

SAFETY AND TECHNO-ECONOMIC ANALYSIS OF
SHALE GAS TO BUTADIENE PROCESS

A Thesis

by

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ABSTRACT

The recent discoveries of substantial reserves of shale gas have significantly impacted butadiene production and prices. Shale gas offers a competitive feedstock that can be used to produce a variety of chemicals and petrochemicals, including butadiene.

The scope of this thesis is to examine the financial and technical viability of converting shale gas to butadiene and design a cost-effective, safe and environmentally friendly process. Traditional and innovative butadiene production routes were investigated and a base case was created for producing butadiene from shale gas via ethylene as an intermediate.

Computer-aided process simulation (Aspen Plus) was used to design the process and to obtain the data necessary for economic evaluation and safety analysis. Two design scenarios were considered and compared in terms of profitability and safety risk level. Hazard Identification and Ranking (HIRA) system was selected to compare risk levels of each scenario since it gives quantitative results for each unit. Additionally, with the help of sensitivity analysis, the impact of price volatility of butadiene on the process profitability was evaluated.

The results of this study show that there is a trade-off between profitability and risk level. Therefore, none of the scenarios are superior to others in terms of both economic and safety considerations.

DEDICATION

To
my parents
and
my sister

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All the research and study for the thesis was completed individually by the thesis student.

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CHAPTER I

INTRODUCTION AND LITERATURE REVIEW

1.1 Shale gas invention

Shale gas invention is one of the most crucial incidents of recent years in the U.S. which has led to big changes in the oil and gas market prices. The history of shale gas extraction and discovery dates back to the 19th century. Due to insufficient technology and market conditions, production of shale gas was considered to be uneconomic and impractical in previous years. In the 1940s, hydraulic fracturing had begun to be used for shale gas extraction which is a technique to stimulate well by applying liquid (mostly water) at high pressure. In the 2000s, typical natural gas production decreased and the demand for it increased, which made shale gas an important source for natural gas production. This emerging demand accelerated technological developments in drilling. Some big oil companies also played a role as a pioneer to begin making investments to extract shale gas. (Q. Wang et al., 2014)

With the help of technological developments, these companies began using hydraulic fracturing and horizontal drilling together which boosted the efficiency of shale production. Furthermore, oil prices increased in years and abundant and cheap shale gas has become more profitable when compared to oil. Finally, shale gas has become to be considered as a reliable natural gas source by all oil and gas companies. (Q. Wang et al., 2014) (Stevens, 2012)

According to the EIA projections for the U.S., shale gas production will increase from 23% to 49% between 2010 and 2035. (Meyer, 2012)

1.1.1 Why Is Shale Gas Revolution Important in the U.S.?

Shale gas revolution is highly significant for the U.S. since it brings several advantages. The U.S. has been a global player for years to determine and control oil supply and demand since it has approximately 32 billion barrels of proved oil reserves. (EIA, 2016) However, there are also other oil supplier countries which can change the global supply and demand balance of oil and oil prices too. Therefore, the U.S. economy has been highly accessible and vulnerable if these other supplier countries decide to change the oil supply and oil price.

According to the EIA Annual Energy Outlook 2017 report, the U.S. may become an energy exporter in the future by using its natural gas reserves. According to the EIA report, the U.S. may not need to import energy in the future. With the help of the shale innovation, the U.S. may become independent and self sufficient in terms of energy. (Hennessy Funds, 2014)

According to the U.S. EPA, eGRID (2000) report, using natural gas as fuel is more environmentally friendly than using coal or oil. Combustion of coal releases twice as much CO₂ as natural gas and combustion of oil releases approximately 30% more CO₂ than natural gas. (Hennessy Funds, 2014) Furthermore, burning natural gas releases much less pollutant gases such as nitrogen oxide and sulfur dioxide than oil and coal. Therefore, in terms of emissions, natural gas is more advantageous than other energy resources.

1.1.2. Shale Gas Effect in the Petrochemical Market

Shale gas has changed the global oil and gas market. Crude oil and coal had been the mainstream energy resources since shale gas discovery. After the invention of a new resource, “shale gas”, economy of traditional production processes has changed.

Naphtha had been the key petrochemical source to produce ethylene and other petrochemical products in previous years and all processes were developed according to the naphtha as the feedstock. Developments in drilling technology and improvements of drilling efficiencies made shale gas producible and started a new era for oil and gas industry.

Entry of the cheap and abundant natural gas has changed the balance of oil and gas market. As producing natural gas became a more profitable resource than naphtha, pioneer companies decided to change their conventional feedstocks and production routes. New production routes using natural gas liquids as feedstock invented. (Thompson, 2013)

Naphtha and heavier feedstocks used to produce petrochemical products. As the price difference between naphtha and natural gas liquids decreased, usage of natural gas liquids to produce petrochemical products increased. Production of NGLs such as butane, propane and ethane has increased and has been used as the new intermediate products. (Thompson, 2013)

Before the 2000s, naphtha steam crackers were used to produce ethylene, the key intermediate product of petrochemical industry. Ethylene is an essential key chemical for petrochemical industry since it has been considered as the beginning step to produce plastics which have a variety of usage areas such as packaging industry, tire industry, conductor industry, and detergent industry.

After the 2000s, companies have begun to use ethane instead of naphtha to produce ethylene. Even if both of these feedstocks give the same ethylene product in the cracker, the output stream has completely different compositions.

Using naphtha yields 23% ethylene whereas using ethane as the feedstock of cracker yields 80% ethylene. More general, using naphtha results in large amounts of by products such as propylene, gasoline, fuel gas, butylene and butadiene. Ethane feed produces 80% ethylene, 13% fuel gas, 3% propylene, 2% butylene, 1% butadiene, 1% gasoline whereas naphtha feed produces 23% of ethylene, 27% fuel gas, 13% propylene, 15% butylene, 4% butadiene, 18% gasoline. (Burdick & Leffler, 2010)

As the petrochemical companies have begun using ethane, the production of ethylene has increased due to high profits. On the other hand, changing the feedstock has changed the by product distribution and decreased the propylene and butadiene production per ethane significantly. The yield for butadiene decreased from 5% to 1%. (Rouilloux et. al, 2014)

This decrease in production of butadiene affects the butadiene prices. Since the supply decreases, price of butadiene increases. In addition, unbalanced NGL market is changing the butadiene price frequently. For such reasons, scientists have changed the direction of their research to on purpose butadiene production processes.

1.2 Butadiene Production and Market Conditions

1.2.1 Butadiene Usage Areas

Butadiene or 1,3 butadiene (C_4H_6) is a colorless diolefin which is gaseous at 298 K. 1,3 butadiene is insoluble in water but soluble in ether and alcohol.

It is a major chemical for chemical market which is used in manufacturing important products such as acrylonitrile-butadiene-styrene resins, polybutadiene, styrene-butadiene latex, chloroprene, adiponitrile and styrene-butadiene rubber (SBR).

Synthetic rubber, the major end product, which is produced from butadiene. Synthetic rubber, styrene-butadiene rubber (SBR) is the key component for automobile industry and tire manufacturing.

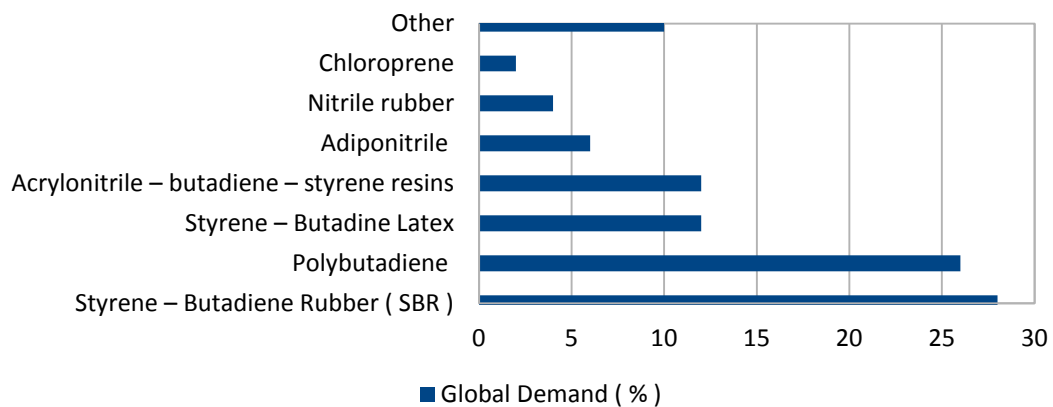


Figure 1: Global Demand of Butadiene End Products (White, 2007)

According to the table above, styrene – butadiene rubber has the highest global demand which is 28% and polybutadiene has the second highest global demand which is 26%. (White, 2007)

The largest consumption area of butadiene is the automotive industry where styrene – butadiene rubber and polybutadiene are used to manufacture tires. (IHS Markit, 2016)

1.2.2 Butadiene Production Routes

There are three common routes to produce 1,3 butadiene. These are (American Chemistry Council, 2010):

- steam cracking or naphtha cracking
- catalytic dehydrogenation (Houdry process)
- oxidative dehydrogenation

Among these production routes, steam cracking is the most conventional production route where naphtha, ethane, propane or butane is cracked to produce ethylene as the main product and 1,3 butadiene as a side product of this process. Naphtha or ethane is fed to a pyrolysis furnace where cracking takes place at a relatively high temperature (around 1,100 K). (American Chemistry Council, 2010). The cracking products such as hydrogen, ethylene, propylene, butadiene, and heavier hydrocarbons are quenched. The cooled gases are compressed and the heavier components are first separated. Next, a separation train is used to obtain relatively pure streams of ethylene, propylene and 1,3 butadiene. (White, 2007)

The type of the pyrolysis furnace depends on the feedstock of the process unit. For example, if the process unit uses naphtha as the feed, then the cracker is designed to produce heavier components and is classified as a heavy cracker. On the other hand, if the process unit utilizes ethane as the feed, the cracker is designed to crack lighter components and is classified as a light cracker. The distribution of the products can be controlled through design and operating conditions (most notably temperature). Market conditions and price gap between ethylene and butadiene are the key factors to determine rate of butadiene production.

