Hxrxn, kj/kg	Methane mole frac	Hydrogen mol frac	pn1	pn2	pn3	pn4	pn5	pn6	pn7	pn8	Damage Potential	FEDI
1	Cracker	105	891100	100	47	1488	0	4	2972220	6.2	316810	9498	1	0	1.95	1.4	1.1	2	1	1	1.45	1.45	14216252	1146
2	Acetylene hydrogenation	1.9	286000	1150	1057	88	0	4	17196	1585	3648	6067	0	1	1.75	1.4	1.1	2	1	1	1.35	1.45	86802	209