REMOVAL OF RESIDUAL ACIDITY FROM VINYL CHLORIDE MONOMER WITHOUT INCREASING MOISTURE CONTENT

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2020

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A THESIS
Submitted to
National University of Sciences and Technology
in partial fulfillment of the requirements
for the degree of

B.E. CHEMICAL ENGINEERING

School of Chemical and Materials Engineering (SCME)
National University of Sciences and Technology (NUST)
July, 2020

CERTIFICATE

This is to certify that work in this thesis has been completed by **Mr. Muhammad Ayub Khan**, **Ms. Uroob Fatima** and **Mr. Muhammad Ziyab** under the supervision of Dr. Erum Pervaiz at the school of Chemical and Materials Engineering (SCME), National University of Science and Technology, H-12, Islamabad, Pakistan.

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DEDICATED

TO

MY LOVING MOTHER

Who is my heaven

Her prayers, guidance and help

Made possible everything

Her hands are always raised for

My success and well-being

MY DEAR FATHER

Whose love is more precious than pearls and diamonds

By the virtue of his prayers

I have been able to reach at this position

MY LOVING SISTERs AND BROTHERs

Who are the world for me

Their love and prayers encouraged me

At every step

MY KIND TEACHERS AND FRIENDS

Whose efforts and guidance

Made possible for me to reach at this position

ACKNOWLEDGEMENTS

We set our humble thanks before Him, who is one and only, the Creator of all skies and earth and Lord of all worlds The Almighty ALLAH, the omnipotent and the omnipresent. All acclamations and praises to Him, who blessed us with good health, zeal of doing work, talented teachers and an opportunity to add a little part to the sphere of knowledge in this world. The humblest and the deepest obligation are also paid, with great honor and esteem to the Holy Prophet Muhammad (PBUH), the cause of creation of Islam, the most perfect in this universe, who is forever, a beacon of perfect guidance and knowledge for humanity as a whole. Who enlightening our conscience with the essence of faith in Allah. Converging all this kindness mercy upon him who guided the mankind to the path of education and research.

We deem it utmost to express our heartiest gratitude and deep sense of obligation to our reverend supervisor, Dr. Erum Pervaiz, for scholastic guidance, ever encouraging attitude and valuable suggestions during our project.

In the end we feel it incomplete if we do not extend our fervent and hearties complement to our family our sweet loving Sisters and brothers whose love and encouragement made us able to reach at this position. No acknowledgement could ever adequately express our obligation to our great affectionate Father and dearest loving Mother for leading their children into intellectual pursuit and wished to see me glittering on the skies of success. May Allah give them a long, prosperous, and happy life (Ameen).

ABSTRACT

Production of Vinyl Chloride Monomer is associated with byproducts formation, one of them being Butadiene. Butadiene is a highly undesirable byproduct as it is a polymerization reaction inhibitor. It is removed by multistep process which includes acid wash, caustic wash, settling and drying. These steps add residual acidity to the final Vinyl Chloride Monomer product. Along with residual acidity, it adds extra moisture content as well. These components are also undesired, hence needs removal. In this project, an alternate route is proposed for the removal of butadiene, where the product stream containing butadiene is treated with hydrogen in the presence of Nickel (Ni) catalyst supported by activated Alumina. Alongside this major change, certain minor but important changes are made to the entire plant in order to minimize the formation of byproducts in the first place, and secondly, ensure energy economy. These changes include, the modification of catalyst in direct chlorination reactor from simple Ferric Chloride ($FeCl_3$) to Ferric Chloride ($FeCl_3$) modified by Sodium (Na). This enabled the operation of direct chlorination at higher temperature while maintaining selectivity. Operation at higher temperature makes it possible to recover heat, which can be used in distillation columns. Carbon Tetrachloride (CCl_4) is introduced deliberately into cracking furnace, to increase the rate of reaction, conversion while maintaining selectivity. All these changes result in an energy efficient, environmentally friendly plant where the requirements of removal of residual acidity and ensuring minimum moisture content are met in an economical way.

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ABBREVIATIONS

VCM- Vinyl Chloride Monomer

EDC-Ethylene Dichloride

TCE-Trichloroethane

OC- Oxychlorination

OCR-Oxychlorination Reactor

DC-Direct Chlorination

DCR-Direct Chlorination Reactor

PVC-Polyvinylchloride

PVDC-Polyvinyledenechloride

LPG-Liquified Petroleum Gas

NFPA-National Fire Protection Association

HTC-High Temperature Chlorination

LTC-Low Temperature Chlorination

CHAPTER 1

INTRODUCTION

Vinyl Chloride Monomer (VCM) is a monomer of the polymer polyvinylchloride (PVC). Vinyl Chloride is an unsaturated hydrocarbon which reacts through chain reaction mechanism to polymerize. It occurs at high pressure and temperature i.e. 1.5 MPa and around 80 ^{0}C[1]. If other unsaturated hydrocarbons are present, they will inhibit the rate of polymerization reaction as well as lower the quality of the final polyvinylchloride (PVC)[2]. Due to this very reason, removal of these impurities is pertinent.

During the removal of butadiene, by acid treatment, some of the acid remains which is not removed. This is residual acidity, i.e. the acidity which was not expected from the process of manufacturing of Vinyl Chloride Monomer (VCM). This acidity or the extra amount of acid needs removal, as it might react with Vinyl Chloride Monomer (VCM) at polymerization conditions, resulting in lower polymerization rates and production of polychlorinated compounds.

Our project deals with this acidity and proposes an alternate route which excludes the steps which add residual acidity to the final product. The proposed process treats butadiene with hydrogen which removes 99.5% of the butadiene present.[2]

1.1 Problem statement

Removal of residual acidity from vinyl chloride monomer without increasing the moisture content.

1.2 Proposed Solution

In the production of vinyl chloride monomer, certain by products are formed. One of the byproducts is 1,3 – Butadiene (C_4H_6). Butadiene (C_4H_6) is a polymerization reaction inhibitor, therefore its removal from the final product is necessary[2]. Currently, to remove butadiene an acid wash followed by caustic treatment is used in the industry. This mixture is then settled to remove the neutralization byproducts. Even then, acid in excess of the requirement is present, accompanied with acid is the production of water, which is also undesired, therefore further treatment is required. Hence an alternative process is proposed which removes butadiene in a single step where it is treated with Hydrogen (H_2) in the presence of Nickel (Ni) catalyst at 1 bar and 160 ^{0}C[2].

The purpose of this project is to design a safe, environment friendly, economically profitable Vinyl Chloride Monomer (VCM) plant. Requirements of environment friendliness are that the design must go beyond the compliance regulations while looking at the plant benefits and profitability. Plant safety incorporated tending to deviation from typical activities that can affect the workers of the plant and the encompassing networks or surroundings.

The project is divided into these major portions:

- Material Balance
- Energy balance
- Equipment design
- Simulation
- Controls and Instrumentations
- Cost Analysis
- HAZOP Analysis
- Conclusion

The proposed solution to this problem fulfilled these objectives:

1. Optimum production of Vinyl chloride monomer with plant capacity of 1200Mt/day.
2. Purification of Vinyl Chloride monomer which includes these three steps:

- Removing Hydrochloric Acid (HCl) via first distillation column
- Removing Ethylene Dichloride (EDC) through a second distillation column
- Treating butadiene (C_4H_6) with Hydrogen (H_2).

Chlorination of hydrocarbons is the basic idea in the production of Vinyl Chloride Monomer (VCM). Chlorinated hydrocarbons are more resilient to biodegradation rather than the normal hydrocarbons. The reason behind is the inherent strength of C-Cl bond present in chlorinated hydrocarbon. Vinyl Chloride Monomer (VCM) is the major chemical in the production of polyvinylchloride (PVC). Vinyl Chloride Monomer (VCM) production is done in a way that it reduces or eliminates the release of chlorinated hydrocarbons in the environment.

Before delving deeper into the process, some of the properties of Vinyl Chloride Monomer (VCM) are studied.

1.3 Vinyl Chloride Monomer (VCM)

Vinyl Chloride Monomer is an organochloride having the formula C_2H_3Cl. It is colorless chemical with pleasant odor. Having molecular mass of 62.5 gmol^{-1}. Gas at standard temperature and pressure. VCM is in the list of the top twenty largest petrochemicals of the world[3].

1.3.1 Production

Its production was started in 1835 but the regular production was promoted in the twentieth century. That method of production of Vinyl Chloride Monomer (VCM) was treating 1,2 dichloroethane or Ethylene Dichloride (EDC) with potassium hydroxide (KOH) solution in ethanol (C_2H_5OH)[4]. In 1917, a German chemist named Fritz Klatte, patented a method to produce Vinyl Chloride Monomer (VCM) using acetylene (C_2H_2) and hydrogen chloride (HCl) in the presence of mercuric chloride ($HgCl_2$) catalyst. This method of production Vinyl Chloride Monomer (VCM) was highly in use in 1930s and 1940s, later a new method was discovered in United States of America (USA) to produce Vinyl Chloride Monomer (VCM) from ethylene (C_2H_4)[4]. After that, this method was adopted in China, as China is one of the largest manufacturers of Vinyl Chloride Monomer (VCM). In 2000, the approximate production of Vinyl Chloride Monomer (VCM) in the world was almost 31.1 million tons. In 2005, it was around 35 million tons. As for now Around 13 billion kgs of Vinyl Chloride Monomer (VCM) are produced per year[5]. Vinyl Chloride Monomer (VCM) is not only produced in industries but small amount of it, can be produced in environment by the breakdown of chlorinated solvents by the soil organisms.

TABLE 1: VINYL CHLORIDE MONOMER (VCM) PROPERTY TABLE [6]

	PROPERTY	**DESCRIPTION**
1.	Description	Colorless
2.	Normal Boiling point	−13 °C
3.	Normal Melting point	−154 °C
4.	Flash point	−78 °C
5.	Relative density	0.9106
6.	Relative vapor density	2.2
7.	Refractive Index	1.37
8.	Auto ignition temperature	472 °C
9.	Volatility	2530 mmHg at 20 °C
10.	Explosion limit in air	3.3 to 30 %
11.	Stability	Soluble in ethanol, ether, benzene and CCl_4. slightly soluble in water
12.	Solubility	Decompose on burning and form peroxides and is explosive.

1.3.2 Uses of Vinyl Chloride Monomer (VCM)

Vinyl Chloride Monomer (VCM) is not a final product, it's an intermediate which is further polymerized to many useful chemicals. Due to its instability and hazardous effects on human health it cannot be used as monomer in any product rather it is polymerized to Polyvinylchloride (PVC) for further applications. In past, Vinyl Chloride Monomer (VCM) was used as refrigerants as in aerosol spray propellants. Some of its applications were as inhalation aesthetics and in Ethyl Chloride (C_2H_5Cl). But due to the high toxicity and instability of Vinyl Chloride Monomer (VCM), these uses were stopped[4]. One of the applications of Vinyl Chloride Monomer (VCM) is in furniture, in wall coverings, in warehouses and in automobile parts. One of the main uses of Vinyl Chloride Monomer (VCM) is the production of polyvinylidene chloride (PVDC) by its reaction with the Chlorine (Cl_2).

1.3.3 Polyvinylchloride (PVC)

Manufactured from Vinyl Chloride Monomer (VCM) when it is sent to the reactor, polymerization occur and liquid Vinyl Chloride Monomer (VCM) is converted to its polymer. Almost 90% of Vinyl Chloride Monomer (VCM) is utilized in the production of Polyvinylchloride (PVC). Polyvinylchloride (PVC) is highly stable, can be stored and transported easily[7]. When Polyvinylchloride (PVC) is formed it is in the pallet form, which is further sold to different industries such as pipe, toys bottle and plastic industries. It is durable and brittle solid also available in the form of granules or powder depending upon its uses and requirement. This is one of the widely used polymer. Materials manufactured from Polyvinylchloride (PVC) are light, need low maintenance and are long lasting. Its products are high weather resistant and resistant towards petroleum products and Ultraviolet radiations. It is flame resistant chemical that's why highly applicable in fire preventions[8].

Due to the greater flexibility it can be very easily used in conversion and fabrication processes such as pippins and fittings, wires and cables windows, doors, toys, sheets, bottles, printers, glasses manufacturing. Commercial, residential, non-residential, pharmaceutical markets are the most important users of Polyvinylchloride (PVC). Product manufactured from Polyvinylchloride (PVC) are also used in agricultural sectors, and health care departments. Some other molecules containing vinyl chains are used in pharmaceutical and thermoplastics industries. Vinyl Chloride Monomer (VCM) and Polyvinylchloride (PVC) technologies are improving day by day in aspects of safety, quality and environment. Applications of Polyvinylchloride (PVC) are as follows:

- In building materials in the construction of roof materials, windows, pipes, wires, fences, coverings of floor and windows, gutters, frames and insulations.
- In industrial process in the construction of landfill, piping, food processing and chemical processing industries[9].
- In medical devices such as in kidney dialysis, blood transfusions, cardiac catheters, tubes for machinery, valves for heart transplant and in blood and intravenous bags.

- In automobile industries in manufacturing various components such as interior upholstery, body molding, wirings, coating under the cars, dashboards and mats.
- In electronic in the manufacturing of air conditioners, floppy disks, housing, keyboards, body of desktops, refrigerators, fiber optics and refrigerators.
- In toys plant in manufacturing flexible, rubbery, rigid and other parts[7].
- In packaging industries in flexible wraps, jar lids, canes, lining in tins or containers, personal care equipment and lubricants[10].

Due to its applications, properties, low cost, availability and durability most of the materials such as metal, wood, rubber, ceramics are getting replaced by Polyvinylchloride (PVC).

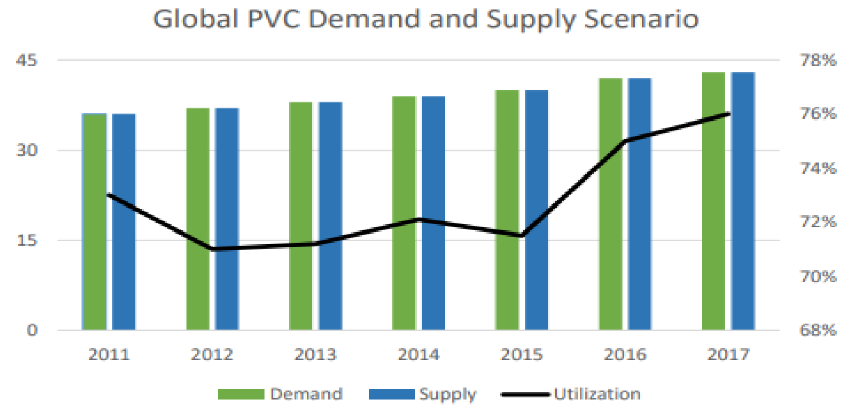


FIGURE 1: GLOBAL DEMAND, SUPPLY AND CONSUMPTION OF POLYVINYLCHLORIDE (PVC) [5]

1.3.4 Consumption of Vinyl Chloride Monomer (VCM)

China is the major contributor of the Vinyl Chloride Monomer (VCM) market as in 2018 it had around 41% of total world capacity as production and consumption. In 2020 china's demand for PVC is almost 50% of the world demand. Other than china, in 2018 North Asian countries consumed around half of the world VCM. They were the largest consumers of VCM. At the second number USA particularly, North America was the main VCM consumer. The development toward lower petroleum gas and feedstock costs for the vinyl chain in the United States and

Canada, by means of shale gas, is setting the North American situation as one of the world's most minimal expense VCM makers. Over 99% of complete worldwide VCM utilization in 2018 was used for PVC manufacturing, VCM, along these lines, follows the PVC advertise pattern intently. These different uses are for the most part in the United States, Western Europe, and Japan[5].

Import and Export of VCM is major issue as VCM is in gaseous state must be stored and transported in liquid state under pressure which increases its cost for transportation. Around 7% of the worldly produced VCM was exported in 2018. The biggest exporters are North America and Northeast Asia, which together represented over 80% of the world's VCM sends out in 2018. The Middle East is additionally a significant wellspring of the world's VCM send out gracefully, with the benefit of minimal effort and less cost manufacturing located close to significant markets. The countries like China, India, and Southeast Asia are significant in the trade of VCM. Throughout the following five-year time frame, VCM exchange is relied upon to decrease as more Vinyl Chloride makers become coordinated[11].

In general, China will be one of the more quickly developing countries for the demand of VCM, with an anticipated normal development of about 4.5% every year throughout the following five years. Utilization will increase at the quickest rates in the Indian Subcontinent and Africa during 2018–23, with expected normal development of about 13% and 10% every year, separately.

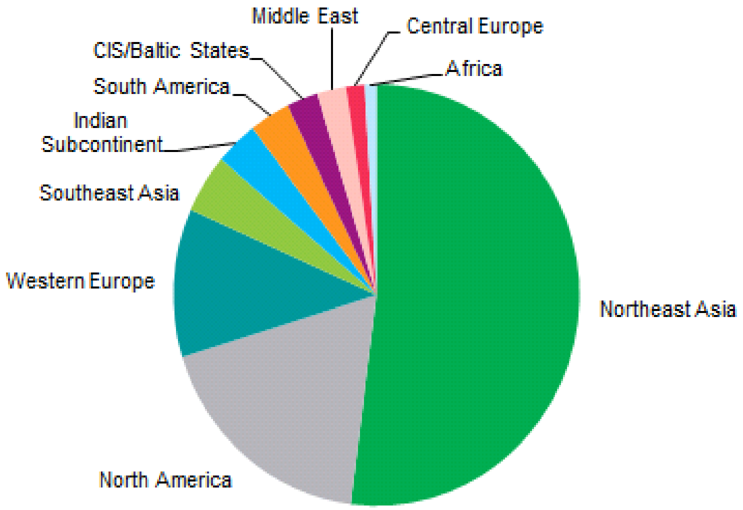


FIGURE 2: GLOBAL CONSUMPTION OF VCM IN 2018[12]

1.3.5 Storage and Transportation of Vinyl Chloride Monomer (VCM)

At ambient conditions VCM is in gas state but it is stored as liquid. The directly acknowledged maximum constraint of safety as a wellbeing peril is 500 ppm. VCM is stored in high capacity spherical containers. They are double layered container with an inside sphere layered by outside sphere with few inches empty space between them. The empty space between two layers are filled with inert gas like nitrogen or argon. As the purge stream of nitrogen gas leave the empty spaces it is allowed to pass through an analyzer which detects the leakage of Vinyl Chloride Monomer if occurring from internal sphere of the container. In case of fire detected or if explosion occur or any leak get detected from the internal sphere the material of sphere is dumped into the ground in another storage.

Tankers used for storing vinyl chloride must be under pressure but at atmospheric temperature. If the vinyl chloride is inhibited it can be stored at normal atmospheric conditions in any suitable pressure vessel[13]. But if vinyl chloride is uninhibited it must be stored in the absence of air and sunlight at any condition maybe refrigeration or atmospheric temperature only for timespan of few days. Incase if vinyl chloride is stored for longer period or months, it must be properly checked and kept under observation.

Transportation is also as difficult as the storage of the vinyl chloride. Like other gases such as propane, butane, LPG, VCM is also flammable for which the same regulations are applicable like other fuel gases[14]. To prevent from corrosion equipment for the transport of VCM is designed properly to provide safety to the environment and to workers.

1.4 Health and Environmental Hazards of Vinyl Chloride Monomer (VCM)

Every chemical need proper handling and some hazards are associated with a specific chemical. In the same manner, Vinyl Chloride Monomer (VCM) has some associated health and environmental hazards which are discussed in this section.

1.4.1 Explosion Hazards of Vinyl Chloride Monomer (VCM)

VCM is in gaseous state at atmospheric pressure and temperature. According to OSHA standards in USA, Vinyl Chloride Monomer is included in 1A (top) flammable liquids. The flammable rating of VCM is 4 according to NFPA (National Fire Protection Association). As it has very low boiling point, it can evaporate or autorefrigerated easily in open environment at ambient conditions. The evaporated part of VCM will form thick clouds which are as thick as twice the air in the atmosphere that's why the danger of explosion or fire is significant. The flash point of VCM is -78 °C according to standards of OSHA[8]. The flammability limits of VCM in air are: 3.6% volume in is lower limit and 33% volume is upper limit. In explosive limits, 4% by volume is the lower limit and 22% by volume in air is the higher limit. On burning and getting fire it releases dangerous chemicals such as Hydrogen Chloride, Carbon Monoxide and hydrogen. Under the presence of air, heat, sunlight, catalysts, oxidizing agents and aluminum or sodium metal, VCM can polymerize rapidly. As soon as VCM is mixed with air, it is hazardous and flammable. On standing it forms peroxides which further can explode. In the presence of moisture, it can react with metals like iron and steel.

1.4.2 Health Hazards of Vinyl Chloride Monomer (VCM)

The major application of VCM is the production of poly vinyl chloride (PVC). VCM has high volatility so that the major health is the through inhalation with food, air or water. In 1974, the workers of industry who were exposed to 1000ppm VCM, got vinyl chloride illness. The effects of VCM hazards are classified by its quantity of vinyl chloride in ppm in air such as if it is ranging from 1000 to 10,000 ppm, it is of acute intensity and the symbols appear will be of nausea, dizziness, headache, fatigue, visual disturbance. If the range of VCM is above 12,000 ppm or above then the chronic symptoms will appear such as narcotic effects, cardiac arrest or cardiac arrhythmias and severe respiratory disorders[15]. Another syndrome caused by exposure to VCM is RADS (Reactive airways Dysfunction Syndrome).