The butadiene production rate may be between 25-50 % or higher which highly depends on the characteristics of the feedstock. (NPTEL, 2011)

Catalytic dehydrogenation process which is also known as Houdry process is the dehydrogenation of n-butane or n-butene to produce butadiene. This process requires high process temperature (around 900 K) for reaction. Dehydrogenation process produces approximately 15 vol% butadiene as a product. (American Chemistry Council, 2010)

Oxidative dehydrogenation of n-butene, O-X-D process, is an alternative process to conventional steam cracking process and dehydrogenation process where reaction takes place in the presence of oxygen. Oxygen improves the dehydrogenation reaction and increases the conversion of 1,3 butadiene up to 80%. Furthermore, the reactor catalyst life increases which is another advantage of oxidative dehydrogenation process.

Catalytic dehydrogenation and oxidative dehydrogenation processes can be more advantageous than steam cracking process if butadiene prices are high and there is a strong demand for butadiene. (Makshina et.al., 2014)

1.2.3 Market Trends of Butadiene

The recent discoveries of substantial reserves of shale gas have resulted in a major impact on butadiene production. Naphtha has been gradually replaced with ethane as a feedstock to the crackers. This shift has led to the increase in the ethylene fraction in the cracking products. The shortfall in butadiene production has led to a global shortage and price increase. Furthermore, the abundant supply of shale gas has offered a competitive feedstock with clear economic and environmental advantages. (Hasaneen & El-Halwagi, 2017)

Therefore, the scope of thesis is to determine the manufacture of butadiene from shale gas. A high-level techno-economic analysis is presented with comparison of two

scenarios to illustrate the potential for using shale gas as a feedstock for the production of butadiene.

As of market conditions in 2012, global butadiene demand was approximately 10 million metric tons. (Makshina et.al., 2014) Recent forecast reports show that global butadiene demand will continue to increase with an annual rate of 3% till 2020. (IHS Markit, 2016)

According to the global market share pie chart (Grand View Research, Inc., 2015), Asia Pacific has the greatest share, 43.84%, in the world which contains China and India due to growth in automobile industry. North America has the second greatest share, 23.62%, in the world whereas Europe has 20.52% share according to the global market in 2013. (Grand View Research, Inc., 2015)

Recent projection reports show that Asia Pacific will be the most quickly developing butadiene market due to several reasons. Increasing population in this region and governmental support for industrial development contribute to the demand. In addition, this region contains developing countries in which the economy is still developing which affects the butadiene demands. (Grand View Research, Inc., 2015)

According to research reports, China has the highest consumption of 1,3 butadiene as of 2015 market conditions. Western Europe, United States and South Korea are also large consumers of 1,3 butadiene. (IHS Markit, 2016)

Asia (China) is the region which has the greatest share in terms of butadiene demand and consumption due to developing demand for automobile industry and polymers.

CHAPTER II

PROCESS DESCRIPTION

The proposed process is based on integrating two concepts: UOP's methane conversion to butadiene (Bricker et al., 2013) and the Synfuels' cracking of methane to ethylene (Hall, 2005)

2.1 Synfuels' Eclairs Process

Eclairs process is developed by a research group at Texas A&M University which converts methane to ethylene. Eclairs process differs from the traditional Fischer Tropsch process since it does not produce syngas like Fischer Tropsch. This difference also makes Eclairs process more profitable since it is a direct conversion of methane to ethylene process. Currently, the process is considered as profitable for small capacities such as 300 kSCMD. (Hall, 2005)

Synfuels' Eclairs process has 4 main steps which are pyrolysis (including quenching), absorber, hydrogenation and purification. (Peterson, 2015)

In the first reaction, pipeline quality shale gas (mostly methane) and oxygen are fed to supersonic reactor whereby combustion first takes place leading to a high rise in temperature (to about 2500 K). At this high temperature, methane is cracked to produce a mixture with acetylene being the main product. Other cracking output gases are H_2 , CO and CO_2 and other hydrocarbon gases. The hot gases leaving the cracker are quenched and the cooled stream is pressurized up to 12 atm before entering an amine sweetening part to remove CO_2 . The separate syngas (H_2 and CO) is recycled back to the cracker to provide some of the heat of

combustion. Next, acetylene is reacted with hydrogen (separated from the cracker products) to produce ethylene which is separated to a 99.99 mol% purity. (Hall, 2005) (Thiruvengataswamy, 2015)

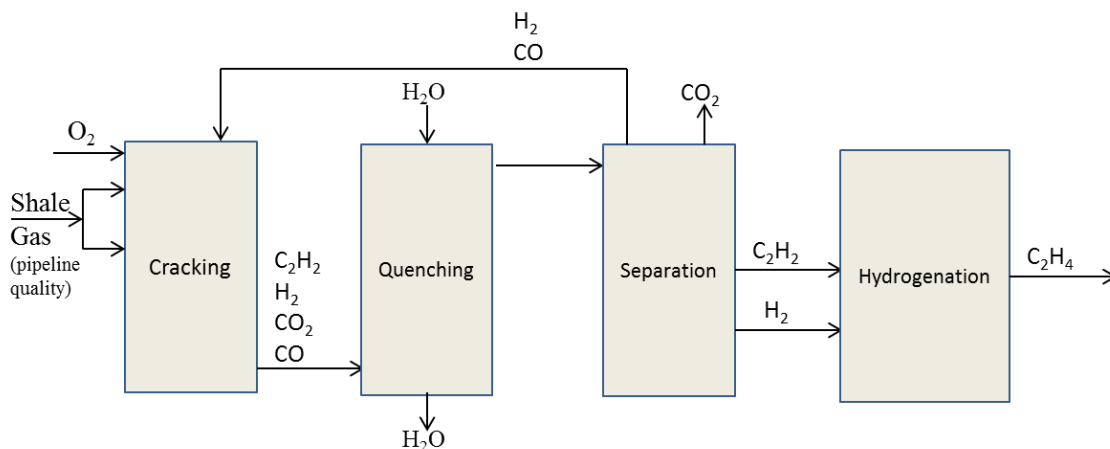


Figure 2: A Block Flow Diagram for the Shale Gas-to-Ethylene Portion of the Process

Figure 2 is a block flow diagram showing the key steps for converting shale gas to ethylene.

2.2 Description of Methane to Butadiene Production Process

Methane to butadiene process can be divided into two parts; methane to ethylene conversion and ethylene to butadiene conversion. For the process of methane to ethylene conversion part, literature data are used. Since, there are previous findings and research results about methane to ethylene conversion; this first part of the process is not designed again. Instead, these previous findings and research results are considered as the start point to design the second part of the process.

Second part of the process; ethylene to butadiene conversion; consists of three main parts. These are ethylene dimerization reactor, water quenching and separation - purification respectively.

Ethylene is dimerized to butadiene and hydrogen. The product distribution is highly impacted by temperature. Table 1 shows the impact of temperature on the product distribution.

Table 1: Effect of Dimerization Temperature on Product Distribution

Temperature(K)	Ethylene(mol%)	Butadiene(mol%)	H2(mol%)
3,273	37.2872	31.3564	31.3564
2,273	43.4089	28.2956	28.2956
1,773	48.6405	25.6798	25.6798
1,573	51.4675	24.2662	24.2662
1,273	56.8765	21.5618	21.5618

As can be seen from Table 1, butadiene yield is enhanced with increasing temperature. Nonetheless, higher temperature entails higher cost. As temperature decreases, conversion of ethylene to butadiene decreases. As temperature increases, amount of hydrogen and butadiene produced increases.

Two different scenarios are defined in this project in order to make comparison in terms of safety performance and economic analysis.

1. Scenario: Dimerization reaction operates at 1273 K and 1 bar.

2. Scenario: Dimerization reaction operates at 2773 K and 1 bar.

For both scenarios, rest of the process is assumed as similar to each other in order to make a good comparison.

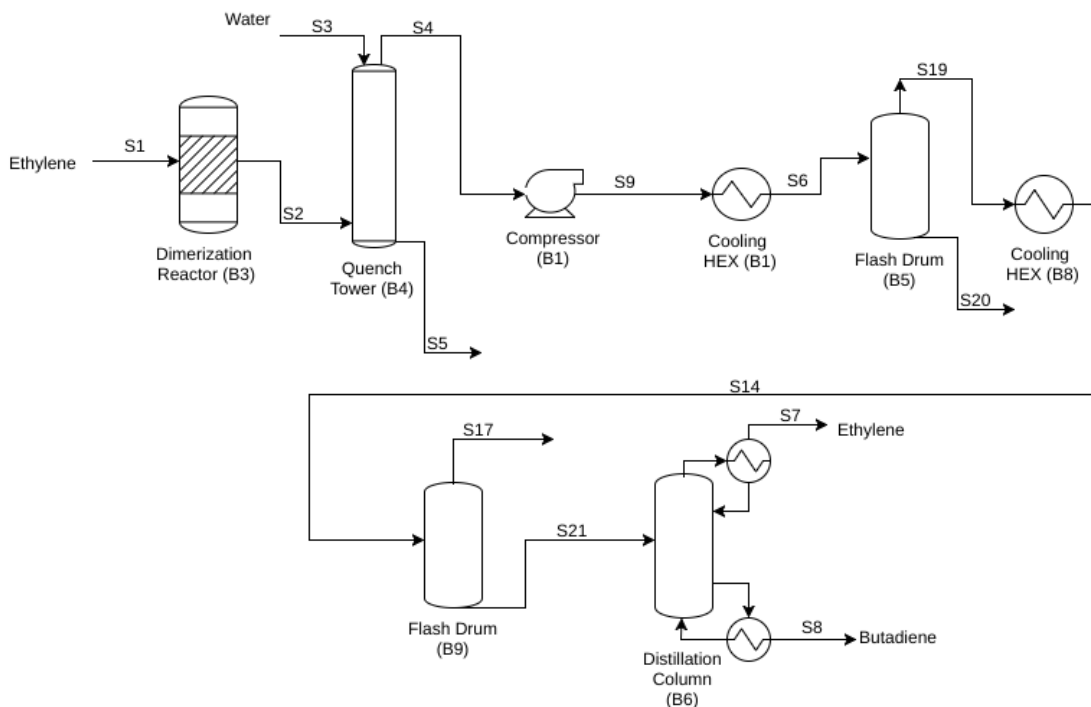


Figure 3: Flowsheet for the Ethylene-to-Butadiene Portion of the Process

In both scenarios, atmospheric pressure is used. To reduce the risk hazards, the hot reactor effluent is cooled down up to 361 K using a water quenching tower. The cooled stream is then compressed to 25 atm then cooled up to 298 K. With the combination of compression and cooling units, water in the stream is liquefied and with a flash separator drum water content is removed from the system.

The remaining process stream contains significant amount of hydrogen besides ethylene and butadiene. In order to separate hydrogen from process stream, cryogenic conditions are required. A refrigeration cycle is used to cool the stream up to 200K for the

first scenario and 120 K for the second scenario. Different refrigeration temperatures are applied for each scenario due to different amount of hydrogen in each process stream. In the second scenario, the amount of hydrogen produced is more than the first scenario, thus separation becomes more difficult for the second scenario. In order to equalize the product stream butadiene purity in each case, lower refrigeration temperature is applied in the second case.

After achieving cryogenic conditions via cooling, hydrogen is removed from the main process stream using a flash separator drum which operates at 25 bars.

As a final step, process stream containing mostly ethylene and butadiene is fed to flash and distillation units to finally obtain butadiene as a bottom product of the distillation column with a 99.5 wt.% purity. Figure 3 is a diagram of the ethylene-to-butadiene portion of the process.

2.3 Process Assumptions

The process was simulated using ASPEN Plus® V.8.8 for a base case processing 10 MM standard cubic feet (SCF) per hour. The following are some of the assumptions used in the simulation:

- Pipeline-quality shale gas was approximated with a methane stream.
- Conversion of acetylene to ethylene in the hydrogenation reactor was assumed to be complete.
- For the ethylene dimerization reactor, RGIBBS model reactor was used. It is based on identifying the equilibrium product distribution by minimizing Gibbs free energy.

- For the butadiene-ethylene distillation column, Radfrac model column was used with 20 stages, a kettle reboiler, and a reflux ratio of 0.9. Feed stream is introduced to 11th stage.
- The number of operating hours per year was taken as 8,160 (corresponding to 93% on-stream efficiency).
- For quench water tower, Radfrac model column was used with 8 stages.
- 100% pure water at 298 K is introduced to the quench water tower and cooling heat exchangers.
- Compressor yield is assumed as 0.72. Polytropic / isentropic conditions are assumed.

2.4 Chemistry of the Overall Processes

Main chemical reactions of methane to butadiene process are tabulated as below.

Table 2: Main reactions of the process

Methane \rightarrow Acetylene + H ₂	Supersonic Reactor
$2\text{CH}_4 \rightarrow \text{C}_2\text{H}_2 + 3\text{H}_2$	
Acetylene + H ₂ \rightarrow Ethylene	Hydrogenation
$\text{C}_2\text{H}_2 + \text{H}_2 \rightarrow \text{C}_2\text{H}_4$	
Ethylene \rightarrow Butadiene	Dimerization
$2\text{C}_2\text{H}_4 \rightarrow \text{C}_4\text{H}_6 + \text{H}_2$	

Initial reaction is the pyrolysis of methane to acetylene which is happening in a supersonic reactor at high reaction temperature. Fuel and oxygen are fed to supersonic

reactor and heated in the combustion chambers. Methane which is mixed with heated combustion gases is fed to the reactor at a different place. Heated combustion gases accelerates methane inside the reactor and helps methane pyrolyzes to acetylene and hydrogen. Reaction occurs at atmospheric pressure and high temperature.

Second important step of the process is the acetylene hydrogenation to ethylene. Reaction happens in liquid phase and required hydrogen is obtained from the pyrolysis reaction section.

Third main reaction of the process is dimerization reaction where ethylene is converted to the butadiene at high temperature and atmospheric pressure.

CHAPTER III

ECONOMIC ANALYSIS

In this chapter, economic analysis of Scenario I and Scenario II are evaluated using the shortcut tools in literature. (El-Halwagi, 2011)

Operating cost is the summation of raw material, energy/utility cost, labor and maintenance cost. Labor and maintenance costs are neglected for this process.

3.1 Raw Materials Cost

Natural gas to butadiene production process uses natural gas as the feedstock. For raw material cost calculation, natural gas price is determined for different time periods.

Table 3: Natural Gas Price Data for Raw Material Cost Calculation (EIA, 2017)

Natural Gas Price Estimation (\$ / thousand cubic feet)	
Jan 2007 – Jan 2017	4.451
Jan 2012 – Jan 2017	3.312
Jan 2015 – Jan 2017	2.511

Natural gas prices are obtained from U.S. Energy Information Administration (EIA). Three different time periods are considered to decide natural gas price which are tabulated as above. For each interval, average natural gas price is calculated. For raw materials cost calculation, Jan 2015 – Jan 2017 natural gas price estimation is used which is 2.511 \$ / thousands cubic feet.

Table 4: Cost Data Used in the Base-Case Assessment

Item	Price	Unit
Shale Gas	2.51	\$/1000 SCF
Oxygen	200	\$/tonne
Hydrogen	1,500	\$/tonne
Butadiene	2,000	\$/tonne
Low pressure steam	4	\$/tonne
Cooling utility	1	\$/MM Btu removed
Electric Energy	0.05	\$/kWh
Refrigerant	12	\$/MM Btu removed

Table 4 summarizes the economic data used for the raw materials, products, and utilities in the base-case assessment.

For total cost of raw materials calculation, it is assumed that the process unit operates 340 days in a year. In addition, the natural gas is considered as 100% methane for the feedstock. Amount of natural gas, oxygen and NMP solvent required is determined according to the production capacity of the process unit. Cost of oxygen and cost of NMP solvent are obtained from the literature and web data.

Raw material cost is calculated as 262.26 MM\$ / yr for this process unit. Raw material cost is assumed as same for both Scenarios I and II.

3.2 Utility Cost

For natural gas to ethylene production process part, utility cost data is obtained from previous studies and optimized according to this project's process capacity. Therefore, for

both Scenario I and Scenario II, the utility cost of natural gas to ethylene part is assumed as 299.25 MM\$ / yr. For ethylene to butadiene process part, utility costs are calculated in the next parts.

Table 5: Raw Material Cost Calculation Details

RAW MATERIAL COST	
Average Price of Natural Gas (\$ / thousand ft3)	2.51
Density of Natural Gas (Methane) (kg / m3)	0.65
Density of Natural Gas (Methane) (kg / ft3)	0.02
Average Price of Natural Gas (\$ / kg)	0.14
Amount of Methane Feed (tonne / hr)	189.5
Cost of Methane (\$ / hr)	25860.57
Cost of Methane (MM\$ / yr)	211.02
Price of Oxygen (\$ / kg)	0.2
Amount of Oxygen Feed (kg / hr)	245685
Cost of Oxygen (MM\$ / yr)	42.10
Price of NMP Solvent (\$ / kg)	4.08
Amount of NMP Solvent Consumed (kg / hr)	274.5
Cost of NMP Solvent (MM\$ / yr)	9.14
Total Cost of Raw Material (MM\$ / yr)	262.26

For both scenarios, amount of utility consumed data were obtained from the Aspen simulation. Utility prices were assumed in accordance with the literature. (El-Halwagi, 2011)

According to the Table 6, annual utility cost of second part (ethylene to butadiene process) is calculated as 18.77 MM\$ / yr. Annual utility cost is calculated as 318.02 MM\$ / yr after adding the first part (natural gas to ethylene process) utility cost data.

According to the Table 7, annual utility cost of second part (ethylene to butadiene process) is calculated as 38.47 MM\$ / yr. Annual utility cost is calculated as 337.72 MM\$ / yr after adding the first part (natural gas to ethylene process) utility cost data.

3.3 Operating Cost

Maintenance costs and labor costs are neglected.

Scenario I : Dimerization reaction operates at 1273 K and 1 bar

$$\text{Total Operating Cost} = 262.26 \text{ MM\$ / yr} + 321.91 \text{ MM\$ / yr} = 584.17 \text{ MM\$ / yr}$$

Scenario II : Dimerization reaction operates at 2773 K and 1 bar

$$\text{Total Operating Cost} = 262.26 \text{ MM\$ / yr} + 347.21 \text{ MM\$ / yr} = 609.47 \text{ MM\$ / yr}$$

3.4 Fixed Capital Investment Cost (FCI)

In order to estimate fixed capital cost, installed equipment cost has to be calculated. For both scenarios major equipment are considered for total equipment cost calculation and all of the delivered equipment cost data is obtained from Aspen simulation results excluding dimerization reactor cost data. Dimerization reactor cost is estimated considering the reactor capacity and similar reactors that are studied in previous research studies.