VCM is a chemical which causes genetic mutation having clastogenic effect which cause chromosomes breakage of human body. VCM is highly hazardous and can cause angiosarcoma, tumors in brain and lungs, lymphatic tumors and tumors that effect the bone marrow and damage immune system cells. Minute exposure to VCM can cause respiratory issues but sever exposure or permanent exposure causes depression and some neurotic disorders. Vinyl chloride monomer also cause some of the reproductive disorders such as birth defects, lower male libido and abortions.

Vinyl Chloride can affect our skin and cause edema, eczema, skin thickening, dryness, itching and irritation, blistering and frostbite and loss of skin elasticity. OSHA has put limit for workers on vinyl chloride exposure to be no more than 1ppm in eight hours or exposure to 5ppm Vinyl Chloride for fifteen minutes. And in drinking water if the limit of VCM will be higher than 0.002 ppm, it will be hazardous.

1.4.2.1 Effect on liver

The danger of vinyl chloride monomer to liver was seen in 1940, when the production of VCM was established in early stages. It was observed that exposure to vinyl chloride cause liver injuries even a short-term exposure can damage the liver. Later it was discovered that about 300 ppm of VCM can damage the liver and it was confirmed by experiment on animals[4]. In a research it was found that expose to 250ppm of VCM for four a day causes liver tumor. That' why proper precautions must be taken in VCM plants.

1.4.2.2 Cancerous Tumors

In 1970s it was reported that if a worker is exposed to 30,000ppm of VCM, there are many chances of developing cancer tumors in his body. After that VCM was also declared as the causes of some bone and liver injuries.

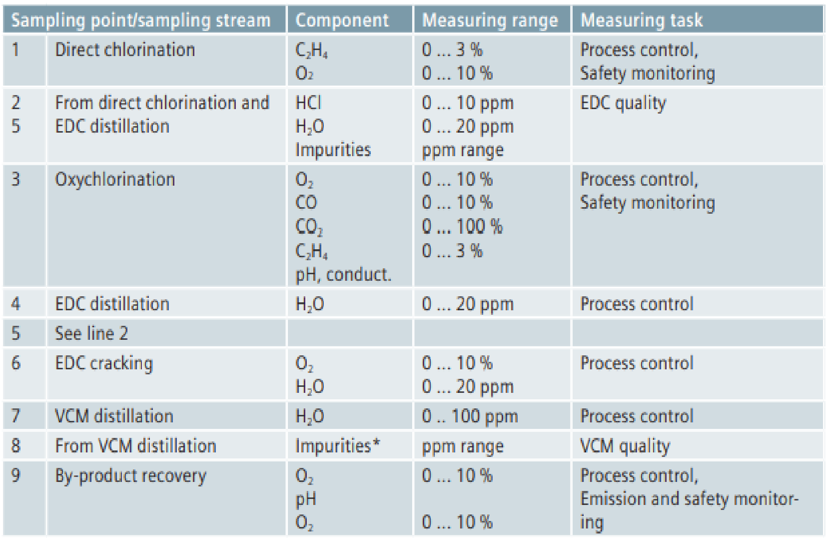
Later in 1997, Centre of Disease Control and Prevention (CDCP) in USA ordered that acceptance of VCM or PVC industry would only possible with the no exposure of the workers to the chemical.

1.4.3 Environmental Hazards

U.S. EPA (United State Environment Protection Agency) declared that vinyl chloride monomer, poly vinyl chloride, ethylene di chloride plants emit vinyl chloride which adds to the environmental pollution which further lead to many problems and illnesses such as liver disease, respiratory disease and rare type of cancers and tumors. EPA estimate liver is the most sensitive to get cancer and protection against its cancer would protect against other tumors and cancers of body[16].

1.4.4 Emission Monitoring of Vinyl Chloride Monomer (VCM)

As we have discussed in detail the hazards of VCM on health of the workers, and on environment. In most of the countries which produce VCM and utilize it in further applications, there are proper regulations and specifications on the amount of VCM which can be released into the atmosphere. There is optimized process of the byproducts oxidation and the recycle process of some chemicals so only low volume flow rates are emitted through the stack. Samples are taken on the daily basis or sometimes monthly basis to measure in laboratory. Sampling rages are given in the figure.



Sampling point/sampling stream		Component	Measuring range	Measuring task
1	Direct chlorination	C_2H_4 O_2	0 ... 3 % 0 ... 10 %	Process control, Safety monitoring
2 5	From direct chlorination and EDC distillation	HCl H_2O Impurities	0 ... 10 ppm 0 ... 20 ppm ppm range	EDC quality
3	Oxychlorination	O_2 CO CO_2 C_2H_4 pH, conduct.	0 ... 10 % 0 ... 10 % 0 ... 100 % 0 ... 3 %	Process control, Safety monitoring
4	EDC distillation	H_2O	0 ... 20 ppm	Process control
5	See line 2			
6	EDC cracking	O_2 H_2O	0 ... 10 % 0 ... 20 ppm	Process control
7	VCM distillation	H_2O	0 .. 100 ppm	Process control
8	From VCM distillation	Impurities*	ppm range	VCM quality
9	By-product recovery	O_2 pH O_2	0 ... 10 % 0 ... 10 %	Process control, Emission and safety monitoring

FIGURE 3: FIGURE INDICATIN MEASURING RANGES[15]

1.5 Raw Materials

Process chosen to produce vinyl chloride monomer is the production of ethylene di chloride by the reaction of ethylene and chlorine in reactors and then conversion of ethylene di chloride (EDC) to vinyl chloride monomer (VCM) by pyrolysis. Further VCM is purified and other solvents and acid is removed.

1.5.1 Ethylene (C_2H_4)

Ethylene is the simplest hydrocarbon which is flammable and exist in gaseous form. It is carbon-carbon double bonded compound colorless compound. If look at its physical properties, its critical temperature is 9 °C and critical pressure is 900lbs. The explosivity limits of ethylene are narrow in range such as 4 to 15 parts ethylene in 100 parts of air. It is highly compressible in nature. It has very low boiling point that's why gaseous in state at ambient conditions.

There are many methods of the production of ethylene such as naphtha cracking, ethane propane cracking, oxidative dehydrogenation of ethane and catalytic dehydration of ethanol. In Pakistan most of the ethylene is manufactured from ethanol as it is sufficient in Pakistan and this process is environment friendly[17].

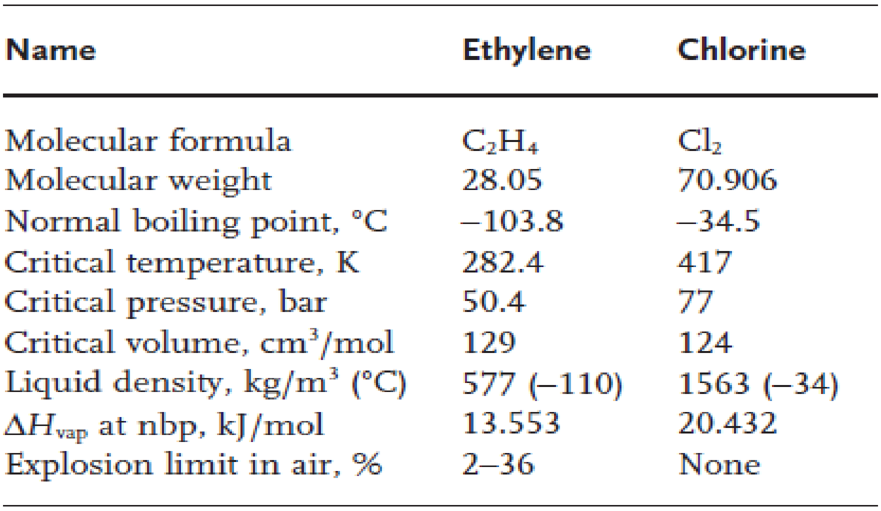
It is widely used in industries in most of the reactions such as alkylation, polymerization, oxidation, hydration, halogenation, hydrohalogenation and many more. It is the main component in the production of VCM. When it reacts with chlorine it forms ethylene dichloride. It is also naturally present in plants and help in ripening of fruits. It is very different from other hydrocarbons. It is often known as olefin gas and in past as marsh gas. It is used as refrigerants, as an anesthetic and in manufacturing other chemicals. Ethylene is used in manufacturing various polymers in which VCM is one of them which is further polymerized to PVC.

1.5.2 Chlorine (Cl_2)

Chlorine is gas at room temperature and pressure. Its boiling point is -100.98 °C. Apparently it has light green color. It is very reactive in nature; it can react with all elements except the noble gases. The reaction of other elements with chlorine is very fast. It is a strong oxidizing agent and it doesn't burn like oxygen but helps other to oxidize and burn.

It has wide applications in industries. It is used as solvent, as bleaching agent and as water disinfectants. As it kills bacteria very fast, so it is used in cleaning pools, and chlorinated water is often used in pools. This gas has been used as weapon in wars. Used in the production of large no of drugs in pharmaceutical industry. In polymer industry when it reacts with ethylene, it forms EDC which further gives

VCM. It is used in the production of various plastics. It is also hazardous for skin, eyes and respiratory track.



Name	Ethylene	Chlorine
Molecular formula	C_2H_4	Cl_2
Molecular weight	28.05	70.906
Normal boiling point, °C	−103.8	−34.5
Critical temperature, K	282.4	417
Critical pressure, bar	50.4	77
Critical volume, cm^3/mol	129	124
Liquid density, kg/m^3 (°C)	577 (−110)	1563 (−34)
ΔH_{vap} at nbp, kJ/mol	13.553	20.432
Explosion limit in air, %	2–36	None

FIGURE 4:PHYSICAL PROPERTIES OF ETHYLENE AND CHLORINE [18]

1.5.3 Oxygen (O_2)

One of the raw materials is oxygen. Oxygen is colorless and odorless gas. Air can be used in place of oxygen, but oxygen is preferred due to environmental and efficiency considerations. Oxygen is reactive and combines with both metals and non-metals and forms acidic or basic solid compounds. Most of the solid compounds are not useful source of oxygen, because separation from tight combination is very difficult and expensive. Oxygen existing naturally is consists of three isotopes which includes oxygen 16 in 99.78%, oxygen 17 in 0.037 %, oxygen 18 in 0.204 %. There are various methods of the production of oxygen on lab scale which includes:

- Thermal decomposition of salts which contain oxygen
- Thermal decomposition of metal oxides
- Thermal decomposition of peroxides
- Water electrolysis

There are wide range of uses of oxygen such as ordinary air is also getting replaced by pure oxygen in industries. It is used in the manufacturing of different compounds of oxides and in kilns. Other than that, it is widely applicable in the field of medicine in inhalation process, in incubators and in ventilators. One of the wide applications is in steel industries and in welding metal cutting, gas cutting, and flame hardening. It is used as raw material of many processes which involve oxidation. Large amount of oxygen is used in coal gasification process in developed countries. It is used to enrich the air feed or cracking regenerators in refineries. More importantly it can be used as source of fuel in many industries including fertilizer industries.

1.5.4 Hydrochloric Acid (HCl)

HCl is a colorless with pungent odor chemical. Its pH is 3.01. It forms fumes in the air. Is very strong acid. It also exists naturally in the stomach of human and animals. It is widely used chemical of industry such as used in the formation of the VCM which further converts to PVC and PVC has tremendous applications. Other than PVC it is used in the production of many chemicals like salts for example calcium chloride, zinc chloride, nickel chloride which are further used in electroplating and in production of batteries. Some organic compounds are also produced from HCl such as poly carbonate, ascorbic acid, activated carbon and various pharmaceutical products. It is also used as cleaning agent in house[19]. It has applications in lather industries. It is used in refining and cleaning metals by pickling. Some other uses are in the manufacturing of glues, glucose and bleaching powder.

It is very corrosive and effect human skin, organs, eyes, tissues and intestines badly. That's why its handling and use must be very careful with proper rubber gloves, overall coats, face shield and goggles. Its transportation and handling are also very important. It transported in bottles (tightly closed) which are coated with PVC. For storage of HCl wood cabinets are preferred. It should be stored in cool and dry places.

1.6 Market Analysis of Vinyl Chloride Monomer (VCM)

Almost around 95% of vinyl chloride is further used in the production of PVC polymer. PVS is highly applicable in industries in numbers of applications such as in many fabrication processes of polymers like extrusion, injection molding, blow molding and coatings[5].

Extrusion molding and injection moldings of polymer are done to mold polymers into different shapes to make pipes, windows, doors, wires and cables, sheets and films. Other than these applications VCM is used in the production of solvents like polyvinylidene chloride and chlorinated solvents, but the involvement in these applications in minute as compare to the production of PVC.

Most of the EDC is consumed in the production of VCM, but the remaining EDC is used in the production of chemicals like chlorinated solvents, adhesives and lead alkyls. But most of the EDC is consumed at VCM plant. In short, the EDC and VCM are very mature industrial segments.

CHAPTER 2

PROCESS SELECTION

There are three different methods that can be used for the production of the vinyl chloride monomer industrially and all of these methods utilize the C_2 hydrocarbon feeds. We will have a look at these methods, their advantages and the drawbacks.

2.1 Vinyl Chloride Monomer (VCM) from Acetylene

This process is considered as the first effective industrial process for the vinyl chloride production. It has been used in the industries extensively since 1940s. This process involves the hydrochlorination of acetylene. The acetylene for the production of VCM is obtained using calcium carbide, but serious draw back associated with the process is high energy requirements, hindering the way for mass production using this method. For the conversion of the acetylene into the vinyl chloride a catalyst is needed to be employed, and most commonly used catalyst is the mercuric chloride deposited on active carbon. To increase the catalytic activity and achieve high conversion of acetylene to VCM, Ruthenium based catalyst supported with N doped carbon is also used. Only use of 1% of Ru/N-AC based catalyst provide high conversion in pass up to 93%. It was suggested that N doped Carbon and Ru/AC catalyst gives a synthetic effect in the production of VCM in one step[20].

In the production of VCM the feed gasses (acetylene & hydrochloric gas) are first purified, dried and then mixed. Then they are entered the tubular fixed bed reactor packed with mercuric chloride on the active carbon pallets serving as catalyst. Reaction take place is as:

$$C_2H_2 + HCl \rightarrow C_2H_3Cl$$

HCl is usually used in the slight excess where acetylene is the limiting reactant in this case. In this process 99% conversion of acetylene and 98% conversion of HCl is obtained, with the selectivity as high as 98%. The only byproduct that is produced in this process is 1,1 –dichloroethane, due further addition of the HCl to the vinyl chloride.

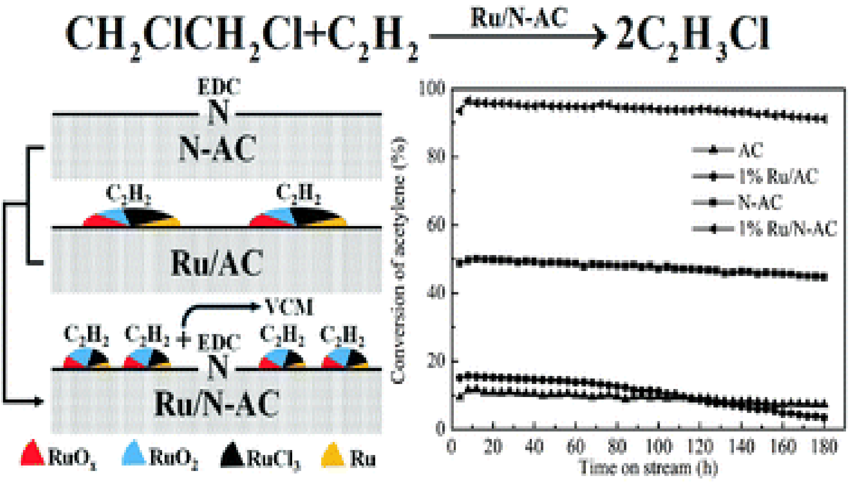


FIGURE 5: ACETYLENE CONVERSION TO VCM USING RU/N-AC CATALYST [20]

2.1.1 Advantages

- Very simple single stage process
- Higher selectivity of desired product
- Higher conversion

2.1.2 Disadvantages

- Mercuric Chloride (catalyst of this process) is of very high volatility
- Production of the acetylene is very costly process
- Storage and transportation of acetylene is hazardous

2.2 Vinyl Chloride Monomer (VCM) from Ethane (C_2H_6)

Ethane is a compound that is relatively much cheaper as compared to ethylene and acetylene. So due to this aspect many attempts have been made to come up with a process that can produce vinyl chloride directly from the ethane. The major problem with the ethane is the symmetry of its molecule, due to which wide range of the byproducts are obtained along with vinyl chloride. One of the routes for the VCM production that seems most promising is oxychlorination at high temperature in the presence of a catalyst. This increases the selectivity of vinyl chloride and produces the by-products that are useful, i.e. ethylene, ethyl chloride and EDC. The EDC produces and be chlorinated and recycled with ethyl chloride[4].

In the past ethane is used in the VCM production in a way that it first converted into ethylene than further ethylene is used by reacting with chlorine. But in order to save money and reducing the cost of conversion of ethane to ethylene, industries were attempting to convert ethane directly in the VCM by the following reactions.

Hight temperature chlorination:

$$C_2H_6 + 2Cl_2 \rightarrow C_2H_3Cl + 3HCl$$

Hight temperature oxychlorination:

$$C_2H_6 + HCl + O_2 \rightarrow C_2H_3Cl + 2H_2O$$

High-temperature oxidative chlorination:

$$2C_2H_6 + 1.5O_2 + Cl_2 \rightarrow 2C_2H_3Cl + 3H_2O$$

In this way the extra manufacturing cost can be saved. Although this method shows promise but is limited to the conceptual stage till now. The reason being, that there are some serious challenges being faced in the design of the oxychlorination reactor. As the temperature of reaction goes as high as 500^0C in the process, chlorine becomes very aggressive at this temperature, making it difficult for any construction material to survive. Kinetics must be controlled, and special catalyst must be used to achieve high yield otherwise only 20 to 45% yield would achieve.

2.2.1 Advantages

- Cheaper Process
- Useful Byproducts

2.2.2 Disadvantages

- Process is still conceptual
- Selectivity of the process towards VCM is low
- Causes environmental pollution

2.3 Vinyl Chloride Monomer (VCM) from Ethylene (C_2H_4)

It was around the 1950s when the ethylene became more readily available, world shifted from acetylene to the ethylene for the vinyl chloride production. The process for the production of the vinyl chloride from the ethylene through the route of EDC is named as **Balanced Ethylene Route**. With the passing time many improvements have been made in the process to reach the one that is being used in the industries today. Ethylene can be converted into the vinyl chloride with EDC as intermediate product by using either oxychlorination or direct chlorination. Reactions of the whole process are as follow.

Direct Chlorination $C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$

Oxychlorination $C_2H_4 + 0.5O_2 + HCl \rightarrow C_2H_4Cl_2 + H_2O$

Pyrolysis $C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$

Overall reaction $2C_2H_4 + Cl_2 + 0.5O_2 \rightarrow 2C_2H_3Cl + H_2O$

For the direct chlorination route, the high temperature and excess of ethylene is required to minimize the soot formation. In the case of oxychlorination route the selectivity and the conversion are good if we use the temperature above 350^0C.

2.3.1 Advantages

- High selectivity can be achieved
- Lower in cost as compared to method using acetylene
- No harmful by-products
- Good conversion rates can be achieved with appropriate catalysts
- Economic process

2.3.2 Disadvantages

- Lengthy process

2.4 Selecting the Best Route

We have to select the best possible route to get to our desired product from the all possible routes. We have to consider some factor on the basis of which we decide, which route suits us the best. Factors to be considered are:

- Choose the route with lower byproducts (better selectivity)
- Choose the process with lesser power requirements (economical)
- Choose the process with lower process time and high conversion rate
- Choose the route with less environmental effect (in the allowed limits)

All of these qualities do not exist in one route mostly, so we have to optimize our process to get best possible efficiency in terms of productivity and economics.

From all of the above-mentioned process, it can be easily deducted that the Balanced Ethylene Route is the best suitable for the application in the industry.

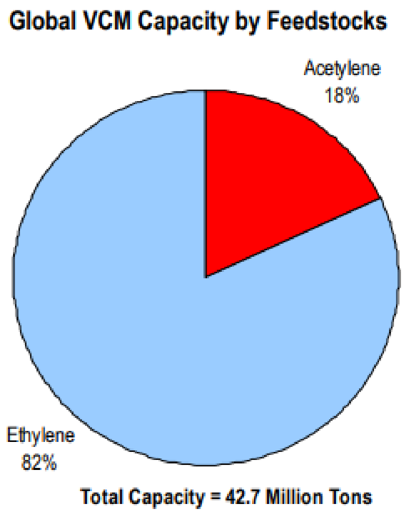


FIGURE 6: PRODUCTION FROM ETHYLENE AND ACETYLENE[21]

As the process of obtaining the vinyl chloride from the ethane is not practically possible and lots of research is going on it to make it possible, on the other hand the production of vinyl chloride from the acetylene is much more expensive than its production from ethylene using the balanced ethylene route. Balanced ethylene routs consist of two reactors, one is direct chlorinator and the other is oxy chlorinator in which recycled HCL is used in this it is also incorporating the acidity content of the process. In this way giving major advantage by utilizing the HCl the main by product during VCM production. About 95% of the world VCM is produced using ethylene.