Table 6: Annual Utility Cost Calculation – Scenario I

Equipment Name	Utility Type	Utility Rate	Rate Units	Utility Price	U.P. Unit	Utility Cost (\$ / hr)
B1 (Compressor)	Electricity	22408.45	kW	0.05	\$ / kW	1120.42
B2 (Cooler HEX)	Cooling Water	207.01	MMBTU / hr	1	\$ / MMBtu	207.01
B3 (Conversion Reactor)	Natural Gas	127.87	MMBTU / hr	4	\$ / MMBtu	511.49
B4 (Quench Tower)	Cooling Water	16.99	MMBTU / hr	1	\$ / MMBtu	16.99
B6 (Distillation Column) – Condenser	Refrigerant	9.78	MMBTU / hr	12	\$ / MMBtu	117.39
B6 (Distillation Column) – Reboiler	Low Pressure Steam	16.56	Tonne / hr	4	\$ / tonne	66.24
B8 (Cooler HEX)	Refrigerant	21.77	MMBTU / hr	12	\$ / MMBtu	261.19
Annual Utility Cost (MM\$/yr) – Second Part						18.77
Annual Utility Cost (MM\$/yr) – First +Second Part						318.02

Table 7: Annual Utility Cost Calculation – Scenario II

Equipment Name	Utility Type	Utility Rate	Rate Units	Utility Price	U.P. Unit	Utility Cost (\$ / hr)
B1 (Compressor)	Electricity	37605.96	kW	0.05	\$ / kW	1880.30
B2 (Cooler HEX)	Cooling Water	617.97	MMBTU / hr	1	\$ / MMBtu	617.97
B3 (Conversion Reactor)	Natural Gas	302.46	MMBTU / hr	4	\$ / MMBtu	1209.82
B4 (Quench Tower)	Cooling Water	56.21	MMBTU / hr	1	\$ / MMBtu	56.21
B6 (Distillation Column) – Condenser	Refrigerant	28.38	MMBTU / hr	12	\$ / MMBtu	340.50
B6 (Distillation Column) – Reboiler	Steam	54.55	Tonne / hr	4	\$ / tonne	218.20
B8 (Cooler HEX)	Refrigerant	32.64	MMBTU / hr	12	\$ / MMBtu	391.69
Annual Utility Cost (MM\$/yr) – Second Part						38.47
Annual Utility Cost (MM\$/yr) – First +Second Part						337.72

For the first part of this process (methane to ethylene process), fixed capital investment is assumed in accordance with literature and recalculated considering this process' capacity using the formula below: (El-Halwagi, 2011)

$$FCI_B = FCI_A \times \left(\frac{Capacity_B}{Capacity_A} \right)^x$$

where x is equal to 0.6 for this process since it is ethylene process. (El-Halwagi, 2011) According to this formula above, fixed capital investment for the first part of the process is estimated as 254.07 MM\$ / yr.

For both scenarios, total installed equipment cost of 254.07 MM\$ / yr is used to calculate overall fixed capital investment.

For Scenario I, total delivered equipment cost for part II is estimated as 37.48 MM\$. FCI Lang factor is used to calculate total installed equipment. FCI Lang factor is assumed as 5.0 since the type of plant is considered as fluid. (El-Halwagi, 2011) Total delivered equipment cost is multiplied with FCI Lang factor and fixed capital investment cost (part II) is calculated as 187.39 MM\$. Total fixed capital investment cost is estimated adding the first part's fixed capital investment cost and resulted as 441.46 MM\$ / yr.

For Scenario II, total delivered equipment cost for part II is estimated as 69.09 MM\$. FCI Lang factor is used to calculate total installed equipment cost. FCI Lang factor is assumed as 5.0 since the type of plant is considered as fluid. (El-Halwagi, 2011) Total delivered equipment cost is multiplied with FCI Lang factor and fixed capital investment cost (part II) is calculated as 345.47 MM\$. Total fixed capital investment cost is estimated adding the first part's fixed capital investment cost and resulted as 599.54 MM\$ / yr.

Table 8: FCI Calculation – Scenario I

Equipment Name	Equipment Cost (MM \$)
B1 (Compressor)	26.68
B2 (Cooler HEX)	0.85
B3 (Conversion Reactor)	9.0
B4 (Quench Tower)	0.32
B5 (Flash Separator)	0.035
B6 (Distillation Column)	0.46
B8 (Cooler HEX)	0.084
B9 (Flash Separator)	0.046
Total Delivered Equipment Cost	37.48
Fixed Capital Investment – Part II	187.39
Fixed Capital Investment – Part I	254.07
Total Fixed Capital Investment	441.46

3.5 Feasibility Analysis of the Process

Economic analysis is performed for both Scenario I and Scenario II. Payback period of each scenario including the annual rate of return and return on investment (ROI) are estimated performing a feasibility study.

Table 9: FCI Calculation – Scenario II

Equipment Name	Equipment Cost (\$)
B1 (Compressor)	55.9
B2 (Cooler HEX)	2.37
B3 (Conversion Reactor)	9.0
B4 (Quench Tower)	0.61
B5 (Flash Separator)	0.063
B6 (Distillation Column)	0.97
B8 (Cooler HEX)	0.15
B9 (Flash Separator)	0.039
Total Delivered Equipment Cost	69.09
Fixed Capital Investment – Part II	345.47
Fixed Capital Investment – Part I	254.07
Total Fixed Capital Investment	599.54

Total operating cost and fixed capital investment are calculated in previous parts. WCI, working capital investment is estimated first which is the 15 / 85 of FCI for both scenarios.

For Scenario I, annual net profit is estimated as 24.36 MM\$, return on investment (ROI) is estimated as 4.69 and payback period is estimated as 18.12 years.

Table 10: Summary of Economic Evaluation – Scenario I

Raw Material Cost (MM\$ / yr)	262.26
Utility Cost (MM\$ / yr)	318.02
Annual Operating Cost (MM\$ / yr)	580.28
Fixed Capital Investment (MM\$)	441.46
Working Capital Investment (MM\$)	77.91
Total Capital Investment (MM\$)	519.37
Annual Sales of Butadiene (MM\$ / yr)	300
Annual Sales of Hydrogen (MM\$ / yr)	296.16
Annual Sales of Products (MM\$ / yr)	596.16
Annual FCI depreciation (annualized fixed cost)	44.15
Total Annualized Cost (MM\$ / yr)	624.43
Annual Net Profit (MM\$)	24.36
ROI	4.69
Payback Period (yr)	18.12

For Scenario II, annual net profit is estimated as 117.48 MM\$, return on investment (ROI) is estimated as 16.66 and payback period is estimated as 5.10 years.

Table 11: Summary of Economic Evaluation – Scenario II

Raw Material Cost (MM\$ / yr)	262.26
Utility Cost (MM\$ / yr)	337.72
Annual Operating Cost (MM\$ / yr)	599.98
Fixed Capital Investment (MM\$)	599.54
Working Capital Investment (MM\$)	105.80
Total Capital Investment (MM\$)	705.34
Annual Sales of Butadiene (MM\$ / yr)	444.06
Annual Sales of Hydrogen (MM\$ / yr)	298.06
Annual Sales of Products (MM\$ / yr)	742.11
Annual FCI depreciation (annualized fixed cost)	59.95
Total Annualized Cost (MM\$ / yr)	659.94
Annual Net Profit (MM\$)	117.48
ROI	16.66
Payback Period (yr)	5.10

An important factor in the butadiene market is the price volatility. Market reports show that between January 2016 and February 2017, butadiene prices have sharply increased from \$750 to \$2,000 per tonne. (Dang, 2017) Such large volatilities can significantly impact

the process viability. Figure 4 shows the ROI for both scenarios as a function of the butadiene selling price.

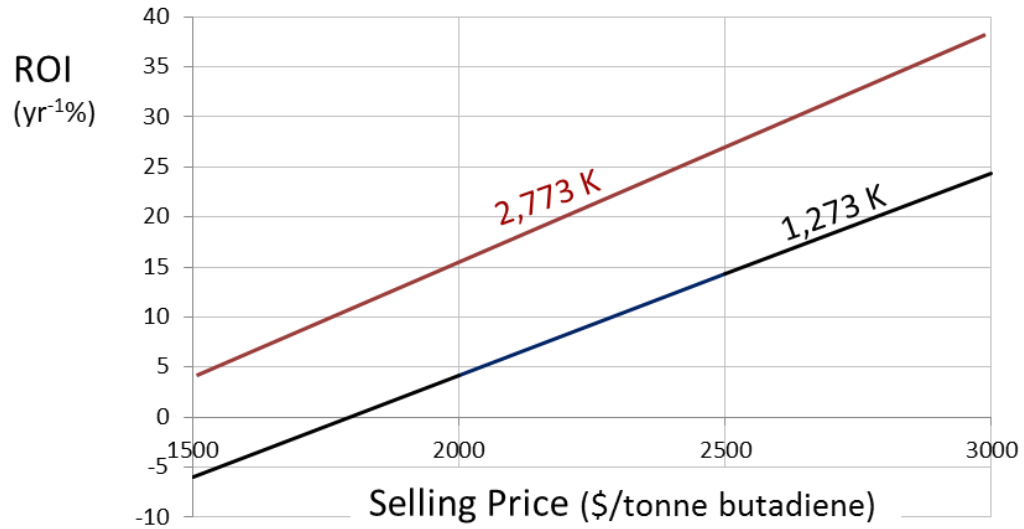


Figure 4: Effect of Price Volatility of Butadiene on ROI for the two Dimerization Temperature Scenarios

For safety reasons, the dimerization temperature was not allowed to exceed 2,773 K. The higher dimerization temperature leads to higher sales of butadiene but incurs additional fixed and operating costs. The benefits from the higher yield at the higher temperature outweigh the additional costs as evident by the higher return on investment (ROI) for Scenario II compared to Scenario I. In many cases, a minimum (threshold) ROI is required before a process is recommended. For a process of this type, the minimum acceptable ROI is typically around 10%. (El-Halwagi, 2011)

CHAPTER IV

SAFETY ANALYSIS

4.1 Metrics for Safety Analysis

There are various types of safety analysis tools that are used for risk assessment. These different types of hazard identification tools are used for different stages of the project. For example, checklists and safety audits are used at all stages whereas fault trees analysis (FTA), HAZOP and failure modes and effect analysis (FMEA) are used at commissioning and operation stages which are later the design stage. (Khan & Abbasi, 1998) In addition to project stage, time and money are also criteria for choosing safety analysis tool. (Heikkilä, 1999)

To perform a HAZOP study, FTA and failure modes and effect analysis, detailed process stream including equipment data is required. Therefore, these studies are not suitable for a process at early design stage.

There are also a variety of hazard indices that aim to define inherent safety level and potential risks of a chemical process using quantitative approach. These hazard indices can be used at early design stages. Some examples of hazard indices are Mond Index and Dow F&EI which can detect potential hazards at earlier stages so that it can be fixed before completion of the project. (Al-Sharrah et al., 2007) There are other tools such as HIRA analysis (Khan & Abbasi, 1998), Hazardous Waste, Toxicity Hazard Index (Amyotte & Khan, 2004) and SWeHI index (Khan et al., 2001) which are less widely used for safety analysis.

4.1.1 Dow Fire and Explosion Index

Dow F&EI is a leading hazard index using a ranking system to define potential hazards and risks. It is an important tool for chemical facilities to determine fire and explosion protection plans. It gives a numerical ranking for equipment and units so that engineers can determine the most dangerous part of the process and take precautions against potential fire and explosions.

Dow F&EI can be easily evaluated using process stream and material data. Detailed stream data including composition, temperature, pressure, equipment data, reaction data, plot plan of the facility, NFPA flammability and instability data are required to calculate the Dow F&EI. (Khan et al, 2003)

The calculation begins with determining of material factor (MF) which is decided according to material's NFPA instability and flammability characteristics. After deciding material factor, penalty factors called F1 and F2 are determined which are namely; general and special process hazards. To calculate F1, 6 different penalties have to be determined according to the information of reaction type (exothermic or endothermic), kind of chemical which is transferred, handled, stored and drainage and spill control of the chemicals in unit. Summation of these six penalties gives F1. (SUARDIN, 2005)

To calculate F2, 12 different penalties have to be determined according to the information of toxicity of handled chemical, maximum pressure released in case of dust explosion, chemicals in storage and process unit, corrosion rate of chemicals, usage of fired equipment, rotating equipment and leakage. Summation of these twelve penalties gives F2. (SUARDIN, 2005)

F3, process unit hazards, is estimated multiplying F1 and F2. (SUARDIN, 2005)

$$Dow\ F\&EI = F3 \times MF$$

$$Damaging\ radii = 0.84 \times Dow\ F\&EI$$

Table 12: Hazard Ratings (Dow, 1994)

F&EI Index	Hazard Degree
1 - 60	Light
61 - 96	Moderate
97 - 127	Intermediate
128 - 158	Heavy
159 - up	Severe

4.1.2 Mond Fire, Explosion and Toxicity Index

The mond index is a hazard index which is like Dow F&EI. It is accepted as an extension of Dow F&EI, can be performed at initial design period to determine potential hazards and determine fire and explosion prevention and toxic release techniques. (Khan & Abbasi, 1998)

Although Mond index is considered similar to Dow F&EI, there are differences in calculation steps which are due to extra hazardous penalties. (Khan & Abbasi, 1998) For example, Mond index is estimating material factor like Dow F&EI but Mond index includes additional special material factors. After calculation of material factor, F1 and F2, general and special process hazard factors have to be estimated similar to Dow F&EI, but again a

new factor called quantity factor, is added to the calculation which covers the chemical inventory and layout hazards. (Khan et al., 2001)

Since Mond index is also a toxicity index, the toxicity evaluation of this index covers additional factors which are related with toxicity such as toxicity of material used in the process, amount of toxic material used and their impacts on human health. (Khan et al, 2003)

Although, Dow F&EI and mond index are very similar to each other, mond index can be more advantageous since it covers more chemical processes and chemicals which have explosive characteristics. Furthermore, mond index is not only a fire and explosion index, it also covers toxicity assessment which makes it a more useful index for some cases. On the other hand, since mond index has relatively more calculation steps when compared to Dow F&EI, it may be take more time to apply it. (Khan et al., 2001)

4.1.3 Safety Weighted Hazard Index (SWeHI)

SWeHI is the newest and updated version of HIRA. SWeHI is performed to give an overall risk assessment of the process including additional factors related to meteorology and social disorders. Performing SWeHI is useful to compare and rank process units and determine which process unit is the most dangerous. Engineers can identify the hazards and take precautions to maintain safety of process units with the help of SWeHI. (Khan et al, 2003)

Evaluation steps of SWeHI are very similar to HIRA. Final calculated the result of SWeHI shows the potential hazard area radius by considering the process materials, process temperature, pressure data, material NFPA ratings, etc. (Khan et al, 2003)

$$\text{SWeHI} = B / A$$

where B shows the potential damage resulted from fire, explosion and toxicity in a specific process unit. 50% probability of damage is assumed to calculate B. “A” is the factor showing the safety precautions and control systems to reduce hazards and decrease the frequency of potential incidents. If the calculated value of SWeHI is high, it means there are potential risks in that process unit and the process unit is unsafe.

Table 13: Classification of SWeHI (Khan et al., 2001)

SWeHI	Degree of Hazards
0 – 1	Non Hazardous
1 - 5	Less Hazardous
5 - 10	Moderately Hazardous
10 - 20	Hazardous
20 - up	Highly Hazardous

Since SWeHI is the updated version of HIRA, new penalties are added to calculation. For example, pn7 is the penalty related with natural effects such as earthquakes or hurricanes. Another different penalty, pn8 represents the vulnerability unit by accidents. (Khan et al. F. I., 2001) All other calculation steps are similar to HIRA evaluation so that the details of calculation steps will be covered in the next section (HIRA).

4.1.4 Hazard Identification and Ranking Analysis (HIRA)

HIRA is a reliable hazard ranking index which is widely used in chemical industry. HIRA is considered as the combination of FEDI and TDI (Khan & Abbasi, 1998). It can be

considered as the previous version of SWeHI. The evaluated result of HIRA gives a numerical value so that responsible engineers can compare all process units with each other and determine the most dangerous unit in the process.

Hazard identification and ranking analysis (HIRA) index considers that there are five different classes for different types of hazards; units used for storage, unit includes physical operations, unit includes chemical reactions, units used for transportation and others respectively. For each class, different calculation steps have to be followed (Khan & Abbasi, 1998).

Calculated result of FEDI is used to assess the degree of hazard according to the table below. For example, if FEDI is greater than 500 shows that that process unit is extremely hazardous, whereas if FEDI is between 100 and 200, means that process unit is moderately hazardous. Also, since FEDI is a ranking system, it provides a comparison of process units.

Table 14: Hazard Ranking according to the Fire and Explosion Damage Index (Khan & Abbasi, 1998)

FEDI	Degree of Hazard
FEDI > 500	Extremely Hazardous
400 < FEDI < 500	Highly Hazardous
200 < FEDI < 400	Hazardous
100 < FEDI < 200	Moderately Hazardous
20 < FEDI < 100	Less Hazardous
FEDI < 20	Not Hazardous

Since HIRA is the combination of both FEDI and TDI. First FEDI has to be calculated. In order to perform Fire, Explosion and Damage Index, five main steps have to be followed. These are namely (Khan & Abbasi, 1998):

1. Classify the units in terms of potential hazards
2. Calculate factors related with energy
3. Calculate penalties using process unit properties
4. Calculate the potential damage using factors and penalties
5. Calculate Fire and Explosion Index (FEDI) using estimated damage.

4.2 Safety Calculations

In order to perform fire, explosion and damage index (FEDI) detailed stream data, equipment data, NPFA rankings, chemical thermodynamic data, process unit layout and chemical reaction data are required. As an initial step, all units are classified into five types described before. (Khan & Abbasi, 1998) Since, this project neglects storage and transportation units, only physical operation and chemical reaction units' calculation steps are explained. In addition, FEDI is performed only for ethylene to butadiene conversion processes both for dimerization reactor at 1273 K and 2773 K.

4.2.1 Energy Factor Calculation

F1, F2, F3 and F4 are energy factors of fire, explosion and damage index. F1 is related with chemical energy, F2 and F3 are related with physical energy and F4 is used only for units where there is a chemical reaction.

For each class, calculation of these energy factors is same. Energy factors are calculated as below: (Khan & Abbasi, 1998)

$$F1 = 0.1 \times M \times H_c / K$$

where M is mass flowrate in kg/s, H_c is in J/mol and K is a constant equal to 3.148.

$$F2 = 1.304 \times 10^{-3} \times PP \times V$$

where PP the pressure of the operation in kPa and V is equipment volume in m³.

$$F3 = 1.0 \times 10^{-3} \times 1 / Temperature \times (Operating Pressure - Vapor Pressure)^2 \times V$$

where T in Kelvin and vapor pressure in kPa.

$$F4 = M \times H_{rxn} / K$$

where H_{rxn} is heat of reaction in kJ/kg.