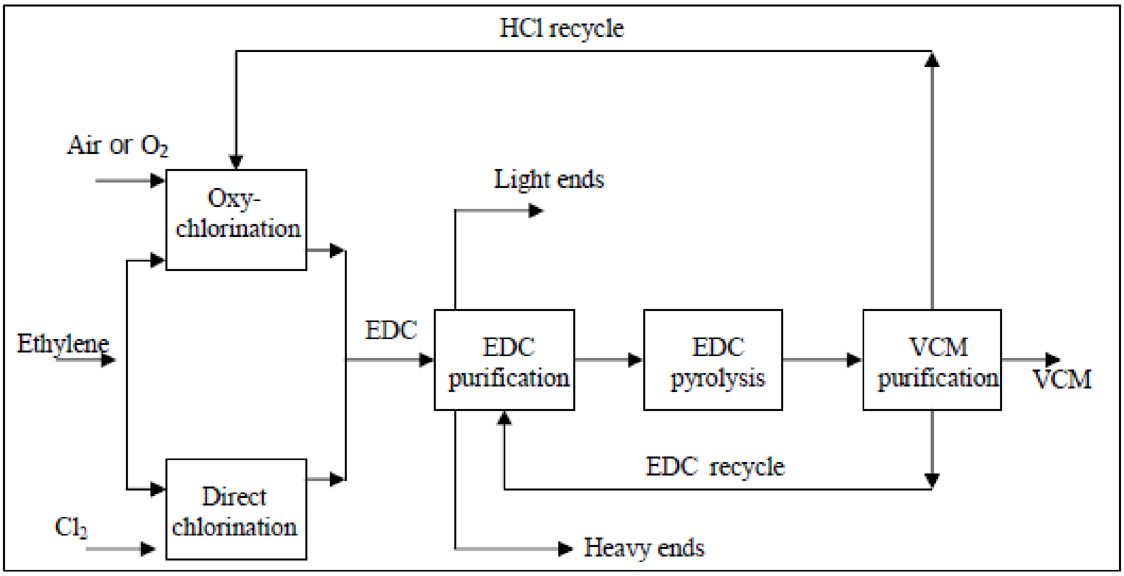


FIGURE 7: BALANCED ETHYLENE ROUTE

If we use this process, we can achieve good selectivity of the desired product at good conversion rates by using appropriate catalysts. And the process does not involve the production of any harmful byproduct.

CHAPTER 3

PROCESS DESCRIPTION

There are two reactors that are being used in this process, in one of them direct chlorination is taking place and oxychlorination reaction is happening. Ethylene is being entered in both the reactors in proportion of 1:1. In the direct chlorination reactor ethylene reacts with chlorine to produce EDC and in oxychlorination reactor ethylene reacts with oxygen in the presence of HCl gas to produce EDC. That HCL is recycled from VCM purification unit. This EDC is further sent to the purification unit to remove unreacted ethylene and the purified EDC is sent further to the furnace for the cracking process. In cracking the EDC breaks down into the vinyl chloride monomer with the production of the HCl as the by-product. The products from the furnace go into the purification unit where HCl is recycled back to the oxychlorination reactor, unreacted EDC is sent back to EDC purification unit and pure vinyl chloride monomer (VCM) is obtained as the product.

Reactions of the whole process are as follows.

Direct Chlorination	$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$
Oxychlorination	$C_2H_4 + 0.5O_2 + HCl \rightarrow C_2H_4Cl_2 + H_2O$
Pyrolysis	$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$
Overall reaction	$2C_2H_4 + Cl_2 + 0.5O_2 \rightarrow 2C_2H_3Cl + H_2O$

The process consists of five sections:

1. Direct Chlorination
2. Oxychlorination
3. EDC Purification
4. EDC Cracking
5. VCM Purification

The process starts with the first two sections which are operating in parallel. Both have the same product, EDC. EDC is produced in both of the sections. In Direct chlorination, ethene reacts with chlorine in the presence of Ferric Chloride modified by Sodium at 116 ^{0}C and 2 bar[22][23] to produce EDC. In oxychlorination ethene reacts with oxygen and Hydrochloric Acid in the presence of alumina supported Cupric Chloride at 300 ^{0}C and 5 bar[24] to produce EDC and water.

The exit stream from direct chlorination reactor is compressed and then mixed with the exit stream from oxychlorination reactor. This stream has significant amount of heat which is exchanged with other process streams and consequently cooling down this stream. This stream is eventually cooled down to 25^{0}C, after which it is sent to three-phase separator.

In three-phase separator, three phases are separated on the basis of difference in density. Vapor phase exits at the top, and two liquid phases drop. They are given enough settling time to divide into two phases, i.e. light liquid and heavy liquid. Light liquid is sent to distillation column where pure EDC is obtained as bottom. This pure EDC is sent to furnace where it is cracked to produce HCl and VCM.

This stream is cooled and sent to distillation column where HCl is obtained as top, and rest of the mixture as bottom, which is sent to another distillation column, where VCM and EDC are separated. EDC is obtained as bottom and is recycled to furnace and VCM with butadiene as top which is sent to a treatment unit where butadiene is treated with hydrogen in the presence of activated alumina supported Nickel at 160^{0}C and 1 bar. After removal of butadiene, final VCM product is obtained.

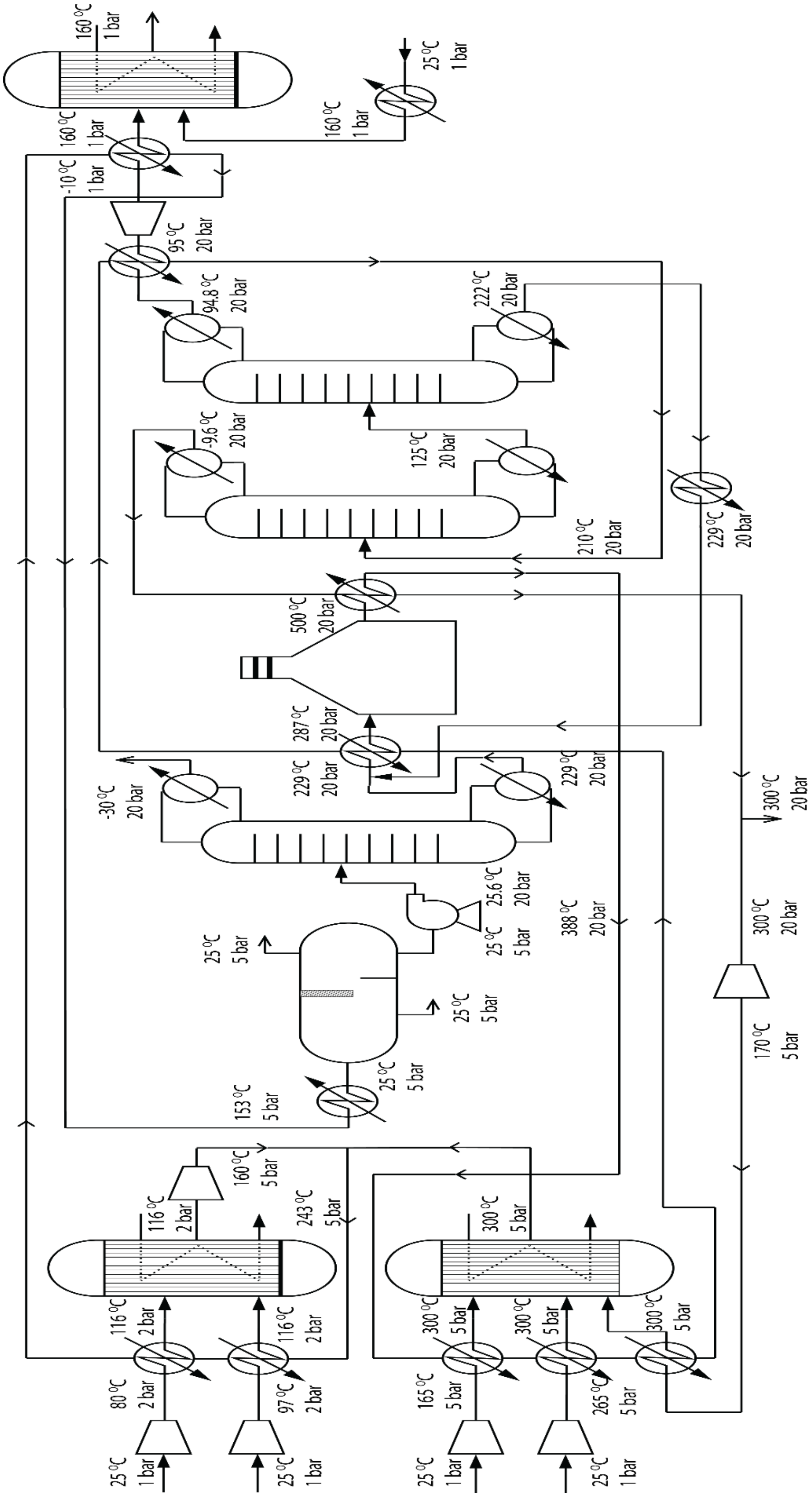


FIGURE 8: PROCESS FLOW DIAGRAM

3.1 Direct Chlorination

In the case of direct chlorination, reactants in the gaseous form react to form EDC in liquid form, the reactor can be fixed bed or fluidized bed but, in this project, we have used packed bed tubular type reactor. The reaction is given as:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Mostly used catalyst is $FeCl_3$, with the concentration of 0.1 to 0.5 wt%. The use of $FeCl_3$ is preferred due to its high selectivity. It uses the electrophilic addition mechanism to catalyze the reaction, it polarizes the chlorine molecule which acts as electrophilic reagent attacking the double bond of ethylene molecule to start the reaction[4]. The process takes place as:

$$FeCl_3 + Cl_2 \rightarrow FeCl_{4-}Cl^+$$

$$FeCl_{4-}Cl^+ + C_2H_4 \rightarrow FeCl_3 + C_2H_4Cl_2$$

There is possibility of the secondary reactions to take place resulting in by-products. Reactions for by-products include:

$$C_2H_4 + 2Cl_2 \rightarrow C_2H_3Cl_3 + HCl$$

$$C_2H_4Cl_2 + Cl_2 \rightarrow C_2H_3Cl_3 + HCl$$

Small amount of oxygen is often present in the chlorine that is produced by the process of electrolysis (or addition of pure oxygen to the chlorine is done in a ratio of 0.5%), this oxygen helps in increasing the selectivity of the process by inhibiting the secondary reactions. Slight excess of chlorine is often used to ensure complete conversion of the ethylene, and highly pure reactants help in avoiding additional by-products that might make the purification more difficult.

There are two techniques that can be used for these reactions:

1. Low-temperature chlorination (LTC)
2. High-temperature chlorination (HTC)

In the case of the LTC the reactor operating temperature is 50-70 ^{0}C, which is below the boiling point of the mixture. Advantage with this method is that it has high selectivity of 99% and due to lesser temperature lesser heat has to be rejected to the environment. But the major problem that comes with this process is that catalyst removal from the product is very difficult and is not environment friendly.

In the HTC the reaction takes places at the boiling point of the EDC. The condition of reaction is 1.5 - 5 bar of pressure and the temperature of 90 – 150 ^{0}C. The heat of the reaction is seven times higher than that need for the vaporization of the ethylene, this additional heat is very helpful in purification process. The drawback is the lower selectivity of the process, but this problem has been overcome by the use of modified catalysts. So, we use HTC with the catalyst $FeCl_3$ modified with Sodium (Na). This catalyst is used because it very high selectivity of around 99% to EDC and very high conversion of around 99.9%.

3.2 Oxychlorination

In the oxychlorination there three reactants ethylene, oxygen and hydrogen chloride gas that react to form EDC and water. The reaction is given as:

$$C_2H_4 + 0.5O_2 + HCl \rightarrow C_2H_4Cl_2 + H_2O$$

The reaction is highly exothermic and is usually carried out in fixed or fluidized bed reactors. The temperature used ranges from 225 to 325 ^{0}C and pressure is 1 – 15bars. Catalyst that is mostly used is the cupric chloride impregnated on alumina. Mostly the fluidized bed reactors are used as there is better heat transfer in them and lesser chances of heat spots. But we are using the Plug Flow Type Reactor as heat recovery is not possible in the case of fluidized bed reactors. The catalyst is in the form of tubes and the reactants flow through it, while water is circulated from the shell side in order to control the temperature. In this reactor both the air and oxygen can be used but oxygen is preferred because of environmental and efficiency aspects[25]. The reactions include:

$$C_2H_4 + 2CuCl_2 \rightarrow 2CuCl + C_2H_4Cl_2$$

$$2CuCl + 0.5O_2 \rightarrow Cu_2OCl_2$$

$$Cu_2OCl_2 + 2HCl \rightarrow \; 2CuCl_2 + H_2O$$

The by-products produced in the case of oxychlorination reactor are much more than that of the direct chlorination reactor. Some of the key impurities are 1,1,2 - trichloroethane (TCE), chloral (CCl 3 - CHO), trichloroethylene (TRI), 1,1 - and 1,2

- dichloroethylenes, ethyl chloride, chloro - methanes (methyl -chloride, methylen - chloride, chloroform), as well as polychlorinated high – boiling components. There is increase in by-product formation with the increase in temperature, this is due to the fact that the oxidation of the ethylene to carbon oxide increases with increased temperature and cracking of EDC is also increased.

In order to limit the nitrous oxide formation and also nitrogenous by-products we use oxygen instead of the air as the feed, though this makes the process expansive but decrease in the by-product formation is of big advantage. Another advantage with the use of oxygen based oxychlorination is that it reduces the amount of off gas produced, reducing the cost for the treatment of vent gasses substantially. In the oxychlorination process the off gas from the reactor is purged in a small amount in order to avoid the accumulation of impurities like carbon oxides, nitrogen, argon, and un-reacted hydrocarbons.

3.3 EDC Purification

The section is subdivided into two equipment:

1. Three-phase Separator
2. Distillation Column (Water Removal Column)

3.3.1 Three-phase Separator

After direct chlorination and oxychlorination, EDC has been produced. This EDC along with all the byproducts is then sent to the horizontal three-phase separator at 25 °C and 5 bar pressure and where the feed stream is separated into three phases. In three phase separators the feed is separated into vapor phase, heavy liquids and light liquids. Vapor phase by products and heavy liquids are separated out and light liquids or organic phase containing the main product EDC is send to the distillation column. It works on the difference of densities of the components, density difference allows it to separate in three parts, vapors, light and heavy liquids.

3.3.2 EDC Purification Column

After three phase separator, organic phase having EDC and some by products such as ethylene, oxygen, hydrochloric acid, TCE, chlorine, carbon tetra chloride, hydrogen, water and carbon dioxide fed to the distillation column which is operating at 5 bar and 147 ^{0}C. Distillation column consists of sieve trays. After separation EDC separate at the bottom and other byproduct at the top. After this the pure EDC is fed to the cracking furnace for pyrolysis.

3.4 EDC Cracking

In the furnace, at high temperature the EDC decomposes into VCM and HCl producing lots of heat. The condition required for this process of cracking are temperature between 480-550^{0}C and pressure around 3 to 30 bar[26]. The main reaction is as follows:

$$\mathrm{ClC}H_2\mathrm{C}H_2\mathrm{Cl} \xrightarrow{heat} CH_2 = CHCl + HCl$$

The furnace is designed as such that a long tubular coil is fitted inside the furnace. In the first section preheating takes place by convection, feed is brought to the temperature where reaction for cracking initiates and the reaction rate becomes significant. In the second stage, heating takes place by radiation process and the diameter of tubes is kept as such, that the gasses move with the superficial velocity of 10 – 20 m/s through it. Length of the tube is kept significant enough to give residence time of 5 – 30 seconds to the gasses.

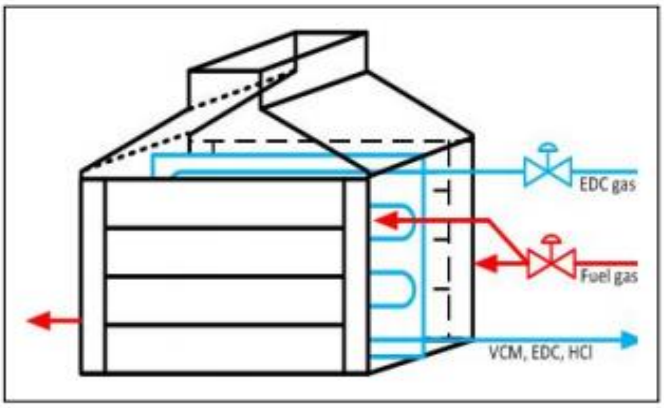


FIGURE 9: EDC CRACKING FURNACE

There is a vast range of side reactions that take place with the main reaction of EDC pyrolysis. Many of these reactions are due to the impurities carried to the furnace with EDC in the feed. Impurities like methyl chloride and butadiene are highly undesired as they are difficult to remove in VCM purification afterwards. And there are some other compounds like chloroprene or polymeric residues that cause fouling in reactor and hence are undesired. So, in order to cope up with that, advanced purification of the feed to the furnace is required. But on the other hand, process of cracking also produces some very good impurities that act as a source to produce radicals that speed up the rate of reaction at relatively lower temperature. Compounds like $CHCl_3$ and CCl_4 are the example of good impurities, and these are added to reactor in required amounts if not already present in the feed.

The formation of the carbon deposits, which is highly undesired in the process of pyrolysis is favored by the high temperature of the furnace. These carbon deposits emerge due to presence of heavy chlorinated compounds and other compounds like trichloroethylene (TRI). So, the prevention of coke formation in a furnace emerges as the major problem, as keeping the reaction temperature below 500 ^{0}C prevents the coke formation but on the other hand it slows down the reaction rate. For this reason, initiators like nitromethane and chloroform are used. During pyrolysis, butadiene and HCl are also formed which are further separated from VCM.

The main reaction of pyrolysis begins at the temperature of about 480 ^{0}C but much higher temperature is required in order to achieve good reaction rate. But this higher temperature gives rise to the secondary reactions that have higher activation energies producing undesired impurities. So, keeping these factors in view we must be careful in optimization of the temperature profile of a furnace.

3.5 VCM Purification

This section is further divided into three sections:

1. HCl Column
2. VCM Column
3. Butadiene Removal

3.5.1 HCl Column

Feed from furnace is cool at 210 ^{0}C and 20 bar and then fed to the distillation column. In this distillation HCl is removed. In the top product there is HCl which is recycled to the oxy chlorinator reactor to react with ethylene. The bottom product of the distillation column consists of EDC, VCM and butadiene. The bottom product is further sent to next distillation column.

3.5.2 VCM Column

In this sieve tray distillation column, the feed enters at 125 ^{0}C and 20 bars. After separation the bottom product is EDC which is recycled to the furnace for pyrolysis. The top feed consists of VCM and butadiene. Which is further sent to the reactor.

3.5.3 Butadiene Removal

As butadiene cannot be separate by simple distillation method. The small amount of this chemical seems unimportant but only about 5 to 10 ppm of butadiene is enough to inhibit the polymerization reaction. That's why its removal is very important. The stream coming from the distillation column is sent to the tubular packed bed reactor at 160 ^{0}C temperature and 1 bar pressure. In this reactor gaseous butadiene allowed to react with gaseous hydrogen in the presence of Ni catalyst supported with active alumina and converted into the n-butane which is not harmful. In this way acidity is removed from the VCM without increasing the moisture content. This is the feasible method to purify vinyl chloride monomer from butadiene and the catalyst is also easily available[2].

Reaction in this reactor is as follows:

$$C_4H_6 + 2H_2 \rightarrow C_4H_{10}$$

CHAPTER 4

MATERIAL BALANCE

Before starting material balance, capacity of the plant is fixed according to the demand of the country. The country's annual demand was 125000 tons of PVC per year in 2009, and EPCL plans to continue exporting 10000 tons of PVC per year. Collectively this adds up to a total of 135000 tons per year. 12% increase per year is expected[27].

4.1 Capacity Calculations

Assuming this percentage increase to be constant, calculating demand

Total demand in 2009: 135000 tons PVC per year

Percent increase per year: 12%

Plant attainment: 96%

Demand in of PVC in 2009 per day: $\frac{135000}{365*0.96} = 385.27$

Predicted demand in 2020: $385.27(1.12)^{10}$ = 1196.6 tons per day = 1200 tons per day approx.

As mass is conserved, this amount of VCM is needed per year. Converting this into kgmoles we get:

Molecular Mass of VCM: 62.5 g $mole^{-1}$

Mass of VCM: 1200000 kg per day

Moles: $\frac{1200000}{62.5}$ = 19200 kgmoles per day = 800 kgmoles per hour

With 60% conversion, 99.5 % Selectivity of the cracking reaction, we get the amount of EDC to be: $\frac{800}{0.96*0.6} = 1340$ kgmoles per hour.