4.2.2 Penalty Calculation

Calculation of penalties for each class is different from each other. Since the project assumes only units with physical and chemical reactions, calculation of penalties for other classes is not covered. Penalties pn1, pn2, pn3, pn4, pn5 and pn6 are used both for physical operation and chemical reaction units, whereas for chemical reaction units two additional penalties have to be calculated; pn7 and pn8 respectively. All penalties are calculated according to the formulas below: (Khan & Abbasi, 1998)

pn1

= ft2 (flash temperature, fire temperature, autoignition temperature, working temperature)

where ft2 is calculated as below;

if (fire point > temperature > flash point)

$$ft2 = 1.45$$

else if (0.75 autoignition temperature > temperature > fire point)

$$ft2 = 1.75$$

else if (process temperature > 0.75 autoignition temperature)

$$ft2 = 1.95$$

else

$$ft2 = 1.1$$

To calculate pn2;

if (Vapor Pressure > Atmospheric Pressure and Operating Pressure > Vapor Pressure)

$$pn2 = fp1 (Operating Pressure, Atmospheric Pressure, Vapor Pressure)$$

$$F = sum(F2, F3)$$

where

$$fp1 = 1 + ((Operating Pressure - Vapor Pressure) / Operating Pressure) \times 0.6$$

otherwise:

$$pn2 = fp2 (Operating Pressure, Atmospheric Pressure, Vapor Pressure)$$

$$F = F2$$

where

$$fp2 = 1 + ((Operating Pressure - Vapor Pressure) / Operating Pressure) \times 0.4$$

if (Atmospheric Pressure > Vapor Pressure and Operating Pressure > Atmospheric Pressure)

$$pn2 = fp3 (Operating Pressure, Atmospheric Pressure, Vapor Pressure)$$

$$F = F3$$

where

$$fp3 = 1 + ((Operating Pressure - Vapor Pressure) / Operating Pressure) \times 0.2$$

otherwise:

$$pn2 = 1.1$$

$$F = F3$$

Penalty pn3 is related with the used chemical in the process unit and its reactivity and flammability ranking. Since, the amount of chemicals in process units are represented as flow rates and changes with respect to time, pn3 is assumed as 1.1 for all calculation steps.

To calculate pn4;

$$pn4 = 1 + 0.25 \times (NFPA \text{ flammability rank} + NFPA \text{ reactivity rank})$$

Penalty pn5 is related to the potential impact of closest unit involving hazards. In this process, it is assumed as 1.2 for all process units.

Penalty pn6 is related to frequency of process units. To calculate pn6;

$$pn6$$

$$= (1$$

$$+ \text{percentage of area inhabited by unit in the r of 30 meter from the nearest process} / 100)$$

For this process, pn6 is assumed as 1.0.

Both pn7 and pn8 are used to calculate FEDI for process units with chemical reactions namely reactors of the process. Penalty pn7 is related to reaction type whereas penalty pn8 is related with undesired side reactions. Both penalties are evaluated in accordance with the literature data. (Khan & Abbasi, 1998)

4.2.3 Damage Calculation (Khan & Abbasi, 1998)

For Physical Operations Unit

$$\text{Potential Damage} = (F1 \times pn1 + F \times pn2) \times pn3 \times pn4 \times pn5 \times pn6$$

For Chemical Reaction Unit

Potential Damage

$$= (F1 \times pn1 + F \times pn2 + F4 \times pn7 \times pn8) \times pn3 \times pn4 \times pn5 \times pn6$$

4.2.4 Fire, Explosion and Damage Index Calculations (Khan & Abbasi, 1998)

$$FEDI = 4.76 \times (Potential\ Damage)^{1/3}$$

$$Damaging\ radii = 0.84 \times Dow\ FEI$$

4.3 Assumptions for Safety Calculations

- Volume of compressors is neglected for calculation steps since simulation results do not contain compressor volume data. Compressor outlet stream data is used to calculate potential damage and FEDI due to higher pressure at the outlet of compressor.
- Volume of heat exchangers is calculated assuming that residence time is 10 seconds which is taken from literature data.
- For all process units, vapor phase stream data is taken into account to calculate potential damage and FEDI rankings since vapor phase conditions are considered more hazardous than liquid phase conditions.
- For flash separators, top outlet stream data is used to calculate potential damage and FEDI ranking in order to consider gas phase conditions.
- For distillation column and quench water tower, top of the column conditions are used to calculate potential damage and FEDI ranking in order to consider gas phase conditions.

- For conversion reactor, reactor effluent stream data is used to calculate potential damage and FEDI ranking due to exothermic reaction inside the reactor and higher temperature at the outlet stream.
- Heat of combustion factor, NFPA reactivity and NFPA flammability are calculated by taking the weighted average of stream components' data.
- For calculating energy factors, molecular weight is included to the calculation steps in order to convert basis from mole to mass unit.
- Penalty pn3 is assumed as 1.1 and pn5 is assumed as 1.2 due to neglecting the potential impact of closest unit involving hazards and process unit density.
- Penalty pn6 is assumed as 1.0 due to lack of information.

4.4 Results for Safety Calculations

For this research, two different reactor temperatures are applied to the dimerization reactor to compare their safety levels. Fire, explosion and damage calculation is performed only for main process equipment. First case is the condition where the ethylene to butadiene conversion reaction takes place at 1273 K, second case is the condition where the ethylene to butadiene conversion reaction takes place at 2773 K. Same process and type of equipment are used at each case.

Scenario I: Dimerization Reactor Temperature at 1273 K

In Case I, the dimerization reactor temperature is 1273 K. Safety calculation is applied to all major equipment and FEDI rankings of each of them is tabulated as below. According to the FEDI ranking results, conversion reactor has the highest FEDI ranking which is 305 and B9 flash drum has the lowest FEDI ranking which are 36.

Dimerization reactor has the highest ranking since it has the highest operation temperature among all equipment.

Table 15: Scenario I: FEDI Rankings of Equipment

No	Equipment Class	FEDI
B1	Compressor	160
B2	Heat Exchanger	161
B3	Reactor	305
B4	Quench Tower	155
B5	Flash Drum	213
B6	Distillation Column	178
B8	Heat Exchanger	212
B9	Flash Drum	36

Scenario II: Dimerization Reactor Temperature at 2773 K

In Case II, the dimerization reactor temperature is 2773 K. Safety calculation is applied to all major equipment and FEDI rankings of each of them is tabulated as below. According to the FEDI ranking results, conversion reactor has the highest FEDI ranking which is 832 and B9 flash drum has the lowest FEDI ranking which are 25.

Dimerization reactor has the highest FEDI ranking since it has the highest operation temperature among all equipment.

Table 16: Scenario II: FEDI Rankings of Equipment

No	Equipment Class	FEDI
B1	Compressor	138
B2	Heat Exchanger	139
B3	Reactor	832
B4	Quench Tower	134
B5	Flash Drum	212
B6	Distillation Column	159
B8	Heat Exchanger	211
B9	Flash Drum	25

In both cases, the highest FEDI ranking equipment is the dimerization reactors and the lowest FEDI ranking equipment are the flash drums (B9).

In general, equipment of Scenario II excluding dimerization reactor have lower FEDI ranking than equipment of Scenario I due to water content in the process streams. Since dimerization reactor operates at very high temperature, a water quench tower is used in the process to cool down the system and mitigate potential risks immediately. However, this adds a great amount of water to the process streams and decreases the molar ratio of hazardous content. At Scenario II, the reactor effluent temperature is more than twice as high Scenario I's reactor. Therefore, more water is used at Scenario II which adds more water to the process streams and affects FEDI results.

In addition, FEDI of reactor at 2773 K is more than twice of FEDI of reactor at 1273 K due to higher temperature at the reactor effluent.

CHAPTER V

CONCLUSIONS

5.1 Results of Economic Analysis

For both Scenario I and II, feasibility analysis is performed and key parameters of feasibility analysis are calculated as Table 17.

According to the table below, the net annual profit of Scenario II is approximately 5 times higher than the Scenario I. It is observed that, utility cost and annual operating cost are higher for Scenario II due to higher dimerization reactor temperature which has a negative impact on annual net profit.

Furthermore, scenario II has higher total capital investment than scenario I which makes an additional negative impact on annual net profit. On the other hand, Scenario II, has higher yields of both hydrogen and butadiene production, which makes a positive impact on annual net profit and dominates the other negative impacts.

It is observed that scenario II has approximately 4 times higher ROI than scenario I and scenario I has approximately 4 times higher payback period than scenario II.

These results seem acceptable for selected market conditions and current prices.

Table 17: Comparison of Economic Analysis Results

	Scenario I (Dimerization Temperature = 1,273 K)	Scenario II (Dimerization Temperature = 2,773 K)
Raw Material Cost (MM\$ / yr)	262.26	262.26
Utility Cost (MM\$ / yr)	318.02	337.72
Annual Operating Cost (MM\$ / yr)	580.28	599.98
Fixed Capital Investment (MM\$)	441.46	599.54
Working Capital Investment (MM\$)	77.91	105.80
Total Capital Investment (MM\$)	519.37	705.34
Annual Sales of Butadiene (MM\$ / yr)	300.00	444.06
Annual Sales of Hydrogen (MM\$ / yr)	296.16	298.06
Annual Sales of Products (MM\$ / yr)	596.16	742.12
Annual After-Tax Profit (MM\$)	24.36	117.48
ROI (yr ⁻¹ %)	4.69	16.66
Payback Period (yr)	18.12	5.10

5.2 Results of Safety Analysis

Table 18: Comparison of Safety Analysis Results

		Scenario I (Dimerization Temperature = 1,273 K)	Scenario II (Dimerization Temperature = 2,773 K)
N	Equipment Class	FEDI	FEDI
B1	Compressor	160	138
B2	Heat Exchanger	161	139
B3	Reactor	305	832
B4	Quench Tower	155	134
B5	Flash Drum	213	212
B6	Distillation Column	178	159
B8	Heat Exchanger	212	211
B9	Flash Drum	36	25

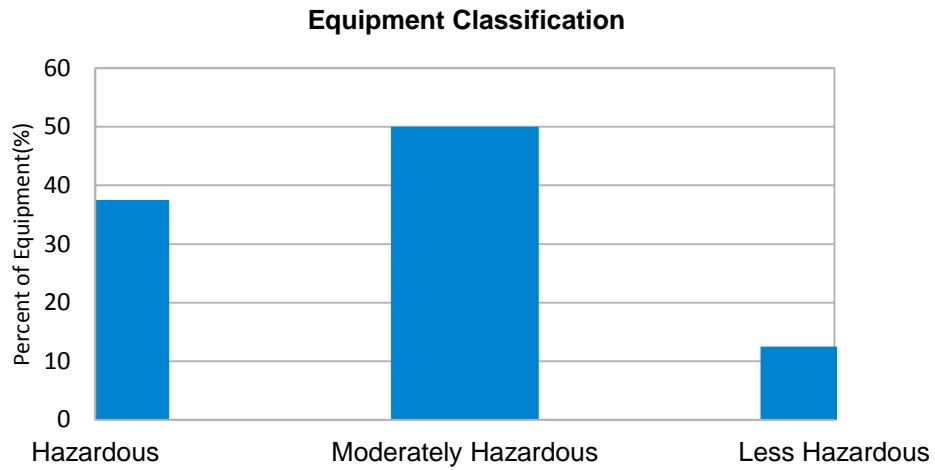


Figure 5: Scenario I – Equipment Classification

According to the equipment classification graphic above, 12.5% of equipment are classified as less hazardous, 50% of equipment are classified as moderately hazardous and 37.5% of equipment are classified as hazardous.