Assuming 10 kgmoles is lost due to the various separation processes, then the net requirement is 1350 kgmoles, of this 1350 kgmoles, 40% is unconverted and is recycled, i.e. 539 kgmoles is recycled by distillation. Amount of HCl formed is

800 kgmoles per hour, this HCl is recycled to oxychlorination reactor. EDC produced from this HCl is calculated:

With 99.7 % conversion,98.5 % selectivity of oxychlorination reactor,

EDC produced: (800)(0.997)(0.985)(0.5) = 392 kgmole EDC

EDC from Direct Chlorination Reactor: 1350 – 539 – 392 = 419 kgmole

With 99.7 % conversion, 99.97% selectivity of direct chlorination reactor,

Amount of Chlorine required: $\frac{419}{0.997*0.9997} = 420\ kgmole$

Additional 3 kgmole, for any losses in the separation section.

Total amount of chlorine: 423 kgmole

4.2 Direct Chlorination Reactor

4.2.1 Reactions

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

$$C_2H_4 + 2Cl_2 \rightarrow C_2H_3Cl_3 + HCl$$

4.2.2 Reactor Data

Conversion: 99.97 %

Selectivity: 99.7 %[22]

Ethylene in 5% excess, to avoid formation of polychlorinated compounds.

4.2.3 Calculations

Amount of Chlorine: 423 kgmole

Amount of Ethylene: (423)(1.05) = 444.15 kgmole

Unreacted chlorine = 423 (0.003) = 0.1269 kg mole

Reacted ethylene = 423 (0.9997 x 0.997) + $\frac{423(9997 \times 0.003)}{2}$ = 422.23 kg mole

Unreacted ethylene = 444.15 - 422.23 = 21.92 kg mole

Amount converted to by-products = 423 (0.9997) – 423 (0.9997 x 0.997) = 1.2686 kg mole

4.2.4 Summary

Summary of the material going in and leaving the reactor is given in the table below:

TABLE 2: MATERIAL BALANCE ON DIRECT CHLORINATION REACTOR

Component	In (kg mole)	Out (kg mole)
C_2H_4	444.15	21.92
Cl_2	423	0.1269
$C_2H_3Cl_3$	0	421
HCl	0	0.6343
$C_2H_4Cl_2$	0	0.6363

4.3 Oxychlorination Reactor

4.3.1 Reactions

$$C_2H_4 + 0.5O_2 + 2HCl \rightarrow C_2H_4Cl_2 + H_2O$$

$$C_2H_4Cl_2 + HCl + 0.5O_2 \rightarrow C_2H_3Cl_3 + H_2$$

$$C_2H_4 + 8HCl \rightarrow 2CCl_4 + H_2$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

4.3.2 Reactor Data

Conversion: 99.7 %

Selectivity: 98.5%[4]

Ethylene in 5% excess, to avoid formation of polychlorinated compounds.

4.3.3 Calculations

HCl introduced = 800 kg mole

So, ethylene = $(\frac{800}{2}) \times 1.05$ = 420 kg mole

Oxygen = $\frac{800}{4}$ = 200 kg mole

Amount of EDC produced = $\frac{800 \times 0.997 \times 0.985}{2}$ = 392.82 kg mole

Amount of water produced = 392.82 kg mole

Unreacted HCl = 2.397 kg mole

HCl converted to by-products = 800 x 0.997 x 0.015 = 11.949 kg mole

60% of HCl converts to CCl_4 and 40% to TCE

TCE = $\frac{11.949 \times 0.4}{3}$ = 1.5932 kg mole

O_2 consumed = 0.7966 kg mole

C_2H_4 consumed = 1.5932 kg mole

Water produced = 1.5932 kg mole

Hydrogen produced = 5932 kg mole

Oxygen converted to by-products = $\frac{799}{4}$ x 0.997 x 0.015

= 2.995 kg mole

Amount left for combustion = 2.995 – 0.7966 = 2.1984 kg mole

Ethylene combusted = 0.7328 kg mole

CO_2 produced = 1.4656 kg mole

H_2O produced = 1.4656 kg mole

Amount of ethylene reacted = 392.33 + 1.5932 + 0.89175 + 0.7328

= 395.55 kg mole

Amount of ethylene unreacted = 419.475 – 395.55

= 27.653764 kg mole

CCl_4 = $\frac{11.949 \times 0.6}{4}$ = 1.79235 kg mole

C_2H_4 consumed = 0.896175 kg mole

H_2 produced = 5.37705 kg mole

4.3.4 Summary

The table below summarizes the material balance on oxychlorination reactor.

TABLE 3: MATERIAL BALANCE ON OXYCHLORINATION REACTOR

Component	In (kgmole/hr)	Out (kgmole/hr)
C_2H_4	419.475	28.9975
O_2	199.75	0.84925
HCl	799	2.397
$C_2H_4Cl_2$	0	392.33
$C_2H_3Cl_3$	0	1.5932
CCl_4	0	1.79325
H_2	0	6.97025
H_2O	0	395.9198
CO_2	0	1.4656

4.4 Three Phase Separator

Three phase separator operates at 25 ^{0}C and 1 bar. Following table summarizes, material balance on the separator.

TABLE 4: MATERIAL BALANCE ON THREE-PHASE SEPARATOR

Components	In (kgmoles)	Vapor (kgmoles)	Light Liquid (kgmoles)	Heavy Liquid (kgmoles)
C_2H_4	45.92	17.3040	29.059	0
Cl_2	0.1269	0.0051	0.1216	0.0002
$C_2H_4Cl_2$	813.8	0.485	813.439	0.0074
H_2O	395.9198	0.1679	61.4203	333.7957
HCl	3.0313	0.5615	2.4601	0.0097
$C_2H_3Cl_3$	2.2275	0.0004	2.2271	0
H_2	6.97025	6.6327	0.3371	0.0005
CCl_4	1.79325	0.002	1.7902	0
CO_2	1.4656	0.3422	1.1112	0.0102
O_2	0.84925	0.6755	0.1688	0.0001

4.5 Distillation Column (EDC Purification)

This distillation column separates EDC from rest of the impurities formed in the two reactors. The table below summarizes the material balance applied on the distillation column.

TABLE 5: MATERIAL BALANCE ON DISTILLATION COLUMN (EDC PURIFICATION)

Components	In (kgmoles)	Tops (kgmoles)	Bottoms (kgmoles)
C_2H_4	29.059	29.059	0
Cl_2	0.1216	0.1216	0
$C_2H_4Cl_2$	813.439	1.9326	813.439
H_2O	61.4203	61.4194	61.4203
HCl	2.4601	2.4601	0
$C_2H_3Cl_3$	2.2271	0.0001	2.2271
H_2	0.3371	0.3371	0
CCl_4	1.7902	0.021	1.7902
CO_2	1.1112	1.1112	0
O_2	0.1688	0.1688	0

4.6 Cracking Furnace

4.6.1 Reactions

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \qquad \text{(Desired Reaction)}$$

$$CCl_4 + 2C_2H_4 \rightarrow 2C_2H_4Cl_2 + C$$

$$C_2H_3Cl_3 + C_2H_4 \rightarrow C_2H_3Cl + C_2H_4Cl_2$$

$$C_2H_4 + C_2H_4Cl_2 \rightarrow C_4H_6 + 2HCl$$

4.6.2 Reactor Data

Conversion: 60%

Selectivity: 99.5%[26]

4.6.3 Calculations

EDC = 1350 kgmoles

VCM = HCl = (0.6)(0.995) = 805.95 kgmole

Remaining EDC = 540kgmole

CCl_4 = 1.7693 kgmole

Ethylene = 3.5386 kgmole

EDC from CCl_4 = 3.5386 kgmole (from stoichiometric ratios)

Carbon from CCl_4 = 1.7693 kgmole (from stoichiometric ratios)

$C_2H_3Cl_3$ = 2.227 kgmoles

Ethylene = 2.227 kgmoles

EDC from $C_2H_3Cl_3$ = 2.227 kgmole

VCM from $C_2H_3Cl_3$ = 2.227 kgmole

EDC to byproducts = (1350) (0.6) (1 – 0.995) = 4.05 kgmole

Ethylene = 4.05 kgmole

Butadiene produced = 4.05 kgmole

HCl produced = 8.1 kgmole

Total Ethylene required = 9.8156 kgmole

(This ethylene is added to the pre-cracking stream, to avoid formation of chlorine, which would affect purification in later stages)

4.6.4 Summary

The following table summarizes material balance of Furnace:

TABLE 6: MATERIAL BALANCE ON CRACKING FURNACE

Components	In (kgmoles)	Out(kgmoles)
C_2H_4	9.8156	0
$C_2H_4Cl_2$	1350	545.7656
C_2H_3Cl	0	808.177
HCl	0	813.95
$C_2H_3Cl_3$	2.2271	0
C_4H_6	0	4.05
CCl_4	1.7693	0

4.7 HCl Column

This distillation column separates HCl from rest of the mixture from cracking furnace. The HCl is recycled back to oxychlorination section. Summary of material balance on this distillation column is given below:

TABLE 7: MATERIAL BALANCE ON HCL COLUMN

Components	In (kgmoles)	Top(kgmoles)	Bottom (kgmoles)
HCl	813.95	813.9499	0.0001
C_2H_3Cl	808.177	0.0081	808.1689
C_4H_6	4.05	0	4.05
$C_2H_4Cl_2$	545.7656	0	545.7656

4.8 VCM Column

This distillation column separates EDC from VCM. EDC is obtained as bottom product and VCM as top product. EDC is recycled back to furnace and VCM is sent for butadiene treatment.

TABLE 8: MATERIAL BALANCE ON VCM COLUMN

Components	In (kgmoles)	Top(kgmoles)	Bottom (kgmoles)
HCl	0.0001	0.0001	0
C_4H_6	4.05	4.05	0
C_2H_3Cl	808.1689	808.1683	0.0005
$C_2H_4Cl_2$	545.7656	0.0008	545.7648

4.9 Butadiene Treatment

4.9.1 Reaction

$$C_4H_6 + 2H_2 \rightarrow C_4H_{10}$$

4.9.2 Reactor Data

Conversion 99.5%

Selectivity 100%[2]

4.9.3 Calculations

Hydrogen Required = (4.05)(2) = 8.1 kgmole

n-butane produced = (4.05)(0.995) = 4.02975 kgmole

Hydrogen unreacted = (8.1)(1 – 0.995) = 0.0405 kgmole

Butadiene unreacted = (4.05)(1 – 0.995) = 0.02025 kgmole

4.9.4 Summary

The following table summarizes material balance on butadiene treatment unit.

TABLE 9: MATERIAL BALANCE ON BUTADIENE REMOVAL UNIT

Components	In(kgmoles)	Out(kgmoles)
HCl	0.0001	0.0001
C_4H_6	4.05	0.02025
C_2H_3Cl	808.1683	808.1683
$C_2H_4Cl_2$	0.0008	0.0008
H_2	8.1	0.0405
n-C_4H_{10}	0	4.02975

CHAPTER 5

ENERGY BALANCE

Energy balance is applied on each equipment using the standard formulae for calculation of work and heat duty. Energy balance is applied on reactor by using standard heat of reactions.

5.1 Ethylene Compressor (Direct Chlorination Reactor)

Polytropic work formula is used to calculate compressor's work.

$$W_s(Molar\ isentropic\ work) = zRT_1\frac{\gamma}{\gamma-1}[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}}-1]$$

$$W_{Ts}(Total\ isentropic\ work) = nW_s$$

$$W_R(Real\ Work) = \frac{W_{Ts}}{\eta}\ [28]$$

To calculate outlet temperature, the following formula is used:

$$T_2 = T_1 + \frac{W_s}{\eta . C_p}$$

TABLE 10: PROPERTY TABLE FOR ETHYLENE (DC)

Property	Value
Inlet Pressure, P_1 (bar)	1
Outlet Pressure, P_2 (bar)	2
Compressibility factor, z	0.9935
γ	0.75
Universal Gas Constant, R (kJ/kgmole.K)	8.314
Molar Flow, n (kgmole/hr)	444.15
Isentropic Work, W_s (MJ/hr)	811
Real Work, W_R (MJ/hr)	1081
Efficiency, η	0.75
Inlet Temperature, T_1 (K)	298
Specific Heat, C_p (kJ/kgmole. K)	49.65

Outlet Temperature, T_2 (K)	353

5.2 Chlorine Compressor (Direct Chlorination Reactor)

Polytropic work formula is used to calculate compressor's work.

$$W_s(Molar\ isentropic\ work) = zRT_1 \frac{\gamma}{\gamma - 1}[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1]$$

$$W_{Ts}(Total\ isentropic\ work) = nW_s$$

$$W_R(Real\ Work) = \frac{W_{Ts}}{\eta}$$

To calculate outlet temperature, the following formula is used:

$$T_2 = T_1 + \frac{W_s}{\eta . C_p}$$

TABLE 11: PROPERTY TABLE FOR CHLORINE (DC)

Property	Value
Inlet Pressure, P_1 (bar)	1
Outlet Pressure, P_2 (bar)	2
Compressibility factor, z	0.9879
γ	1.336
Universal Gas Constant, R (kJ/kgmole.K)	8.314
Molar Flow, n (kgmole/hr)	435
Isentropic Work, W_s (MJ/hr)	806
Real Work, W_R (MJ/hr)	1075
Efficiency, η	0.75
Inlet Temperature, T_1 (K)	298
Specific Heat, C_p (kJ/kgmole. K)	34.37
Outlet Temperature, T_2 (K)	370

5.3 Ethylene Preheater (Direct Chlorination Reactor)

Cold Fluid: Ethylene

Hot Fluid: Post reactors' stream

Formula for Heat Duty: $\Delta H = nC_p\Delta T$

TABLE 12: ENERGY BALANCE ON ETHYLENE PPREHEATER (DC)

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^{0}C)	243	80
Outlet Temperature (^{0}C)	235	116
C_p (kJ/kgmole.^{0}C)	82.515	50.165
Molar Flow (kgmole/hr)	1272	444.1
ΔH (MJ/hr)	799	799

5.4 Chlorine Preheater (Direct Chlorination Reactor)

Cold Fluid: Chlorine

Hot Fluid: Post reactors' stream

Formula for Heat Duty: $\Delta H = nC_p\Delta T$

TABLE 13: ENERGY BALANCE ON CHLORINE PREHEATER (DC)

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^{0}C)	235.4	97
Outlet Temperature (^{0}C)	232.7	116
C_p (kJ/kg.^{0}C)	82.64	35.49
Molar Flow (kgmole/hr)	1272	433
ΔH (MJ/hr)	284	284

5.5 Direct Chlorination Reactor

Direct chlorination is an exothermic reaction and for maximum selectivity, requires efficient temperature control. Therefore, the flow rate of cooling water is critical for efficient operation of the reactor.

5.5.1 Reactions

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

$$C_2H_4 + 2Cl_2 \rightarrow C_2H_3Cl_3 + HCl$$

5.5.2 Calculations

Hess's law is used to calculate heat of reaction at conditions other than standard temperature and pressure.

$$\Delta H_{rxn,T} = \Delta H^0_{rxn} + \Delta H_{products} - \Delta H_{reactants}$$

Sensible enthalpy change is calculated using the formula:

$$\Delta H = C_{pm,Tf}\, T_f - C_{pm,Ti}\, T_i$$

Where $C_{pm,T}$ is mean heat capacity at temperature T.

$$\Delta H^0_{rxn} = \sum_{k=1}^{m} n_k \Delta H^0_{rxn,k} \text{ [28]}$$

$$\Delta H^0_{rxn} = \text{-91928 MJ/hr}$$

TABLE 14: TEMPERATURE DATA FOR DIRECT CHLORINATION REACTOR

	Products	Reactants
T_f (^{0}C)	116	25
T_i (^{0}C)	25	116

TABLE 15: SPECIFIC HEAT DATA FOR DIRECT CHLORINATION RECTOR COMPONENTS [29]

Component	C_{pm} @25^{0}C (kJ/kgmole.K)	C_{pm} @ 116^{0}C (kJ/kgmole.K)
Chlorine	44.16	35.37
Ethylene	44.16	31.54
TCE	152.2	152.7
EDC	136.9	147.3
HCl	29.76	29.95

$$\Delta H_{products} = 18452 \text{ MJ/hr}$$

$$\Delta H_{reactants} = 3531 \text{ MJ/hr}$$

$$\Delta H_{rxn,T} = -61483 \text{ MJ/hr}$$

5.6 Ethylene Compressor (Oxychlorination Reactor)

Polytropic work formula is used to calculate compressor's work.

$$W_s(Molar\ isentropic\ work) = zRT_1 \frac{\gamma}{\gamma - 1} [\left(\frac{P_2}{P_1}\right)^{\frac{\gamma - 1}{\gamma}} - 1]$$

$$W_{Ts}(Total\ isentropic\ work) = nW_s$$

$$W_R(Real\ Work) = \frac{W_{Ts}}{\eta}$$

To calculate outlet temperature, the following formula is used:

$$T_2 = T_1 + \frac{W_s}{\eta . C_p}$$

TABLE 16: PROPERTY TABLE FOR ETHYLENE (OC)

Property	Value
Inlet Pressure, P_1 (bar)	1
Outlet Pressure, P_2 (bar)	5
Compressibility factor, z	0.9935
γ	1.289
Universal Gas Constant, R (kJ/kgmole.K)	8.314
Molar Flow, n (kgmole/hr)	419.475
Isentropic Work, W_s (MJ/hr)	1948
Real Work, W_R (MJ/hr)	2597
Efficiency, η	0.75
Inlet Temperature, T_1 (K)	298
Specific Heat, C_p (kJ/kgmole. K)	44.16
Outlet Temperature, T_2 (K)	438

5.7 Oxygen Compressor (Oxychlorination Reactor)

Polytropic work formula is used to calculate compressor's work.

$$W_s(Molar\ isentropic\ work) = zRT_1\frac{\gamma}{\gamma-1}[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1]$$

$$W_{Ts}(Total\ isentropic\ work) = nW_s$$

$$W_R(Real\ Work) = \frac{W_{Ts}}{\eta}$$

To calculate outlet temperature, the following formula is used:

$$T_2 = T_1 + \frac{W_s}{\eta.C_p}$$

TABLE 17: PROPERTY TABLE FOR OXYGEN (OC)

Property	Value
Inlet Pressure, P_1 (bar)	1
Outlet Pressure, P_2 (bar)	5
Compressibility factor, z	0.991
γ	1.401
Universal Gas Constant, R (kJ/kgmole.K)	8.314
Molar Flow, n (kgmole/hr)	199.75
Isentropic Work, W_s (MJ/hr)	1011
Real Work, W_R (MJ/hr)	1348
Efficiency, η	0.75
Inlet Temperature, T_1 (K)	298
Specific Heat, C_p (kJ/kgmole. K)	29.22
Outlet Temperature, T_2 (K)	529

5.8 HCl Expander (Oxychlorination Reactor)

Polytropic work formula is used to calculate compressor's work.

$$W_s(Molar\ isentropic\ work) = zRT_1\frac{\gamma}{\gamma-1}[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1]$$

$$W_{Ts}(Total\ isentropic\ work) = nW_s$$

$$W_R(Real\ Work) = \frac{W_{Ts}}{\eta}$$

To calculate outlet temperature, the following formula is used:

$$T_2 = T_1 + \frac{W_s}{\eta . C_p}$$

TABLE 18: PROPERTY TABLE FOR HCL (OC)

Property	Value
Inlet Pressure, P_1 (bar)	20
Outlet Pressure, P_2 (bar)	5
Compressibility factor, z	0.9878
γ	1.417
Universal Gas Constant, R (kJ/kgmole.K)	8.314
Molar Flow, n (kgmole/hr)	799
Isentropic Work, W_s (MJ/hr)	-5356.6
Real Work, W_R (MJ/hr)	-3210
Efficiency, η	0.75
Inlet Temperature, T_1 (K)	573
Specific Heat, C_p (kJ/kgmole. K)	44.16
Outlet Temperature, T_2 (K)	443

5.9 Ethylene Preheater (Oxychlorination Reactor)

Cold Fluid: Ethylene

Hot Fluid: Post Cracking Stream

TABLE 19: ENERGY BALANCE ON ETHYLENE PREHEATER (OCR)

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^{0}C)	388.9	165
Outlet Temperature (^{0}C)	367.4	300
C_p (kJ/kg.^{0}C)	75.16	62.03
Molar Flow (kgmole/hr)	2168	419.5
ΔH (MJ/hr)	3438	3438

5.10 Oxygen Preheater (Oxychlorination Reactor)

Cold Fluid: Oxygen

Hot Fluid: Post Cracking Stream

TABLE 20: ENERGY BALANCE ON OXYGEN PREHEATER (OCR)

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^{0}C)	367.4	265
Outlet Temperature (^{0}C)	366	300
C_p (kJ/kg.^{0}C)	74.72	31.67
Molar Flow (kgmole/hr)	2168	199.8
ΔH (MJ/hr)	221	221

5.11 HCl Preheater (Oxychlorination Reactor)

Cold Fluid: HCl

Hot Fluid: Post Cracking Stream

TABLE 21: ENERGY BALANCE ON HCL PREHEATER (OCR)

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^{0}C)	366	170
Outlet Temperature (^{0}C)	346.6	300
C_p (kJ/kg.^{0}C)	74.31	30.085
Molar Flow (kgmole/hr)	2168	799.
ΔH (MJ/hr)	3162	3162