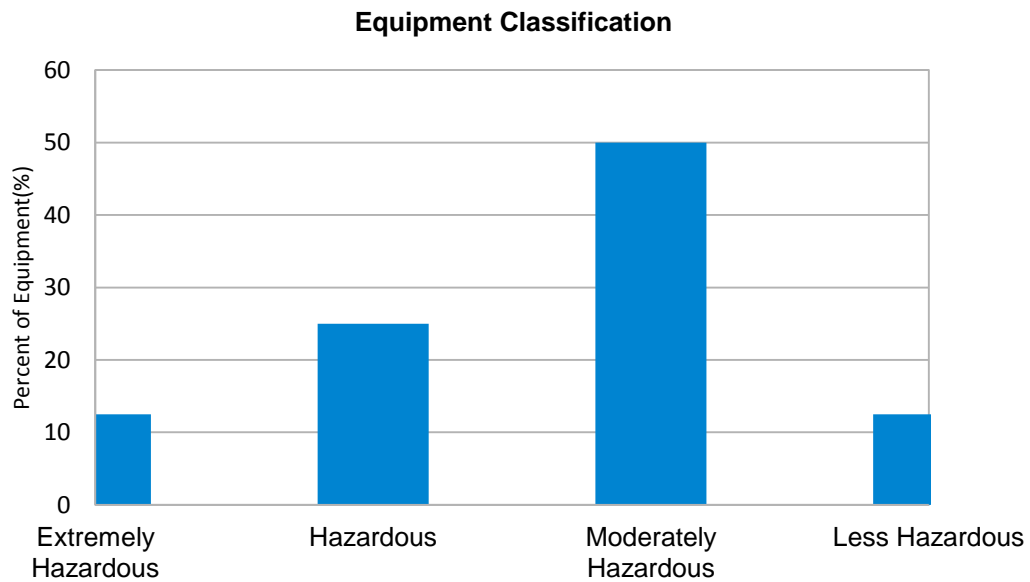


Figure 6: Scenario II: Equipment Classification

According to the equipment classification graphic above, 12.5% of equipment are classified as less hazardous, 50% of equipment are classified as moderately hazardous, 25% of equipment are classified as hazardous and 12.5% of equipment are classified as extremely hazardous.

5.3 Conclusions

This work has assessed the techno-economic viability and safety performance of manufacturing butadiene from shale gas. A process flowsheet was synthesized to convert shale gas to ethylene which is subsequently dimerized to butadiene. Computer-aided process simulation was used to design the process and to obtain the data necessary for economic evaluation. Capital and operating expenses were evaluated for two scenarios involving two dimerization temperatures (1,273 and 2,773). The second scenario was shown to be more profitable because of the enhanced yield of butadiene which results in higher sales that offset the increment in capital and operating costs. In order to assess the impact of price volatility of butadiene on the economic feasibility of the process a sensitivity analysis was performed.

On the other hand, the first scenario was found safer because of lower FEDI ranking for dimerization reactor.

All in all, there is a tradeoff between profitability and safety risk level of the scenarios.

5.4 Recommendations

For further study, these recommendations below are listed according to the results obtained in this thesis:

- a. In this study, 4 different safety metrics are investigated and hazard identification and ranking analysis (HIRA) is performed only for the dimerization reactor. For future work, a better and more comprehensive safety metric can be selected which gives more accurate results for the whole plant.
- b. The conclusion is made according to the 2 different scenarios which are obtained from 2 different operating temperatures for the dimerization reactor. To obtain better results, more operating temperatures can be applied and simulated for the dimerization reactor.
- c. To improve inherent safety level of the whole plant, different dimerization reactor configurations can be considered and simulated such as using two small parallel working reactors instead of one reactor.
- d. Sustainability analysis including carbon footprint calculations can be performed for each scenario to make a more realistic conclusion in the end.
- e. Heat and mass integration techniques can be applied to the system to minimize energy consumption, fresh water usage and waste discharge.

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APPENDIX

Table 19: Safety Data of Chemicals

Name	Fire Point (C)	Autoignition Temperature (C)	Flash Point (C)	NFPA Flammability	NFPA Reactivity	Heat Of Combustion (kj/mol)
Ethylene	-126	490	-136	4	2	-1400
Butadiene	-75	415	-85	4	2	-2540
Hydrogen	-190	570	-200	4	0	-285

Table 20: Aspen simulation stream data – Scenario I

	Units	S1	S14	S17	S19	S2	S20	S21	S3	S4	S5	S6	S7	S8	S9
From			B8	B9	B5	B3	B5	B9		B4	B4	B2	B6	B6	B1
To		B3	B9		B8	B4		B6	B4	B1		B5			B2
Substream: MIXED															
Phase:		Vapor	Mixed	Vapor	Vapor	Liquid	Liquid	Liquid	Liquid	Vapor	Liquid	Mixed	Vapor	Liquid	Vapor
Component Mole Flow															
ETHYLENE	KMOL/HR	1683.315	970.4187	62.3229	970.4187	970.4369	0.0170738	908.0958	0	970.4357	0.0011349	970.4357	908.0893	0.0065796	970.4357
BUTADIEN	KMOL/HR	0	356.4386	0.188337	356.4386	356.4391	0.0003345	356.2502	0	356.4389	0.0001528	356.4389	18.47516	337.7749	356.4389
H2	KMOL/HR	0	356.4379	343.8721	356.4379	356.4391	0.0011189	12.5658	0	356.439	5.26E-05	356.439	12.5658	4.87E-12	356.439
WATER	KMOL/HR	0	0.5285489	7.67E-05	0.5285489	0	2731.761	0.5284723	3366.63	2732.289	634.3408	2732.289	0.0002556	0.5282164	2732.289
Mole Flow	KMOL/HR	1683.315	1683.824	406.3834	1683.824	1683.315	2731.779	1277.44	3366.63	4415.603	634.3422	4415.603	939.1305	338.3097	4415.603
Mass Flow	KG/HR	47223.32	47232.3	2451.786	47232.3	5	49213.93	44780.51	60650.78	96446.23	11427.87	96446.23	26500.01	18280.5	96446.23
Volume Flow	L/MIN	2970530	5717.567	4469.252	19803.41	3920.958	805.9251	1248.314	1016.992	2199630	205.0902	24131.26	10013.57	664.9128	177401
Temperature	C	1000	-73.15	-73.15	0	1000	0	-73.15	25	88.80075	90.11547	25	-8.701455	118.9733	462.9901
Pressure	BAR	1	25	25	25	1	25	25	1	1	1	25	25	25	25
Vapor Fraction		1	0.2413456	1	1	0	0	0	0	1	0	0.3817999	1	0	1
Liquid Fraction		0	0.7586544	0	0	1	1	1	1	0	1	0.6182001	0	1	0
Solid Fraction		0	0	0	0	0	0	0	0	0	0	0	0	0	0
Molar Enthalpy	CAL/MOL	31231.68	8836.551	1203.258	12093.95	32618.03	-69202.68	11264.88	-68725.85	-30274.28	-67454	-37765.3	11887.44	24174.09	-25951.49
Mass Enthalpy	CAL/GM	1113.28	315.0216	199.44	431.1472	1162.697	-3841.319	321.3498	-3814.865	-1386.049	-3744.261	-1729.011	421.2776	447.3799	-1188.138
Enthalpy Flow	MMBTU/HR	208.6257	59.04542	1.940445	80.81117	217.8862	-750.1969	57.10497	-918.1683	-530.4819	-169.8001	-661.7434	44.30177	32.45423	-454.7356
Molar Entropy	CAL/MOL-K	12.47247	-33.31037	-10.46099	-20.52812	1.336322	-41.83414	-40.57929	-40.11986	-8.058812	-36.26272	-32.18164	-21.29392	-41.96282	-6.304887
Mass Entropy	CAL/GM-K	0.4445918	-1.187509	-1.733909	-0.731824	0.0476343	-2.32214	-1.157593	-2.22699	-0.368957	-2.012884	-1.473374	-0.7546326	-0.7765887	-0.288657
Molar Density	MOL/CC	9.44E-06	0.0049083	0.0015155	0.0014171	0.0071552	0.0564936	0.0170555	0.055173	3.35E-05	0.0515498	0.0030497	0.0015631	0.0084801	0.0004148
Mass Density	GM/CC	0.000264955	0.1376818	0.0091432	0.0397509	0.2007303	1.017752	0.5978797	0.993957	0.0007308	0.9286863	0.0666122	0.0441068	0.458218	0.009061
Average Molecular Weight		28.05376	28.05062	6.033183	28.05062	28.05376	18.01534	35.05488	18.01528	21.84214	18.01531	21.84214	28.2176	54.03481	21.84214