5.12 Oxychlorination Reactor

5.12.1 Reactions

$$C_2H_4 + HCl + 0.5O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

$$C_2H_4Cl_2 + HCl + 0.5O_2 \rightarrow C_2H_3Cl_3 + H_2$$

$$C_2H_4 + 8HCl \rightarrow 2CCl_4 + H_2$$

$$C_2H_4 + 3O_2 \rightarrow 2CO_2 + 2H_2O$$

5.12.2 Calculations

Hess's law is used to calculate heat of reaction at conditions other than standard temperature and pressure.

$$\Delta H_{rxn,T} = \Delta H^0_{rxn} + \Delta H_{products} - \Delta H_{reactants}$$

Sensible enthalpy change is calculated using the formula:

$$\Delta H = C_{pm,Tf}\, T_f - C_{pm,Ti}\, T_i$$

Where $C_{pm,T}$ is mean heat capacity at temperature T.

$$\Delta H^0_{rxn} = \sum_{k=1}^{m} n_k \Delta H^0_{rxn,k}$$

$$\Delta H^0_{rxn} = \text{-2118 MJ/hr}$$

TABLE 22: TEMPERATURE DATA FOR OXYCHLORINATION REACTOR

	Products	Reactants
T_f (^{0}C)	300	25
T_i (^{0}C)	25	300

TABLE 23: SPECIFIC HEAT DATA FOR OXYCHLORINATION REACTOR COMPONENTS

Component	C_{pm} @ 25^{0}C(kJ/kgmole.K)	C_{pm} @ 300^{0}C (kJ/kgmole.K)
Oxygen	29.22	31.87
Ethylene	44.16	67.87
HCl	29.76	29.95
EDC	113.7	147.3
H_2O	36.7	82.5
CO_2	46.14	39.14
TCE	126.3	120.55
H_2	29.15	28.46
CCl_4	102	108.15

$$\Delta H_{products} = \text{46476 MJ/hr}$$

$$\Delta H_{reactants} = \text{16485 MJ/hr}$$

$$\Delta H_{rxn,T} = \text{-65308 MJ/hr}$$

5.13 Post Chlorinator Compressor

Polytropic work formula is used to calculate compressor's work.

$$W_s(Molar\ isentropic\ work) = zRT_1 \frac{\gamma}{\gamma - 1}[\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1]$$

$$W_{Ts}(Total\ isentropic\ work) = nW_s$$

$$W_R(Real\ Work) = \frac{W_{Ts}}{\eta}$$

To calculate outlet temperature, the following formula is used:

$$T_2 = T_1 + \frac{W_s}{\eta . C_p}$$

TABLE 24: PROPERTY TABLE FOR DCR EXIT STREAM

Property	Value
Inlet Pressure, P_1 (bar)	2
Outlet Pressure, P_2 (bar)	5
Compressibility factor, z	0.9592
γ	1.119
Universal Gas Constant, R (kJ/kgmole.K)	8.314
Molar Flow, n (kgmole/hr)	456.9
Isentropic Work, W_s (MJ/hr)	1364
Real Work, W_R (MJ/hr)	1819
Efficiency, η	0.75
Inlet Temperature, T_1 (K)	389
Specific Heat, C_p (kJ/kgmole. K)	90.16
Outlet Temperature, T_2 (K)	433

5.14 Pre-three-phase-separator Heat Removal

Cold Fluid: Cooling Water

Hot Fluid: Reactor's Effluent

TABLE 25: HEAT REMOVAL REQUIREMENT FOR PRE-THREE-PHASE SEPARATOR FLUID

Property	Fluid
Inlet Temperature (^{0}C)	132.9
Outlet Temperature (^{0}C)	25
C_p (kJ/kg.^{0}C)	91.32
Molar Flow (kgmole/hr)	1271
ΔH (MJ/hr)	-2.2×10^5

5.15 Three Phase Separator

Enthalpy balance is applied on three-phase separator.

TABLE 26: ENERGY BALANCE ON THREE-PHASE SEPARATOR

	In	Vapor	Light Liquid	Heavy Liquid
Enthalpy (kJ/hr)	2.745×10^8	1.514×10^8	5.912×10^5	9.554×10^7

5.16 Distillation Column (EDC Purification)

5.16.1 Condenser

$$Q_C = H_V - H_L - H_D$$

$$Q_C = (1.863 - 2.719 - 2.914) \text{ x } 10^3$$

$$Q_C = -3.77 \text{ x } 10^3 \text{ MJ/hr}$$

5.16.2 Reboiler

$$Q_B = Q_C + H_W + H_D - H_F$$

$$Q_B = (-0.377 + 4.789 + 0.2914 - 2.0454) \text{ x } 10^4$$

$$Q_B = 3.412 \times 10^4 \text{ MJ / hr}$$

5.17 Pre-Cracking Heat Exchanger

Cold Fluid: Pre-Cracking Fluid

Hot Fluid: Post-Cracking Fluid

TABLE 27: ENERGY BALANCE ON PRE-CRACKING HEAT EXCHANGER

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^{0}C)	346.6	228.5
Outlet Temperature (^{0}C)	286.1	287
C_p (kJ/kg.^{0}C)	72.725	121.2
Molar Flow (kg mole/hr)	2168	1354
ΔH (MJ/hr)	9613	9613

5.18 Cracking Furnace

5.18.1 Reactions

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl \qquad \text{(Desired Reaction)}$$

$$CCl_4 + 2C_2H_4 \rightarrow 2C_2H_4Cl_2 + C$$

$$C_2H_3Cl_3 + C_2H_4 \rightarrow C_2H_3Cl + C_2H_4Cl_2$$

$$C_2H_4 + C_2H_4Cl_2 \rightarrow C_4H_6 + 2HCl$$

5.18.2 Calculations

Hess's law is used to calculate heat of reaction at conditions other than standard temperature and pressure.

$$\Delta H_{rxn,T} = \Delta H^0_{rxn} + \Delta H_{products} - \Delta H_{reactants}$$

Sensible enthalpy change is calculated using the formula:

$$\Delta H = C_{pm,Tf}\, T_f - C_{pm,Ti}\, T_i$$

Where $C_{pm,T}$ is mean heat capacity at temperature T.

$$\Delta H^0_{rxn} = \sum_{k=1}^{m} n_k \Delta H^0_{rxn,k}$$

$$\Delta H^0_{rxn} = 58862\ MJ/hr$$

TABLE 28: TEMPERATURE DATA FOR CRACKING FURNACE

	Products	Reactants
T_f (^{0}C)	500	25
T_i (^{0}C)	25	500

TABLE 29: SPECIFIC HEAT DATA FOR COMPONENTS OF CRACKING FURNACE

Component	C_{pm} @ 25^{0}C (kJ/kgmole.K)	C_{pm} @ 500^{0}C (kJ/kgmole.K)
EDC	89	198
VCM	38.3	68.7
TCE	48.1	135
HCl	23.2	49.3
CCl_4	53.2	157
C_4H_6	23	86
C_2H_4	44.16	132

$$\Delta H_{products} = 106957 MJ/hr$$

$$\Delta H_{reactants} = 111388\ MJ/hr$$

$$\Delta H_{rxn,T} = 88883\ MJ/h$$

5.19 Post-Cracking Heat Exchanger

Cold Fluid: HCl

Hot Fluid: Post-Cracking Stream

TABLE 30: ENERGY BALANCE ON POST-CRACKING HEAT EXCHANGER

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^{0}C)	286.1	96
Outlet Temperature (^{0}C)	209.6	94
C_p (kJ/kg.^{0}C)	71.48	102.42
Molar Flow (kgmole/hr)	2168	808
ΔH (MJ/hr)	11514	11514

5.20 HCl Column

5.20.1 Condenser

$$Q_C = H_V - H_L - H_D$$

$$Q_C = (2.386 – 3.819 – 3.753) \text{ x } 10^4$$

$$Q_C = -5.186 \text{ x } 10^4 \text{ MJ/hr}$$

5.20.2 Reboiler

$$Q_B = Q_C + H_W + H_D - H_F$$

$$Q_B = (-5.186 + 5.779 +3.753 – 1.2) \text{ x } 10^4$$

$$Q_B = 3.146 \text{ x } 10^4 \text{ MJ / h}$$

5.21 VCM Column

5.21.1 Condenser

$$Q_C = H_V - H_L - H_D$$

$$Q_C = (1.8 – 2.8 – 1.564) \text{ x } 10^4$$

$$Q_C = -2.564 \text{ x } 10^4 \text{ MJ/ hr}$$

5.21.2 Reboiler

$$Q_B = Q_C + H_W + H_D - H_F$$

$$Q_B = (-2.564 + 4.946 + 1.564 - 0.8) \times 10^4$$

$$Q_B = 3.146 \times 10^4 \text{ MJ/ hr}$$

5.22 VCM Reboiler

Heat of Vaporization of VCM @ 20 bar = 1.425×10^4 kJ/kgmole

Total Heat Required to vaporize = (808) (1.425×10^4) = 1.15×10^4 MJ/ hr

5.23 VCM Expander

Polytropic work formula is used to calculate compressor's work.

$$W_s(Molar\ isentropic\ work) = zRT_1 \frac{\gamma}{\gamma - 1} [\left(\frac{P_2}{P_1}\right)^{\frac{\gamma-1}{\gamma}} - 1]$$

$$W_{Ts}(Total\ isentropic\ work) = nW_s$$

$$W_R(Real\ Work) = \frac{W_{Ts}}{\eta}$$

To calculate outlet temperature, the following formula is used:

$$T_2 = T_1 + \frac{W_s}{\eta . C_p}$$

TABLE 31: PROPERTY TABLE FOR VCM

Property	Value
Inlet Pressure, P_1 (bar)	20
Outlet Pressure, P_2 (bar)	1
Compressibility factor, z	0.9454
γ	1.176
Universal Gas Constant, R (kJ/kgmole.K)	8.314
Molar Flow, n (kgmole/hr)	817.8
Isentropic Work, W_s (MJ/hr)	-3509.33
Real Work, W_R (MJ/hr)	-2632
Efficiency, η	0.75
Inlet Temperature, T_1 (K)	218.3
Specific Heat, C_p (kJ/kgmole. K)	70.67
Outlet Temperature, T_2 (K)	95.15

5.24 VCM Preheater

Cold Fluid: VCM

Hot Fluid: Pre-Three-Phase Separator Stream

TABLE 32: ENERGY BALANCE ON VCM PREHEATER

Property	Hot Fluid	Cold Fluid
Inlet Temperature (^0C)	232.7	-10
Outlet Temperature (^0C)	152	160
C_p (kJ/kg.^0C)	82.51	59.615
Molar Flow (kgmole/hr)	1272	808
ΔH (MJ/hr)	8187	8187

5.25 Hydrogen Heater

Cold Fluid: Hydrogen

Hot Fluid: Steam

TABLE 33: HEAT REQUIREMENT FOR HYDROGEN HEATER

Property	Value
Inlet Temperature (^0C)	160
Outlet Temperature (^0C)	25
C_p (kJ/kg.^0C)	28.43
Molar Flow (kgmole/hr)	8.519
ΔH (kJ/hr)	-0.9242

5.26 Butadiene Removal

5.26.1 Reaction

$$C_4H_6 + 2H_2 \rightarrow C_4H_{10}$$

5.26.2 Calculations

Hess's law is used to calculate heat of reaction at conditions other than standard temperature and pressure.

$$\Delta H_{rxn,T} = \Delta H^0_{rxn} + \Delta H_{products} - \Delta H_{reactants}$$

Sensible enthalpy change is calculated using the formula:

$$\Delta H = C_{pm,Tf}\, T_f - C_{pm,Ti}\, T_i$$

Where $C_{pm,T}$ is mean heat capacity at temperature T.

$$\Delta H^0_{rxn} = \sum_{k=1}^{m} n_k \Delta H^0_{rxn,k}$$

$$\Delta H^0_{rxn} = -2257 \text{ MJ/hr}$$

TABLE 34: TEMPERATURE DATA FOR BUTADIENE REMOVAL UNIT

	Products	Reactants
T_f (^{0}C)	160	25
T_i (^{0}C)	25	160

TABLE 35: SPECIFIC HEAT DATA FOR BUTADIENE REMOVAL UNIT COMPONENTS

Component	C_{pm} @ 25^{0}C (kJ/kgmole.K)	C_{pm} @ 160^{0}C (kJ/kgmole.K)
Butadiene	124.1	183
Hydrogen	28.57	28.82
n-butane	146.4	146.75

$$\Delta H_{products} = 242 \text{ MJ/hr}$$

$$\Delta H_{reactants} = 407 \text{ MJ/hr}$$

$$\Delta H_{rxn,T} = \text{-}2422 \text{ MJ/hr}$$

CHAPTER 6

DESIGN CALCULATIONS

Design calculations for major components of the process flow diagram are carried out in this section.

6.1 Oxychlorination Reactor Design [30]

Temperature control is very critical in the operation of oxychlorination reactors. It is required that hot spots are not produced during the reaction. Cupric chloride supported on alumina is used as a catalyst. To cater for this, a multi-tubular reactor with minimum tube diameter practically possible is designed, to ensure efficient heat transfer and avoid the problem of temperature hot spots.

6.1.1 Data for design

Reaction:

$$C_2H_4 + 2HCl + 0.5O_2 \rightarrow C_2H_4Cl_2 + H_2O$$

A is HCl, B is O_2 & C is C_2H_4

TABLE 36: DESIGN DATA FOR OCR

Property	Value
Temperature, T (K)	573
Pressure, (bar)	5
Molar Flow, HCl (kgmole/hr)	800
C_{Ao} (kgmole/m^3 of catalyst)	0.06
C_{Bo} (kgmole/m^3 of catalyst)	0.015
C_{Co} (kgmole/m^3 of catalyst)	0.03
Conversion, X_A	0.997
Tube ID, (mm)	22.1
Tube OD, (mm)	25.4
Tube Length, (m)	6.1
Universal Gas Constant, R (kJ/kgmole.K)	8.314

Rate Equation:

$$r = \frac{k_1 k_2 P_A^2 P_C^2}{1 + k_1 P_A^2 (1 + \frac{k_2 P_C}{k_3 P_B})}$$

Using P = CRT, convert the equation in terms of concentration.

From Stoichiometric equations,

$$\frac{C_{Ao} X_A}{2} = \frac{C_{Bo} X_B}{0.5} = \frac{C_{Co} X_C}{1}$$

We get, $X_A = X_B = X_C$

Using the relation,

$$C_A = C_{Ao}(1 - X_A)$$

The final form of the rate equation becomes:

$$r = \frac{\alpha(1 - X_A)^3}{1 + \beta (1 - X_A)^2 + \gamma\beta(1 - X_A)^2}$$

Here,

$$\alpha = R^3T^3k_1k_2C_{Ao}^2C_{Co}$$

$$\beta = \mathrm{R^2T^2C_{Ao}^2}$$

$$\gamma = \frac{k_2C_{Co}}{k_3C_{Bo}}$$

Putting in performance equation,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

Where V is volume of Catalyst

F_{Ao} = 800 kgmole / hr

X_A = 0.997

T = 573 K

$$k_1 = e^{-7.27+\frac{19300}{RT}}$$

$$k_2 = e^{24.87-\frac{21400}{RT}}$$

$$k_3 = e^{12.8-\frac{6200}{RT}}$$

Volume of catalyst turns out to be:

7.216 m^3

Additional 20% volume for supporting material we get,

8.7 m^3

Number of tubes,

$$N_t\pi r^2 l = 8.7$$

r =11.05mm

l = 6.1m

Converting to meters and solving we get N_t = 4331

Shell Diameter 3.63m (from TEMA standards)

Pressure Drop:

Pressure drop is calculated via shell and tube equations

$\Delta P_t = \frac{fGt^2Ln}{5.22\times10^{10}D_s\varphi_t}$

$$\Delta P_r = \frac{4n}{s}\frac{V^2}{2g}$$

Putting in values, we get

$$\Delta P_T = 0.0646\, psi$$

Which is well below the allowable pressure drop of 10 psi.

TABLE 37: SPECIFICATION SHEET FOR OCR

Specification Sheet of Reactor	
Volume of Catalyst (m^3)	7.22
Number of Tubes	4331
Tube OD (cm)	2.54
Shell ID (m)	3.63
Length of Tubes (m)	6.09
Voidage	0.23
Density (kg/m^3)	3390
Mass of catalyst (kg)	22709

6.2 Direct Chlorination Reactor Design [30]

Reaction:

$$C_2H_4 + Cl_2 \rightarrow C_2H_4Cl_2$$

Cl_2 is A, C_2H_4 is B

TABLE 38 DESIGN DATA FOR DCR

Property	Value
Temperature, T (K)	389
Pressure, (bar)	2
Molar Flow, HCl (kgmole/hr)	423
C_{Ao} (kgmole/m^3 of catalyst)	0.3
C_{Bo} (kgmole/m^3 of catalyst)	0.32
Conversion, X_A	0.9997
Tube ID, (mm)	22.1
Tube OD, (mm)	25.4
Tube Length, (m)	6.1
Universal Gas Constant, R (kJ/kgmole.K)	8.314

Rate Equation:

$$-r_A = kC_AC_B$$

$$\text{k} = 11493000e^{\frac{-2156.58}{T}} \left(\frac{m^3 of\ catalyst}{kgmole.hr}\right)$$

From Stoichiometric equations,

$$\frac{C_{Ao}X_A}{1} = \frac{C_{Bo}X_B}{1}$$

We get, $X_A = X_B$

Using the relation,

$C_A = C_{Ao}(1 - X_A)$

Final form of the equation becomes:

$$-r_A = kC_{Ao}^2(1 - X_A)^2$$

Putting in performance equation,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

Where V is volume of Catalyst

Volume of catalyst turns out to be:

8.327 m^3

Additional 20% volume for supporting material we get,

10 m^3

Number of tubes,

$$N_t \pi r^2 l = 10$$

r =11.05mm

l = 6.1m

Converting to meters and solving we get N_t = 5000

Shell Diameter 4.1m (from TEMA standards)

Pressure Drop:

Pressure drop is calculated via shell and tube equations

$$\Delta P_t = \frac{fGt^2Ln}{5.22\times10^{10}D_s\varphi_t}$$

$$\Delta P_r = \frac{4n}{s}\frac{V^2}{2g}$$

Putting in values, we get

$$\Delta P_T = 0.08557\ psi$$

Which is well below the allowable pressure drop of 10 psi.

TABLE 39: SPECIFICATION SHEET FOR DCR

Specification Sheet of Direct Chlorination Reactor	
Volume of Catalyst (m^3)	8.34
Number of Tubes	5000
Tube OD (cm)	2.54
Shell ID (m)	3.63
Length of Tubes (m)	6.09
Voidage	0.32
Density (kg/m^3)	2900
Mass of catalyst (kg)	16446

6.3 Three Phase Separator Design [31]

Design Equation for 3-Phase Separator:

$$d^2 l = 420\left(\left(\frac{TzQ_g}{P}\right)\left(\frac{\rho_g}{\rho_l - \rho_g}\right)\frac{C_D}{d_m}\right)$$

Here,

d_m = 200 µm

T = 298.15 K

z = 0.9811

$Q_g = 3 \times 10^4 \ m^3 / hr$

P = 5 bar

ρ_g = 4.74 kg / m^3

ρ_l = 1216 kg / m^3

We get value of L/D of 5.5 from literature, by putting this, we get:

d= 1.06 m

l= 5.84 m

Oil Pad Thickness:

$$h_o = 320\frac{t_r \Delta(S.G)}{\mu}$$

t_r = 0.008 hrs

Δ(S.G) = 0.275

μ = 7.02 x 10^{-4} Pa.s

h_o = 12 cm

TABLE 40: SPECIFICATION SHEET FOR THREE-PHASE SEPARATOR

Specification Sheet of 3-phase separator	
Vessel Diameter (m)	1.06
Vessel Length (m)	5.84
Liquid Pads Thickness (cm)	12
Percent Liq Volume	50
Gas Capacity (m^3/hr)	3 x 10^4
Material of Construction	Carbon Steel

6.4 Distillation Column (EDC Purification)[28]

Key components for this distillation column are EDC and Water, Water being the light component and EDC being the heavy component.

Top and bottom temperatures are calculated via hit and trial, using the equations of bubble point and dew point.

Calculation of Bottom Temperature using the relation:

(Bubble Point)

$$\sum y_i = \sum K_i x_i = 1$$

Calculation of Top Temperature using the relation:

(Dew Point)

$$\sum x_i = \sum \frac{y_i}{K_i} = 1$$

Top Temperature: -30 ^{0}C

Bottom Temperature: 147 ^{0}C

TABLE 41: DISTILLATION COLUMN (EDC PURIFICATION) COMPONENT FRACTIONS

Components	In (kgmole/hr)	Mole Frac.	Top (kgmole/hr)	Mole Frac.	Bottom (kgmole/hr)	Mole Frac.
Ethylene	29.059	0.0318	29.059	0.3	0	0
Oxygen	0.1688	0.0002	0.1688	0.002	0	0
HCl	2.4601	0.003	2.4601	0.03	0	0
Chlorine	0.1216	0.0001	0.1216	0.0013	0	0
Hydrogen	0.3371	0.0004	0.3371	0.0035	0	0
Carbon Dioxide	1.1112	0.001	1.1112	0.011	0	0
Water	61.4203	0.067	61.4194	0.635	0.0008	9.8×10^{-7}
EDC	813.439	0.89	1.9326	0.020	811.50	0.995
TCE	2.2271	0.002	0	0	2.2271	0.0027
CCl_4	1.7902	0.0019	0	0	1.7902	0.0021
Total	912.1344	1	96.6098	1	815.52	1

TABLE 42: DISTILLATION COLUMN (EDC PURIFICATION) COMPONENT RELATIVE VOLATILITY DATA

Minimum number of stages are calculated by Fenske's Equation

Components	K (Top)	K (Bottom)	Alpha (Top)	Alpha (Bottom)	Alpha Avg
Ethylene	1.51	9.35	2.32	9.3	5.82
Oxygen	20.02	18.85	3.07	8.83	5.89
HCl	0.9897	7.985	1.52	7.97	4.75
Chlorine	0.1558	4.102	2.39	4.09	2.17
Hydrogen	127.8	28.59	1.96	8.56	4.32
Carbon Dioxide	1.349	9.785	2.07	9.77	5.92
Water	9.00E-01	7	1.38	6.99	4.19
EDC	6.52E-01	1.001	1.00	1	1.00
TCE	1.76E-01	0.6596	0.027	0.65	0.046
CCl_4	1.00E-01	1.033	0.0154	1.031	0.059

Calculation of Minimum Number of Stages:

$$N_m = \frac{\log\left[\frac{x_{LK}}{x_{HK}}\right]_d \log\left[\frac{x_{HK}}{x_{LK}}\right]_b}{\log \alpha_{LK}}$$

$$N_m = 12$$

Calculation of Minimum Reflux Ratio:

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q$$

$$\theta = 3.1$$

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1$$

$$R_m = 2.18$$

Here

θ is the root of the first equation which is calculated by hit and trial, reflux ratio is selected. Theoretical number of plates are calculated from the graph below.

Number of Stages:

$$\frac{R_m}{R_m + 1} = 0.7$$

$$\frac{R}{R + 1} = 0.8$$

$$\frac{N_m}{N} = 0.7$$

$$N = 17$$

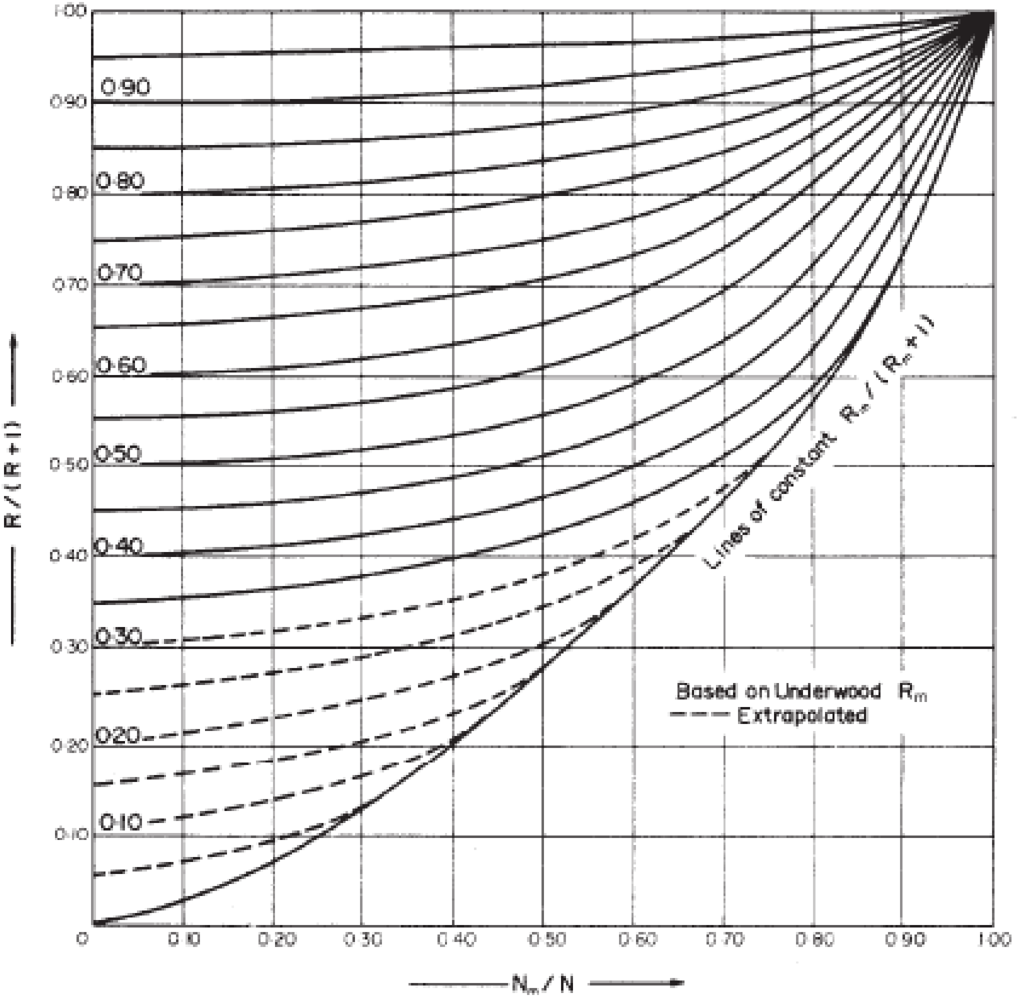


FIGURE 10: ERBAR MADDOX CORRELATION

Feed Point:

$$\log \frac{N_r}{N_s} = 0.206 \log[(\frac{B}{D})\left(\frac{x_{f,HK}}{x_{f,LK}}\right)\left(\frac{x_{b,LK}}{x_{d,HK}}\right)^2]$$

$$N_r = 0.82\ N_s$$

Hence, feed entry stage is 14.

Efficiency:

$$\mu = 3.1 \times 10^{-2}\ \text{cp}$$

$$\alpha = 4.76$$

$$\mu\alpha = 0.147$$

Corresponding to this, $E_o = 0.83$

Hence actual stages:

24

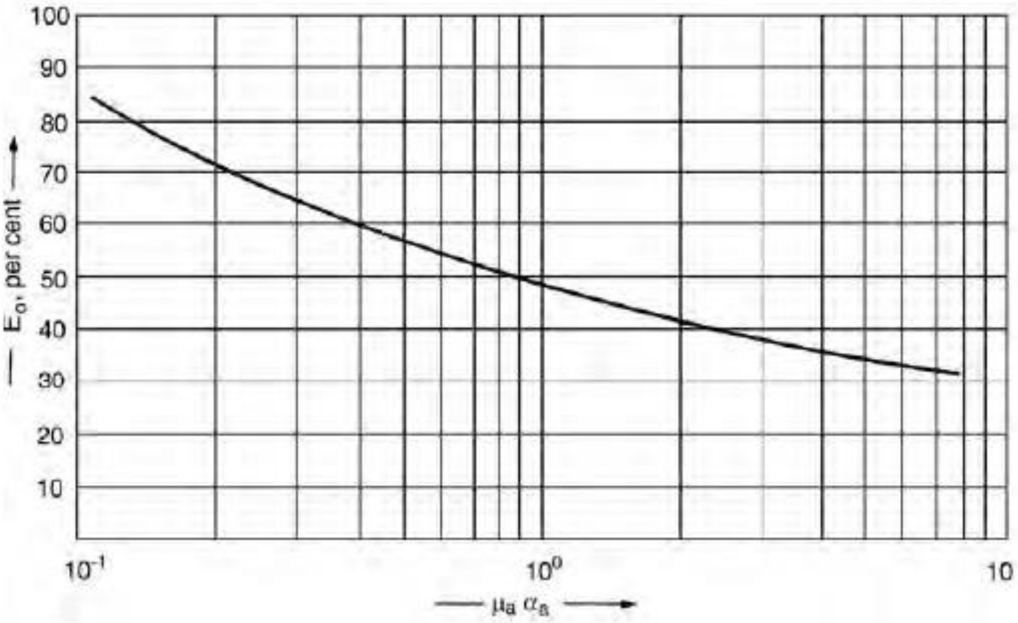


FIGURE 11: O'CONNEL'S CORRELATION

Height & Diameter:

$$u_v = (-0.171 l_t^2 + 0.27 l_t \; - 0.047)\left[\frac{\rho_l - \rho_v}{\rho_v}\right]^{0.5}$$

$$D_C = \left(\frac{4V_w}{\pi \rho_v u_v}\right)^{0.5}$$

$\rho_L = 1077$ kg/m^3

$\rho_V = 13.4$ kg/m^3

$l_t = 0.6$ m

$u_v = 0.48$ m/s

$V_W = 17.21$ kg /s

$D_c = 1.85$ m

H = 12.7 m

TABLE 43: SPECIFICATION SHEET FOR DISTILLATION COLUMN (EDC PURIFICATION)

Specification Sheet of Distillation Column	
No. of Theoretical Plates	17
No. of Actual Plates	20
Type of Plates	Sieve Plates
Hole Size (mm)	4
Reflux Ratio	4
Column Diameter (m)	1.85
Column Height (m)	12.7

6.5 Catalyst requirement for Furnace [30]

Reaction:

$$C_2H_4Cl_2 \rightarrow C_2H_3Cl + HCl$$

Reactor Data:

Conversion: 60%

TABLE 44: DESIGN DATA FOR FURNACE

Property	Value
Temperature, T (K)	573
Pressure, (bar)	20
Molar Flow, HCl (kgmole/hr)	1350
C_{Ao} (kgmole/m^3 of catalyst)	0.33
Conversion, X_A	0.6
Tube ID, (mm)	22.1
Tube OD, (mm)	25.4
Tube Length, (m)	6.1
Universal Gas Constant, R (kJ/kgmole.K)	8.314

Rate Equation:

$$-r_A = \; kC_A$$

$$k = 124e^{\frac{-4200}{RT}}$$

Using the relation,

$$C_A = C_{Ao}(1 - X_A)$$

Final form of the equation becomes:

$$-r_A = kC_{Ao}^{1}(1 - X_A)^1$$

Putting in performance equation,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

Where V is volume of Catalyst

Volume of catalyst turns out to be:

24.12 m^3

Number of tubes,

$$N_t \pi r^2 l = 24.12$$

r =11.05mm

l = 6.1m

Converting to meters and solving we get N_t = 12000

6.6 HCl Column [28]

Key components for this distillation column are VCM and HCl, HCl being the light component and VCM being the heavy component.

Top and bottom temperatures are calculated via hit and trial, using the equations of bubble point and dew point.

Calculation of Bottom Temperature using the relation:

(Bubble Point)

$$\sum y_i = \sum K_i x_i = 1$$

Calculation of Top Temperature using the relation:

(Dew Point)

$$\sum x_i = \sum \frac{y_i}{K_i} = 1$$

Top Temperature: -9.6 ^{0}C

Bottom Temperature: 125 ^{0}C

TABLE 45: HCL COLUMN COMPONENT FRACTIONS

Components	In (kgmole/hr)	Mole Frac.	Top (kgmole /hr)	Mole Frac.	Bottom (kgmole/hr)	Mole Frac.
Chlorine	0	0	0	0	0	0
HCl	813.95	0.371	813.94	0.999	0.0001	$7.36\text{x}10^{-8}$
VCM	808.177	0.372	0.0081	$9.95\text{x}10^{-6}$	808.1	0.595
Butadiene	4.05	0.002	0	0	4.05	0.002
EDC	545.765	0.251	0	0	545.7	0.401
Total	2172	1	814	1	1358	1

TABLE 46: HCL COLUMN RELATIVE VOALTILITY DATA

Components	K (Top)	K (Bottom)	Alpha (Top)	Alpha (Bottom)	Alpha Avg
Chlorine	0	0	0	0	0
HCl	1	5.28	9.29	3.50	6.39
VCM	0.1076	1.50	1	1	1
Butadiene	$7.98\text{x}10^{-2}$	1.38	7.42E-01	0.92	0.083
EDC	N/A	0.244	N/A	0.16	0.160

Minimum number of stages are calculated by Fenske's Equation

Calculation of Minimum Number of Stages:

$$N_m = \frac{\log\left[\frac{x_{LK}}{x_{HK}}\right]_d \log\left[\frac{x_{HK}}{x_{LK}}\right]_b}{\log \alpha_{LK}}$$

$$N_m = 15$$

Calculation of Minimum Reflux Ratio:

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q$$

$$\theta = 4.556$$

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1$$

$$R_m = 2.47$$

Here

θ is the root of the first equation which is calculated by hit and trial, reflux ratio is selected. Theoretical number of plates are calculated from the graph below.

Number of Stages:

$$\frac{R_m}{R_m + 1} = 0.7$$

$$\frac{R}{R + 1} = 0.8$$

$$\frac{N_m}{N} = 0.67$$

N= 22 (refer to figure 10)

Feed Point:

$$\log \frac{N_r}{N_s} = 0.206 \log[(\frac{B}{D})\left(\frac{x_{f,HK}}{x_{f,LK}}\right)\left(\frac{x_{b,LK}}{x_{d,HK}}\right)^2]$$

$$N_r = 0.15\ N_s$$

Hence, feed entry stage is 18.

Efficiency:

$$\mu = 1.86 \times 10^{-2} \text{ cp}$$

$$\alpha = 6.4$$

$$\mu\alpha = 0.119$$

Corresponding to this, $E_o = 0.83$ (refer to figure 11)

Hence actual stages:

27

Height & Diameter:

$$u_v = (-0.171 l_t^2 + 0.27 l_t - 0.047)\left[\frac{\rho_l - \rho_v}{\rho_v}\right]^{0.5}$$

$$D_C = \left(\frac{4V_w}{\pi \rho_v u_v}\right)^{0.5}$$

$\rho_L = 997 \text{ kg/m}^3$

$\rho_V = 36.74 \text{ kg/m}^3$

$l_t = 0.6$ m

$u_v = 0.27$ m/s

$V_W = 40.6$ kg /s

$D_c = 2.26$ m

H = 15.9m

TABLE 47: SPECIFICATION SHEET FOR HCL COLUMN

Specification Sheet of HCl Column	
No. of Theoretical Plates	22
No. of Actual Plates	27
Type of Plates	Sieve Plates
Hole Size (mm)	4
Reflux Ratio	4
Column Diameter (m)	2.26
Column Height (m)	15.9

6.7 VCM Column [28]

Key components for this distillation column are VCM and HCl, HCl being the light component and VCM being the heavy component.

Top and bottom temperatures are calculated via hit and trial, using the equations of bubble point and dew point.

Calculation of Bottom Temperature using the relation:

(Bubble Point)

$$\sum y_i = \sum K_i x_i = 1$$

Calculation of Top Temperature using the relation:

(Dew Point)

$$\sum x_i = \sum \frac{y_i}{K_i} = 1$$

Top Temperature: 94.8 ^{0}C

Bottom Temperature: 222 ^{0}C

TABLE 48: VCM COLUMN COMPONENT FRACTION

Components	In	Mole Frac.	Top	Mole Frac.	Bottom	Mole Frac.
HCl	0.0001	7.36×10^{-8}	0.0001	1.2×10^{-7}	0	0
Butadiene	4.05	0.003	4.05	0.005	0	0
VCM	808.1689	0.6	808.16	0.995	0.0005	9.161
EDC	545.7656	0.4	0.0008	9.84×10^{-7}	545.76	0.999
Total	1357.984	1	812.21	1	545.76	1

TABLE 49: VCM COLUMN RELATIVE VOLATILITY DATA

K (Top)	K (Bottom)	Alpha (Top)	Alpha (Bottom)	Alpha Avg
3.68	8.27	22.66	8.27	15.46
0.864	3.35	5.31	3.35	4.33
1.001	3.37	6.15	3.37	4.76
0.162	0.999	1	1	1

Minimum number of stages are calculated by Fenske's Equation

Calculation of Minimum Number of Stages:

$$N_m = \frac{\log\left[\frac{x_{LK}}{x_{HK}}\right]_d \log\left[\frac{x_{HK}}{x_{LK}}\right]_b}{\log \alpha_{LK}}$$

$$N_m = 18$$

Calculation of Minimum Reflux Ratio:

$$\sum \frac{\alpha_i x_{i,f}}{\alpha_i - \theta} = 1 - q$$

$$\theta = 1.46$$

$$\sum \frac{\alpha_i x_{i,d}}{\alpha_i - \theta} = R_m + 1$$

$$R_m = 0.44$$

Here,

θ is the root of the first equation which is calculated by hit and trial, reflux ratio is selected. Theoretical number of plates are calculated from the graph below.

Number of Stages:

$$\frac{R_m}{R_m + 1} = 0.3$$

$$\frac{R}{R + 1} = 0.7$$

$$\frac{N_m}{N} = 0.88$$

N= 20 (refer to figure 10)

Feed Point:

$$\log \frac{N_r}{N_s} = 0.206 \log[(\frac{B}{D}) \left(\frac{x_{f,HK}}{x_{f,LK}}\right) \left(\frac{x_{b,LK}}{x_{d,HK}}\right)^2]$$

$N_r = 0.82\ N_s$

Hence, feed entry stage is 10.

Efficiency:

$\mu = 3.1 \times 10^{-2}$ cp

$\alpha = 4.76$

$\mu\alpha = 0.147$

Corresponding to this, $E_o = 0.83$ (refer to figure 11)

Hence actual stages: 24

Height & Diameter:

$$u_v = (-0.171 l_t^2 + 0.27 l_t \ - 0.047) \left[\frac{\rho_l - \ \rho_v}{\rho_v}\right]^{0.5}$$

$$D_C = \left(\frac{4V_w}{\pi \rho_v u_v}\right)^{0.5}$$

$\rho_L = 743.9$ kg/m^3

$\rho_V = 55.94\ kg/m^3$

$l_t = 0.6\ m$

$u_v = 0.19\ m/s$

$V_W = 43.06\ kg\ /s$

$D_c = 2.28\ m$

$H = 14.5\ m$

TABLE 50: SPECIFICATION SHEET FOR VCM COLUMN

Specification Sheet of VCM Column	
No. of Theoretical Plates	18
No. of Actual Plates	20
Type of Plates	Sieve Plates
Hole Size (mm)	4
Reflux Ratio	2.5
Column Diameter (m)	2.28
Column Height (m)	14.5

6.8 Butadiene Removal Unit [30]

6.8.1 Reaction:

$$C_4H_6 + 2H_2 \rightarrow C_4H_{10}$$

Where C_4H_6 is A, H_2 is B.

6.8.2 Calculations:

Rate Equation:

$$-r_A = kC_AC_B$$

$$\mathrm{k} = e^{6400+\frac{-323.4}{RT}} \left(\frac{m^3 of\ catalyst}{kgmole.hr}\right)$$

TABLE 51: DESIGN DATA FOR BUTADIENE REMOVAL UNIT

Property	Value
Temperature, T (K)	389
Pressure, (bar)	1
Molar Flow, HCl (kgmole/hr)	4.05
C_{Ao} (kgmole/m^3 of catalyst)	1.39×10^{-4}
C_{Bo} (kgmole/m^3 of catalyst)	2.77×10^{-4}
Conversion, X_A	0.995
Tube ID, (mm)	22.1
Tube OD, (mm)	25.4
Tube Length, (m)	6.1
Universal Gas Constant, R (kJ/kgmole.K)	8.314

From Stoichiometric equations,

$$\frac{C_{Ao}X_A}{1} = \frac{C_{Bo}X_B}{1}$$

We get, $X_A = X_B$

Using the relation,

$C_A = C_{Ao}(1 - X_A)$

Final form of the equation becomes:

$$-r_A = kC_{Ao}^2(1 - X_A)^2$$

Putting in performance equation,

$$\frac{V}{F_{Ao}} = \int_0^{X_A} \frac{dX_A}{-r_A}$$

Where V is volume of Catalyst

Volume of catalyst turns out to be:

$$25.5\ m^3$$

Number of tubes,

$$N_t \pi r^2 l = 25.5$$

$$r = 11.05mm$$

$$l = 6.1m$$

Converting to meters and solving we get

$$N_t = 12750$$

Shell Diameter

9.87m (from TEMA standards)

Pressure Drop:

Pressure drop is calculated via shell and tube equations

$$\Delta P_t = \frac{fGt^2Ln}{5.22\times10^{10}D_s\varphi_t}$$

$$\Delta P_r = \frac{4n}{s}\frac{V^2}{2g}$$

Putting in values, we get

$$\Delta P_T = 0.286\, psi$$

Which is well below the allowable pressure drop of 10 psi.

TABLE 52: SPECIFICATION SHEET FOR BUTADIENE REMOVAL UNIT

Specification Sheet of Butadiene Removal Unit	
Volume of Catalyst (m^3)	25.5
Number of Tubes	12750
Tube OD (cm)	2.54
Shell ID (m)	3.63
Length of Tubes (m)	6.09
Voidage	0.48
Density (kg/m^3)	8900
Mass of catalyst (kg)	11801

6.9 Ethylene Preheater (DCR)[32]

Heat is exchanged between the outlet stream of reactors, and inlet cold ethylene. Ethylene is at shell side and post reactor stream is at tube side. This is done to equalize mass velocities.

Data required to design the heat exchangers is given in the following tables.