Table 21: Aspen simulation stream data – Scenario II

	Units	S1	S14	S17	S19	S2	S20	S21	S3	S4	S5	S6	S7	S8	S9			
From			B8	B9	B5	B3	B5	B9		B4	B4	B2	B6	B6	B1			
To		B3	B9		B8	B4		B6	B4	B1		B5			B2			
Substream: MIXED																		
Phase:		Vapor	Mixed	Vapor	Vapor	Liquid	Liquid	Liquid	Liquid	Vapor	Liquid	Mixed	Vapor	Liquid	Vapor			
Component Mole Flow																		
ETHYLENE	KMOL/HR	1683.315	675.417	0.2916998	675.417	675.5221	0.1045989	675.1253		0	675.5216	0.0005637	675.5216	675.1225	0.0028205	675.5216		
BUTADIEN	KMOL/HR		0	503.8885	1.14E-05	503.8885	503.8964	0.0077504	503.8885	0	503.8963	0.0001678	503.8963	0.8661751	503.0223	503.8963		
H2	KMOL/HR		0	503.8836	497.2255	503.8836	503.8964	0.0127994	6.658062	0	503.8964	5.37E-05	503.8964	6.658062	3.43E-12	503.8964		
WATER	KMOL/HR		0	2.606007	9.87E-10	2.606007		0	9039.706	2.606007	10000	9042.312	957.6884	9042.312	8.96E-05	2.605918	9042.312	
Mole Flow	KMOL/HR	1683.315	1685.795	497.5172	1685.795	1683.315	9039.831	1188.278	10000	10725.63	957.6891	10725.63	682.6468	505.6311	10725.63			
Mass Flow	KG/HR	47223.32	47266.86	1010.531	47266.86	47223.32	162856	46256.33	180153	210123	17253.05	210123	19000	27256.33	210123			
Volume Flow	L/MIN	2970530	4371.539	3297.281	23425.05	4024.866	2730.818	1074.258	3020.801	5457110	312.2215	26155.87	6546.976	990.487	486966			
Temperature	C	1000	-153.15	-153.15		25	2500	25	-153.15	25	96.88343	97.45347		25	-20.28678	119.0322	557.1701	
Pressure	BAR		1	25	25	25	1	25	25	1	1	1	1	25	25	25	25	
Vapor Fraction			1	0.2951232		1	0	0	0	0	1	0	0	0.1571745		1	0	1
Liquid Fraction			0	0.7048768		0	1	1	1	1	0	1	0.8428255		0	1	0	0
Solid Fraction			0	0		0	0	0	0	0	0	0	0		0	0	0	0
Molar Enthalpy	CAL/MOL	31231.68	7560.754	-1208.643	12439.92	76509.9	-68714.87	11232.39	-68725.85	-46058.56	-67309.31	-55959.4		11539.2	23863.33	-41440.3		
Mass Enthalpy	CAL/GM	1113.28	269.6579	-595.0541	443.6758	2727.26	-3814.229	288.5487	-3814.865	-2351.036	-3736.232	-2856.42	414.5894	442.6878	-2115.299			
Enthalpy Flow	CAL/SEC	14603600	3540520	-167030	5825320	35775100	17255000	3707560	190910000	137220000	-17906000	166720000	2188110	3351680	123460000			
Molar Entropy	CAL/MOL-K	12.47247	-41.21995	-12.60525	-19.68727	22.02398	-40.12712	-53.20057	-40.11986	-8.168241	-35.86812	-36.9145	-21.75846	-41.87009	-6.49392			
Mass Entropy	CAL/GM-K	0.4445918	-1.470129	-6.205975	-0.702156	0.7850635	-2.227378	-1.366668	-2.22699	-0.4169437	-1.990982	-1.884282	-0.7817551	-0.7767305	-0.3314789			
Molar Density	MOL/CC	9.44E-06	0.0064272	0.0025148	0.0011994	0.0069705	0.0551717	0.0184356	0.055173	3.28E-05	0.0511223	0.0068344	0.0017378	0.0085081	0.0003671			
Mass Density	GM/CC	0.000265	0.1802068	0.0051079	0.0336298	0.1955482	0.9939405	0.717648	0.993957	0.0006417	0.9209833	0.1338916	0.0483683	0.4586351	0.0071916			
Average Molecular Weight		28.05376	28.03832	2.031147	28.03832	28.05376	18.0154	38.9272	18.01528	19.59075	18.01529	19.59075	27.83284	53.90556	19.59075			

Table 22: Safety Calculation for Physical Units – Scenario I

No	Equipment Class	Mass Flowrate (kg/s)	Heat of Combustion (J/mol)	Operating Pressure (kPa)	Volume (m3)	Temperature (C)	NFPA Reactivity	NFPA Flammability	F1	F2	Ethylene	Butadiene	Hydrogen	Water	pn1	pn2	pn3	pn4	pn5	pn6	Damage Potential	FEDI
B1	Compressor	26.791	533.528	2500	0	462.99	0.601	1.525	9915.33	0.00	0.2198	0.0807	0.0807	0.6188	1.95	1.4	1.1	1.5315	1.2	1	39086.24	160.97
B2	Heat Exchanger	26.791	533.528	2500	14.783	462.99	0.601	1.525	9915.33	48.19	0.2198	0.0807	0.0807	0.6188	1.95	1.4	1.1	1.5315	1.2	1	39222.63	161.16
B4	Quench Tower	26.791	533.528	100	366.605	88	0.601	1.525	9915.33	47.81	0.2198	0.0807	0.0807	0.6188	1.75	1.4	1.1	1.5315	1.2	1	35212.69	155.47
B5	Flash Drum	13.120	1399.856	2500	8.618	25	1.577	4.000	16369.79	28.09	0.5763	0.2120	0.2117	0.0000	1.75	1.4	1.1	2.3941	1.2	1	90656.87	213.02
B6	Distillation Column	7.361	1397.821	2500	6.080	-8.701	1.973	4.000	9221.84	19.82	0.9669	0.0197	0.0134	0.0000	1.75	1.4	1.1	2.4933	1.2	1	53204.60	178.38
B8	Heat Exchanger	13.120	1399.094	2500	3.301	25	1.576	3.999	16354.38	10.76	0.5763	0.2117	0.2117	0.0003	1.75	1.4	1.1	2.3937	1.2	1	90477.95	212.88
B9	Flash Drum	0.681	455.508	2500	14.011	-73.15	0.308	4.000	59.40	45.68	0.1534	0.0005	0.8462	0.0000	1.75	1.4	1.1	2.0769	1.2	1	460.30	36.68

Table 23: Safety Calculation for Physical Units – Scenario II

No	Equipment Class	Mass Flowrate (kg/s)	Heat of Combustion (J/mol)	Operating Pressure (kPa)	Volume (m3)	Temperature (C)	NFPA Reactivity	NFPA Flammability	F1	F2	Ethylene	Butadiene	Hydrogen	Water	pn1	pn2	pn3	pn4	pn5	pn6	Damage Potential	FEDI
B1	Compressor	58.368	220.895	2500	0	557.17	0.220	0.628	8021.6052	0	0.0630	0.0470	0.0470	0.8431	1.95	1.4	1.1	1.2119	1.2	1	25023.346	138.757
B2	Heat Exchanger	58.368	220.895	2500	40.5805	557.17	0.220	0.628	8021.6052	132.29	0.0630	0.0470	0.0470	0.8431	1.95	1.4	1.1	1.2119	1.2	1	25319.633	139.302
B4	Quench Tower	58.368	220.895	100	727.615	96.88	0.220	0.628	8021.6052	94.881	0.0630	0.0470	0.0470	0.8431	1.75	1.4	1.1	1.2119	1.2	1	22669.347	134.267
B5	Flash Drum	13.130	1405.312	2500	23.430	25.00	1.399	3.994	16431.828	76.382	0.4007	0.2989	0.2989	0.0015	1.75	1.4	1.1	2.3482	1.2	1	89464.51	212.083
B6	Distillation Column	5.278	1390.571	2500	23.975	-20.29	1.980	4.000	6487.9615	78.158	0.9890	0.0013	0.0098	0.0000	1.75	1.4	1.1	2.4951	1.2	1	37755.272	159.126
B8	Heat Exchanger	13.130	1405.312	2500	3.904	25.00	1.399	3.994	16431.828	12.728	0.4007	0.2989	0.2989	0.0015	1.75	1.4	1.1	2.3482	1.2	1	89188.281	211.865
B9	Flash Drum	0.281	285.649	2500	11.101	-153.15	0.001	4.000	5.1583087	36.188	0.0006	0.0000	0.9994	0.0000	1.75	1.4	1.1	2.0003	1.2	1	157.60476	25.6683

Table 24: Safety Calculation for Units with Reaction – Scenario I and Scenario II

Scenario	No	Equipment Class	Mass Flowrate (kg/s)	Heat of Combustion (J/mol)	Operating Pressure (kPa)	Volume (m3)	Temperature (C)	NFPA Reactivity	NFPA Flammability	F1	F2	F4	Ethylene	Butadiene	Hydrogen	Water	pn1	pn2	pn3	pn4	pn5	pn6	pn7	pn8	Damage Potential	FEDI
I	B3	Reactor	13.118	1411.741	100	27.244	1000	1.576	4.000	16500.825	3.5526	24182.47	0.5765	0.2117	0.2117	0	2	1.4	1.1	2.4	1.2	1	1.5	1.45	267920.329	305.586
II	B3	Reactor	13.118	1412.065	100	27.244	2500	1.401	4.000	16504.658	3.5526	789804	0.4013	0.2993	0.2993	0	2	1.4	1.1	2.4	1.2	1	1.5	1.45	5429294.594	832.294