TABLE 53: HOT FLUID DATA FOR ETHYLENE PREHEATER (DCR)

Hot Fluid Data	
Inlet Temp(T_1) ^0C	387.8
Exit Temp(T_2) ^0C	366.8
Mass Flow Rate(W) (kg/hr)	1.34×10^5
C_p (kJ/kg.^{0}C)	1.21
Specific gravity	12.02
Thermal Conductivity (W/m.K)	0.03
Dirt Factor(m^2. K/ W)	4.4×10^{-5}
Viscosity (Pa.s)	2.44×10^{-5}

TABLE 54: COLD FLUID DATA FOR ETHYLENE PREHEATER (DCR)

Cold Fluid Data	
Inlet Temp(t_1) ^0C	165
Exit Temp(t_2) ^0C	300
Mass Flow Rate(W) (kg/hr)	1.17×10^4
C_p (kJ/kg.^{0}C)	2.22
Specific gravity	2.68
Thermal Conductivity (W/m.K)	0.046
Dirt Factor (m^2.K/ W)	4.4×10^{-5}
Viscosity (Pa.s)	1.7×10^{-5}

TABLE 55: ETHYLENE PREHEATER EXCHANGER SPECIFICATIONS

Exchanger Data			
Shell Side		Tube Side	
ID (cm)	63.5	Number & Length (m)	238, 1.22
Baffle Space (cm)	15.24	OD (cm), BWG, & Pitch (cm)	2.54, 16, 3.18 (Square)
Passes	1	Passes	4

6.9.1 Heat Duty

$$Q = mc_p\Delta T$$

Hot Fluid Heat: 3.2 x 10^6 kJ/hr

Cold Fluid Heat: 3.2 x 10^6 kJ/hr

6.9.2 Calculation of LMTD

$$\text{LMTD} = \frac{\Delta t_2 - \Delta t_1}{2.3\log\left(\frac{\Delta t_2}{\Delta t_1}\right)}$$

LMTD = 246.74 ^{0}C

Ft = 0.95

Corrected LMTD = 234.4 ^{0}C

6.9.3 Flow Areas

Shell Side: 0.019 m^2

Tube Side: 0.022 m^2

6.9.4 Mass Velocity

$$G = \frac{m^{\cdot}}{a}$$

Shell Side: 6.1 x 10^5 kg/hr. m^2

Tube Side: 5.85 x 10^6 kg/hr. m^2

6.9.5 Reynolds Number

$$Re = \frac{DG}{\mu}$$

Shell Side: 2.5×10^5

Tube Side: 1.48×10^6

6.9.6 Obtaining j_H

$$h_0 = j_h \frac{k}{D_e} \left(\frac{c\mu}{k}\right)^{1/3} \varphi_s$$

Shell Side: 320

Tube Side: 390

6.9.7 Calculate h values

Using j_H formula, h is calculated.

$h_i = 557$ W/m^2 K

$h_o = 572$ W/m^2 K

$h_{io} = 498$ W/m^2 K

6.9.8 Get U_C

$$\text{Uc} = \frac{h_{io} h_0}{h_{io} + h_0}$$

Uc = 263 W/m^2 K

6.9.9 Get U_D

$$\frac{1}{U_D} = \frac{1}{U_C} + R$$

$U_D = 257$ W/m^2 K

6.9.10 Calculate Area

$$A = \frac{Q}{U\Delta T}$$

A =28.38 m^2

6.9.11 Calculate Pressure Drop

$$\Delta Ps = \frac{fGs^2 D_S(N+1)}{5.22\times10^{10} D_e S\ \varphi_S}$$

Shell Side Pressure Drop = 0.02 psi

$$\Delta Ps = \frac{fGs^2 D_S(N+1)}{5.22\times10^{10} D_e S\ \varphi_S}$$

Tube Side Pressure Drop: 2.91 psi

Both pressure drops are well below the acceptable limits of 10 psi.

CHAPTER 7

SIMULATION

The entire process was simulated on Aspen HYSYS using Peng Robinson as the fluid package because we were dealing with pressures higher than 10 bar to verify results which were obtained manually, and to opt for some process conditions by hit and trial method. Most important results to be verified were:

1. Verification of output of reactors
2. Verification of distillation column parameters

Some simplifications that were employed are:

- Multi tubular reactor was not present in HYSYS so simulation was done via PFR
- Furnace was unavailable, so it was also simulated as a PFR

7.1 Results

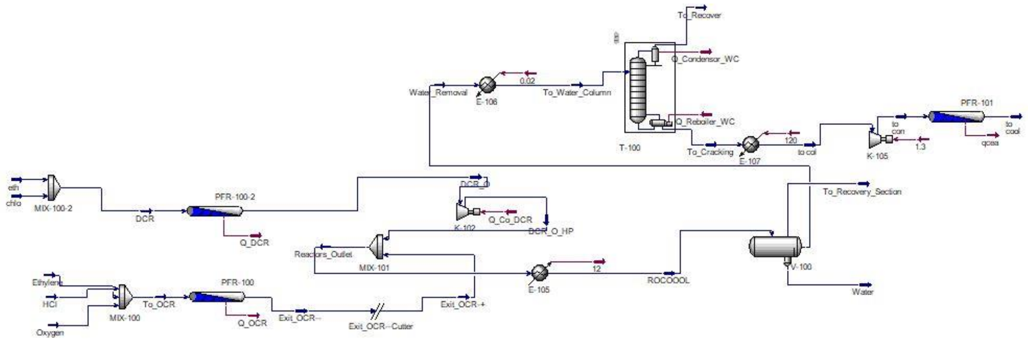


FIGURE 12: PLANT SIMULATION PART 1

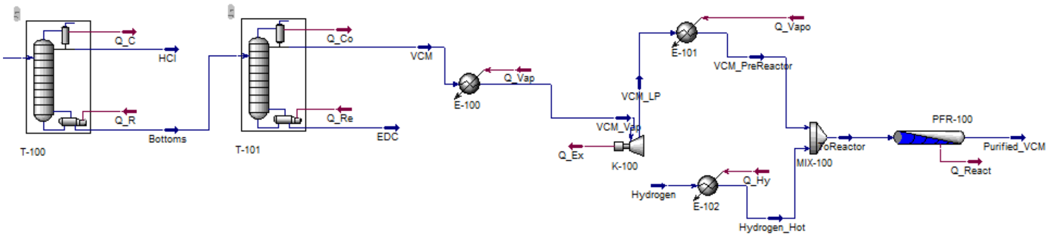


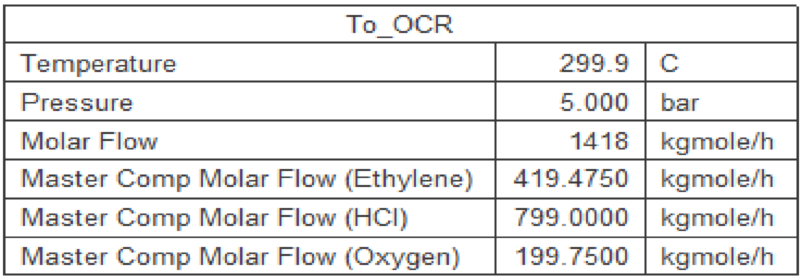
FIGURE 13: PLANT SIMULATION PART 2

First of all, manual calculations and simulation results are compared.

7.1.1 Oxychlorination Reactor

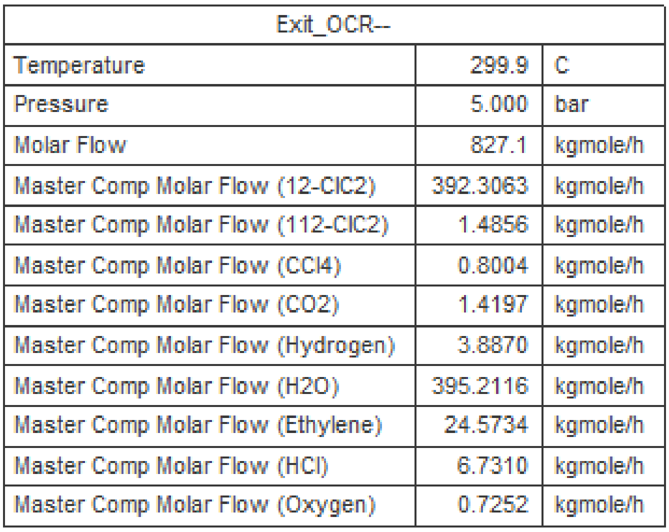
TABLE 56: MATERIAL BALANCE ON OCR DONE MANULALLY

Component	In (kgmole/hr)	Out (kgmole/hr)
C_2H_4	444.15	21.92
Cl_2	423	0.1269
$C_2H_4Cl_2$	0	421
$C_2H_3Cl_3$	0	0.6343
HCl	0	0.6343



To_OCR		
Temperature	299.9	C
Pressure	5.000	bar
Molar Flow	1418	kgmole/h
Master Comp Molar Flow (Ethylene)	419.4750	kgmole/h
Master Comp Molar Flow (HCl)	799.0000	kgmole/h
Master Comp Molar Flow (Oxygen)	199.7500	kgmole/h

FIGURE 14: MATERIAL BALANCE ON OCR (IN) SIMULATION RESULTS



Exit_OCR--		
Temperature	299.9	C
Pressure	5.000	bar
Molar Flow	827.1	kgmole/h
Master Comp Molar Flow (12-ClC2)	392.3063	kgmole/h
Master Comp Molar Flow (112-ClC2)	1.4856	kgmole/h
Master Comp Molar Flow (CCl4)	0.8004	kgmole/h
Master Comp Molar Flow (CO2)	1.4197	kgmole/h
Master Comp Molar Flow (Hydrogen)	3.8870	kgmole/h
Master Comp Molar Flow (H2O)	395.2116	kgmole/h
Master Comp Molar Flow (Ethylene)	24.5734	kgmole/h
Master Comp Molar Flow (HCl)	6.7310	kgmole/h
Master Comp Molar Flow (Oxygen)	0.7252	kgmole/h

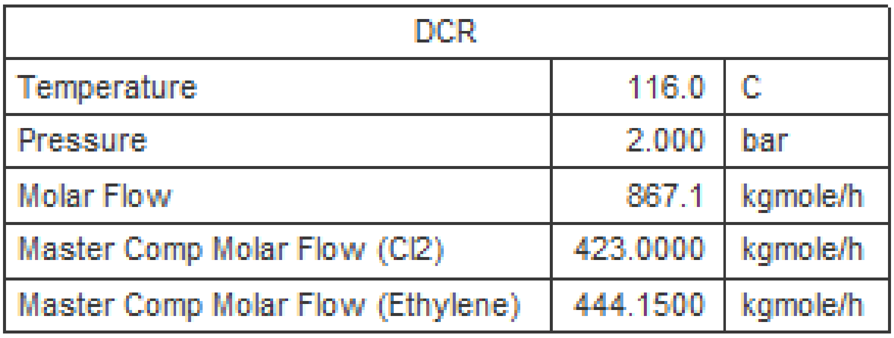
FIGURE 15: MATERIAL BALANCE ON OCR (OUT) SIMULATION RESULTS

The values show a very little difference, hence confirming the kinetics of the reaction. Secondly, to cater for the catalyst, heterogenous catalytic reaction was employed. Catalyst data was also fed to the plug flow reactor, as well as its sizing. Similar results will be shared for each reactor.

7.1.2 Direct Chlorination Reactor

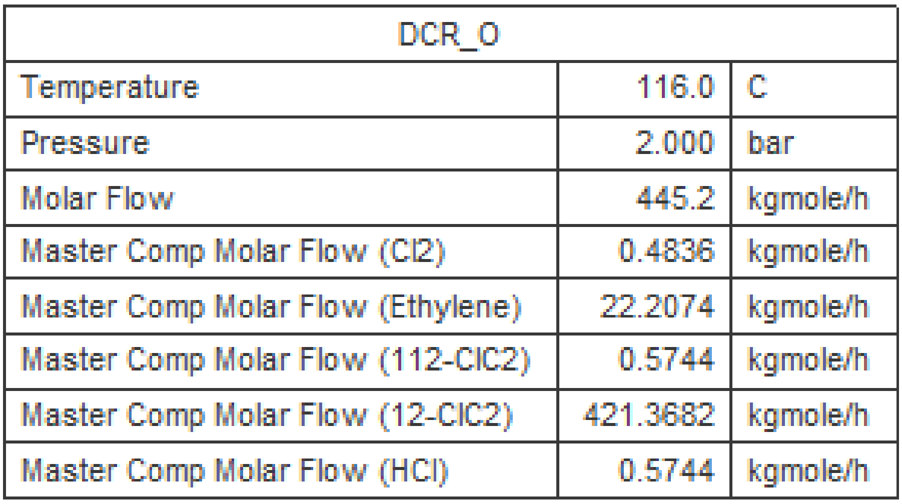
TABLE 57: MATERIAL BALANCE ON DCR DONE MANUALLY

Component	In (kgmole/hr)	Out (kgmole/hr)
C_2H_4	444.15	21.92
Cl_2	423	0.1269
$C_2H_4Cl_2$	0	421
$C_2H_3Cl_3$	0	0.6343
HCl	0	0.6343



DCR		
Temperature	116.0	C
Pressure	2.000	bar
Molar Flow	867.1	kgmole/h
Master Comp Molar Flow (Cl2)	423.0000	kgmole/h
Master Comp Molar Flow (Ethylene)	444.1500	kgmole/h

FIGURE 16: MATERIAL BALANCE ON DCR (IN) SIMULATION RESULTS



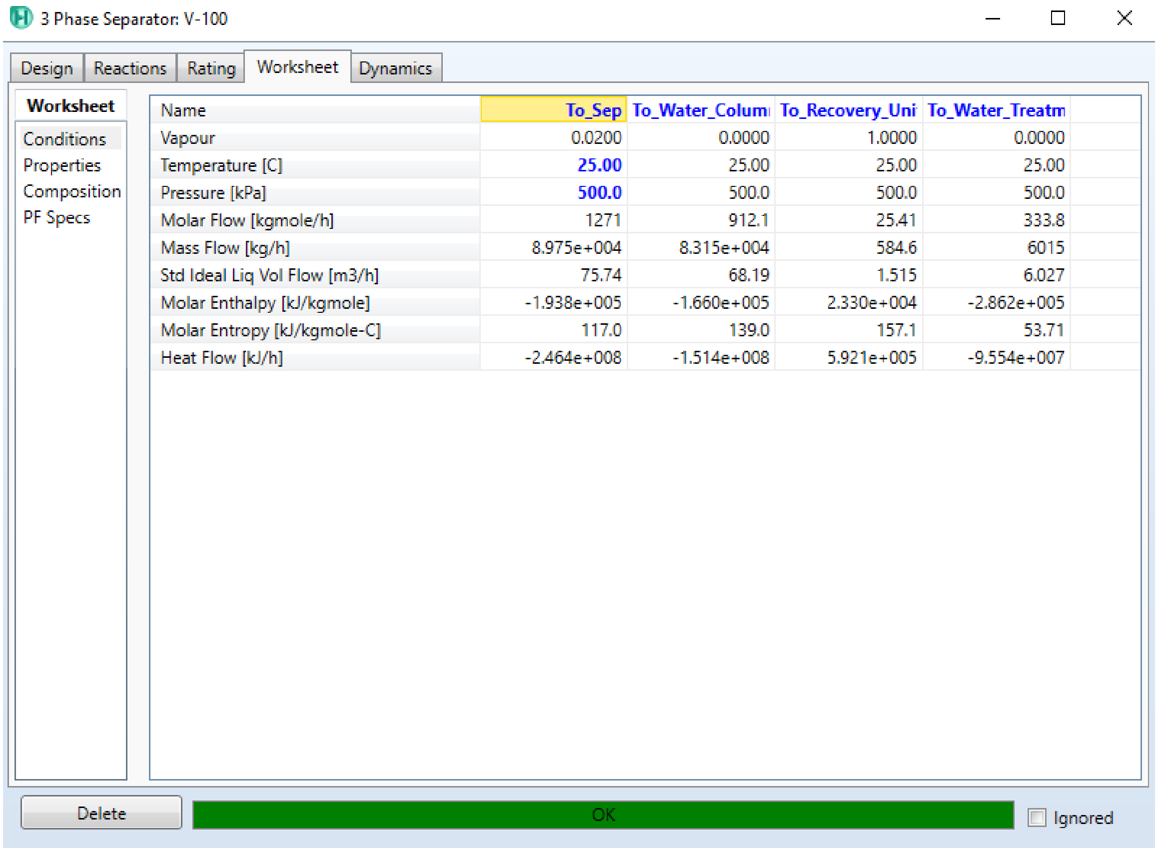
DCR_O		
Temperature	116.0	C
Pressure	2.000	bar
Molar Flow	445.2	kgmole/h
Master Comp Molar Flow (Cl2)	0.4836	kgmole/h
Master Comp Molar Flow (Ethylene)	22.2074	kgmole/h
Master Comp Molar Flow (112-ClC2)	0.5744	kgmole/h
Master Comp Molar Flow (12-ClC2)	421.3682	kgmole/h
Master Comp Molar Flow (HCl)	0.5744	kgmole/h

FIGURE 17: MATERIAL BALANCE ON DCR (OUT) SIMULATION RESULTS

In this reactor as well, the results are comparable and have a very little difference.

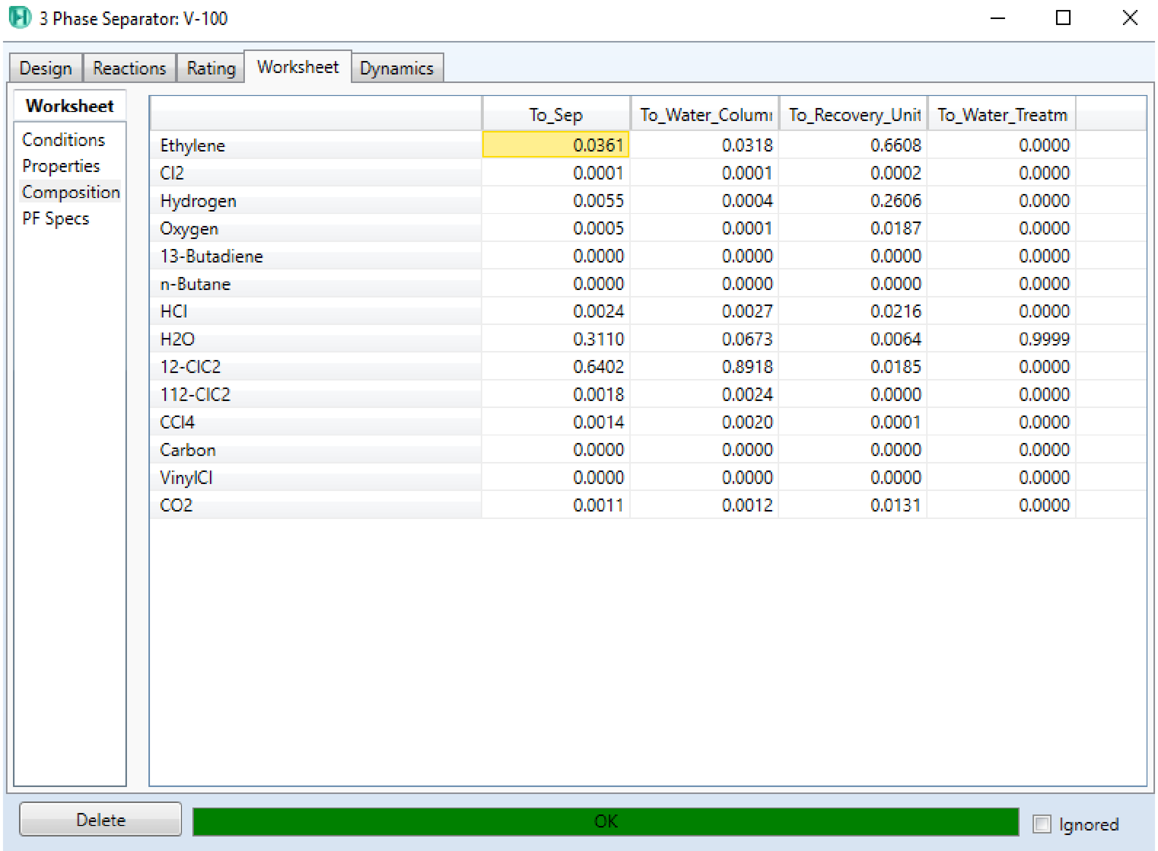
7.1.3 Three Phase Separator

In three phase separator, operating condition were selected by hit and trial, to give maximum concentration of EDC in light liquid stream while keeping the other two streams low in concentration of EDC.



Name	To_Sep	To_Water_Colum	To_Recovery_Uni	To_Water_Treatm
Vapour	0.0200	0.0000	1.0000	0.0000
Temperature [C]	25.00	25.00	25.00	25.00
Pressure [kPa]	500.0	500.0	500.0	500.0
Molar Flow [kgmole/h]	1271	912.1	25.41	333.8
Mass Flow [kg/h]	8.975e+004	8.315e+004	584.6	6015
Std Ideal Liq Vol Flow [m3/h]	75.74	68.19	1.515	6.027
Molar Enthalpy [kJ/kgmole]	-1.938e+005	-1.660e+005	2.330e+004	-2.862e+005
Molar Entropy [kJ/kgmole-C]	117.0	139.0	157.1	53.71
Heat Flow [kJ/h]	-2.464e+008	-1.514e+008	5.921e+005	-9.554e+007

FIGURE 18: THREE-PHASE SEPARATOR OPERATING CONDITONS OBTAINED FROM SIMULATION

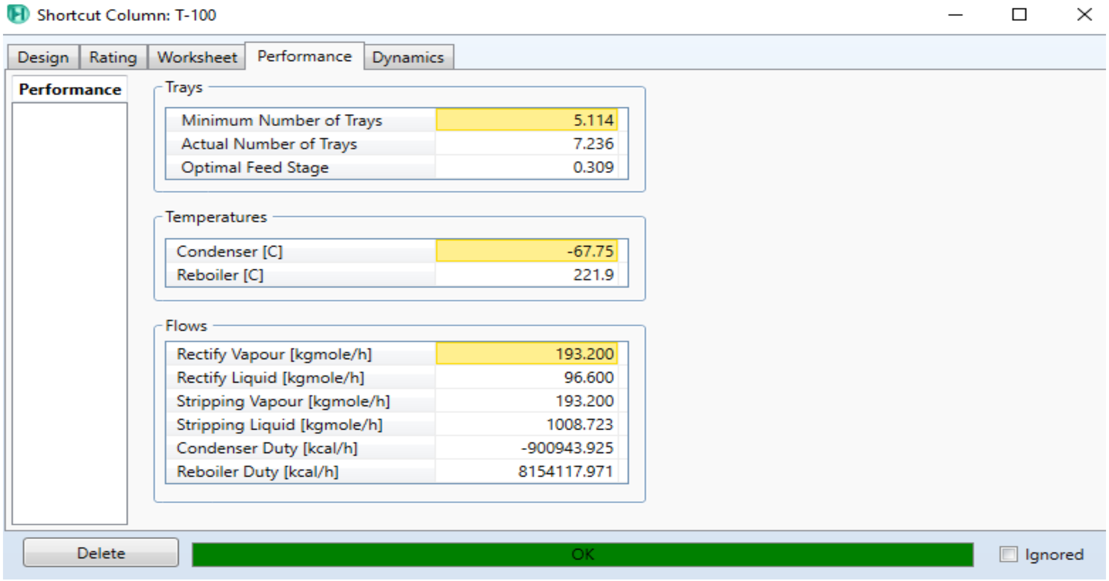


	To_Sep	To_Water_Colum	To_Recovery_Unit	To_Water_Treatm
Ethylene	0.0361	0.0318	0.6608	0.0000
Cl2	0.0001	0.0001	0.0002	0.0000
Hydrogen	0.0055	0.0004	0.2606	0.0000
Oxygen	0.0005	0.0001	0.0187	0.0000
13-Butadiene	0.0000	0.0000	0.0000	0.0000
n-Butane	0.0000	0.0000	0.0000	0.0000
HCl	0.0024	0.0027	0.0216	0.0000
H2O	0.3110	0.0673	0.0064	0.9999
12-ClC2	0.6402	0.8918	0.0185	0.0000
112-ClC2	0.0018	0.0024	0.0000	0.0000
CCl4	0.0014	0.0020	0.0001	0.0000
Carbon	0.0000	0.0000	0.0000	0.0000
VinylCl	0.0000	0.0000	0.0000	0.0000
CO2	0.0011	0.0012	0.0131	0.0000

FIGURE 19: THREE PHASE SEPARATOR OUTLET COMPOSITION (SIMULATION)

The results show that at 25 ^{0}C and 5 bar, it gives acceptable results keeping composition of EDC as a reference.

7.1.4 Distillation Column (EDC Purification)



Trays

Minimum Number of Trays	5.114
Actual Number of Trays	7.236
Optimal Feed Stage	0.309

Temperatures

Condenser [C]	-67.75
Reboiler [C]	221.9

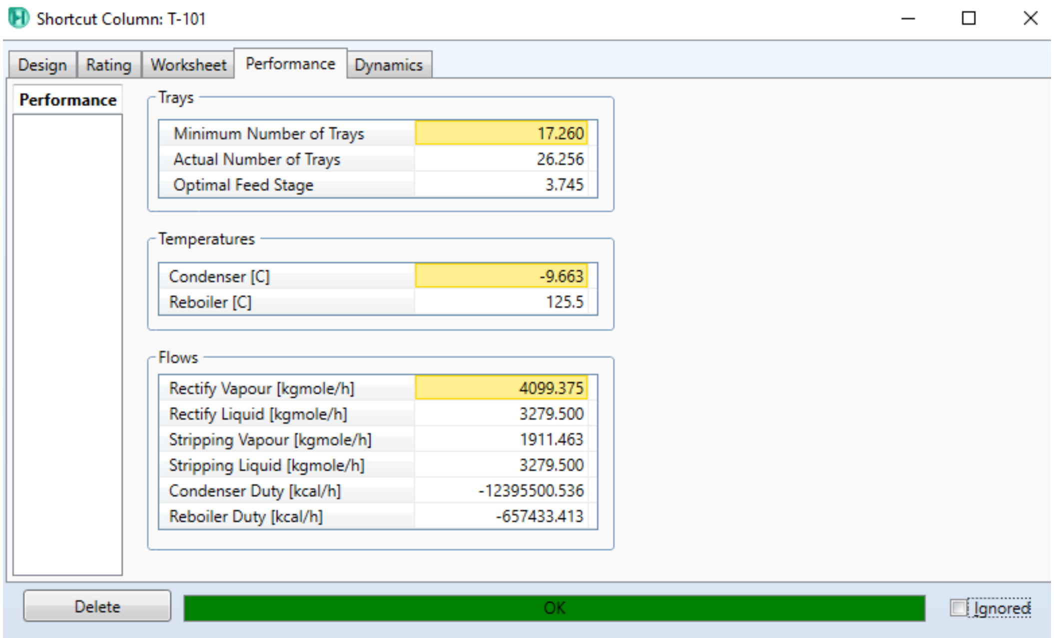
Flows

Rectify Vapour [kgmole/h]	193.200
Rectify Liquid [kgmole/h]	96.600
Stripping Vapour [kgmole/h]	193.200
Stripping Liquid [kgmole/h]	1008.723
Condenser Duty [kcal/h]	-900943.925
Reboiler Duty [kcal/h]	8154117.971

FIGURE 20: DISTILLATION COLUMN (EDC PURIFICATION) SIMULATION RESULTS

For this distillation column, the results were quite different from the calculated values. The reason being, a huge difference in volatility of the components throughout the column. These types of multicomponent systems require rigorous computer models to solve, hence cannot be solved by the classical methods. Design of this distillation column is given in the design section.

7.1.5 HCl Column



Trays

Minimum Number of Trays	17.260
Actual Number of Trays	26.256
Optimal Feed Stage	3.745

Temperatures

Condenser [C]	-9.663
Reboiler [C]	125.5

Flows

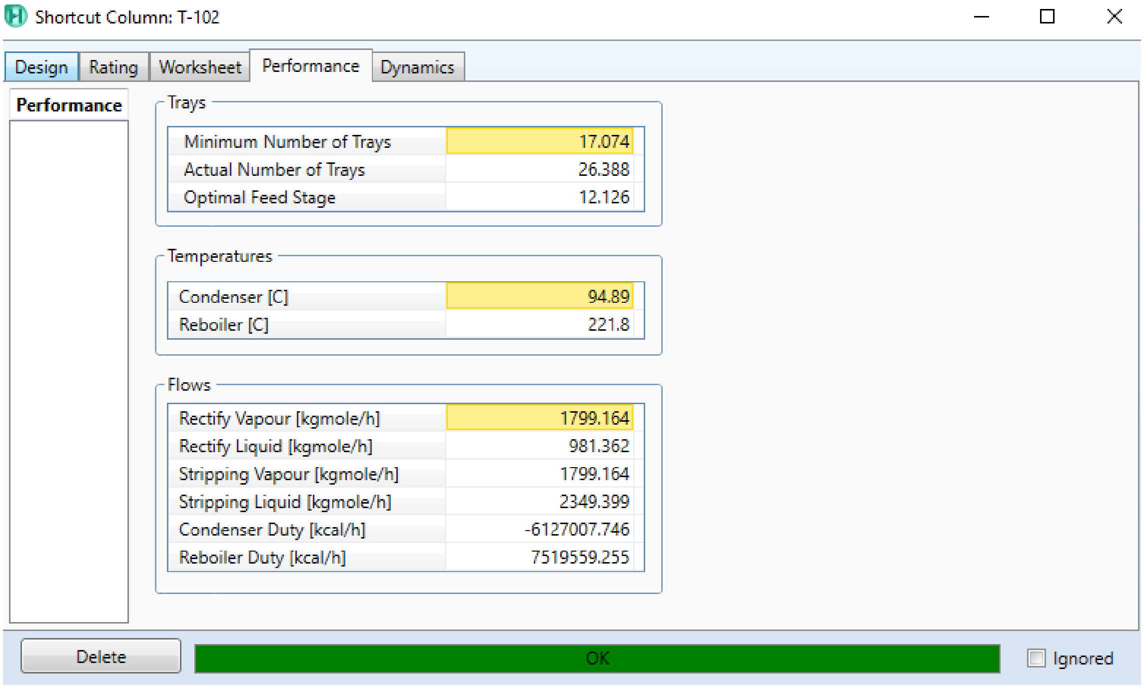
Rectify Vapour [kgmole/h]	4099.375
Rectify Liquid [kgmole/h]	3279.500
Stripping Vapour [kgmole/h]	1911.463
Stripping Liquid [kgmole/h]	3279.500
Condenser Duty [kcal/h]	-12395500.536
Reboiler Duty [kcal/h]	-657433.413

FIGURE 21: HCL COLUMN SIMULATION RESULTS

The results of this column are comparable. The reason being the relative volatility of the components throughout the column do not vary. Therefore, the methods applied give comparable results to the distillation column.

7.1.6 VCM Column

The results of this column are also comparable to the results calculated manually, the reason being the same, smaller difference in relative volatility throughout the column.



Minimum Number of Trays	17.074
Actual Number of Trays	26.388
Optimal Feed Stage	12.126

Condenser [C]	94.89
Reboiler [C]	221.8

Rectify Vapour [kgmole/h]	1799.164
Rectify Liquid [kgmole/h]	981.362
Stripping Vapour [kgmole/h]	1799.164
Stripping Liquid [kgmole/h]	2349.399
Condenser Duty [kcal/h]	-6127007.746
Reboiler Duty [kcal/h]	7519559.255

FIGURE 22: VCM COLUMN SIMULATION RESULTS

7.2 Why Compare the Results?

HYSYS is a white box model, i.e. whatever it calculates, is based on a mathematical model derived from various branches of chemical engineering such as thermodynamics, heat transfer, mass transfer, fluid mechanics and the list is long. During manual calculations, we apply the very same models, or variants of the model, therefore, our results should be comparable to the HYSYS simulation results, if not comparable, there should be a logical explanation for it.

CHAPTER 8

CONTROL AND INSTRUMENTATION [33]

The assumptions we take during calculations are not applicable in industry and corrections are made. Similarly, process variables do not remain constant and vary due to disturbances, foreseen or unforeseen. But it is required to maintain the process variables at their desired values. For this reason, control loops and control systems are installed in industry, to reject the disturbance by varying any other process variable which will help in maintaining the process variable at set point.

VCM plant is no different from other plants, therefore control loops are applied on main components of the Process Flow Diagram. Along with applying control loops, transfer functions are derived, and response of the controllers is simulated on Simulink.

8.1 Control Loop on Direct Chlorination Reactor

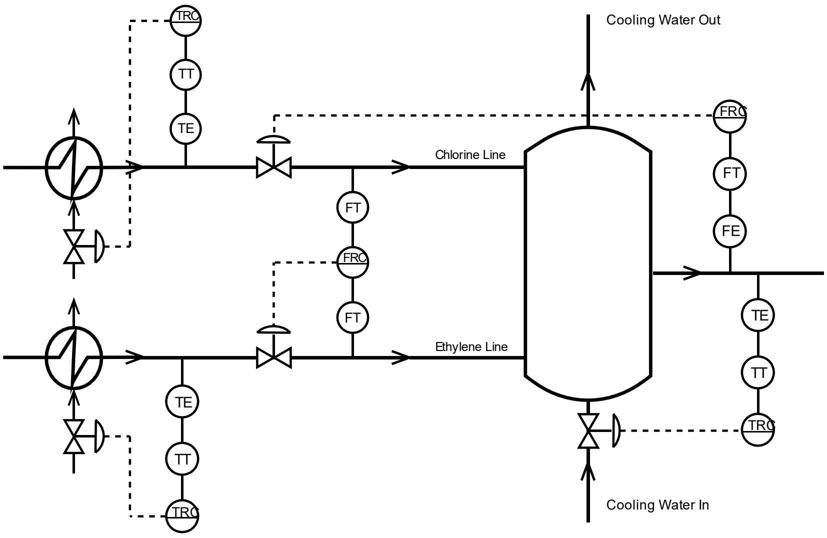


FIGURE 23: CONTOL LOOPS ON DCR

Here temperature control loops are applied on heat exchangers. The control loops maintain the temperature of reactants at 116^0C by manipulating the inflow of heating medium.

Ratio control loop is applied on the raw materials line of this reactor. It maintains a specific ratio between the reactants. It regulates the flow of ethylene relative to chlorine, the limiting reactant.

Temperature and flow control loops are applied on the reactor. In temperature control loop, the outlet temperature is sensed, and the coolant flow rate is accordingly regulated. For flow control, the loop senses the outlet flow rate and manipulates the flow of chlorine only, as flow of ethylene is controlled accordingly with respect to chlorine's flow.

8.2 Control Loop on Oxychlorination Reactor

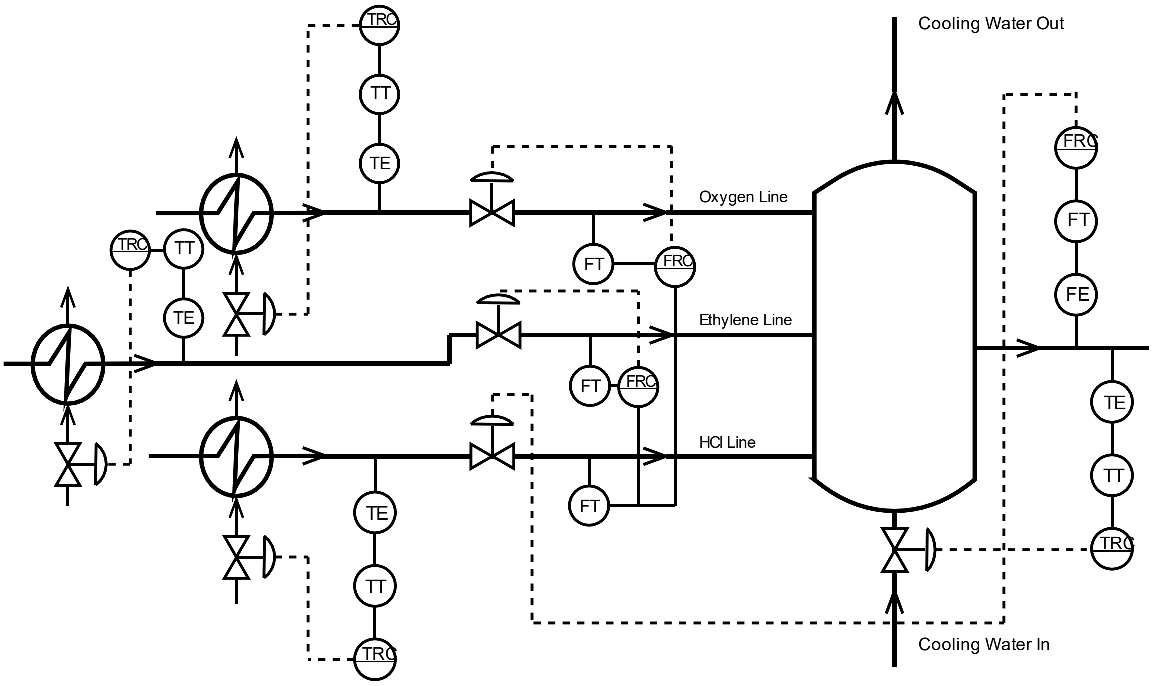


FIGURE 24: CONTROL LOOPS ON OCR

In similar fashion, control loops are applied on oxychlorination reactor. The difference is in ratio control. Here a specific ratio is maintained between HCl and Oxygen, and HCl and Ethylene, i.e. two ratio control loops are applied.

Temperature control loop is identical to that of direct chlorination reactor. In flow control loop, the manipulated variable in this case is HCl, as it is the limiting reactant, and relative to its flow, other raw materials' flows are adjusted.

8.3 Control Loop on Three-Phase Separator

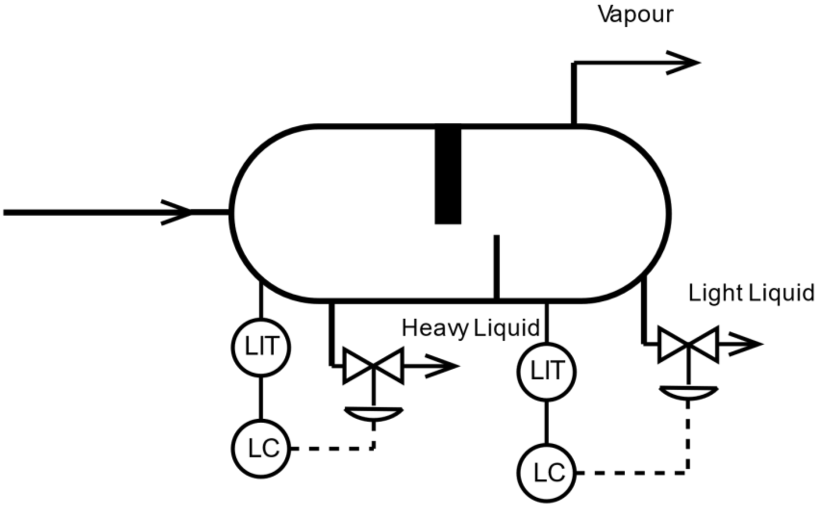


FIGURE 25: LEVEL CONTROL LOOPS ON THREE-PHASE SEPARATOR

Two level control loops are applied on three-phase separator. Both control loops control level, one senses the level of light liquid, other senses the level of heavy liquid. The controllers are fed with certain set points; they operate the outlet valve to maintain that value of level inside the separator.

8.4 Control Loop on Distillation Column

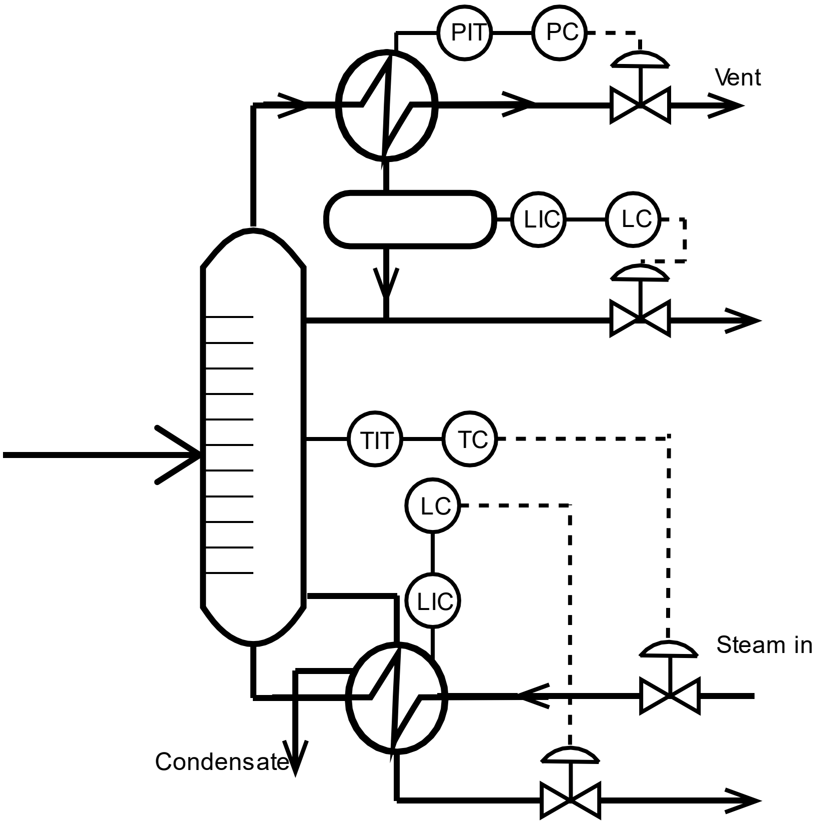


FIGURE 26: CONTROL LOOPS ON DISTILLATION COLUMN

Pressure control loop is applied on condenser, pressure sensor senses pressure, feeds it to the controller and controller acts accordingly. If pressure gets exceedingly high, a vent valve is opened, and gases are vented into a tank.

Level control loop is applied on accumulator, where it controls the level of liquid in the accumulator. To maintain the liquid level, it manipulates the outlet flow rate of top product.

In similar fashion, level controller is installed on reboiler, which maintains the liquid flow rate by controlling the bottoms product outflow rate. Temperature control for the interior of distillation column is applied, where it senses temperature, and accordingly manipulates flow of steam into the reboiler.

8.5 Simulating Controllers’ Response

Temperature, Flow and Pressure control loops were applied on a heat exchanger. Level control loop was applied on three-phase separator. For each of them, sensor and process transfer functions were derived, the model was simulated on Simulink and results were obtained.

8.5.1 Temperature Control Loop

Consider the following temperature control loop:

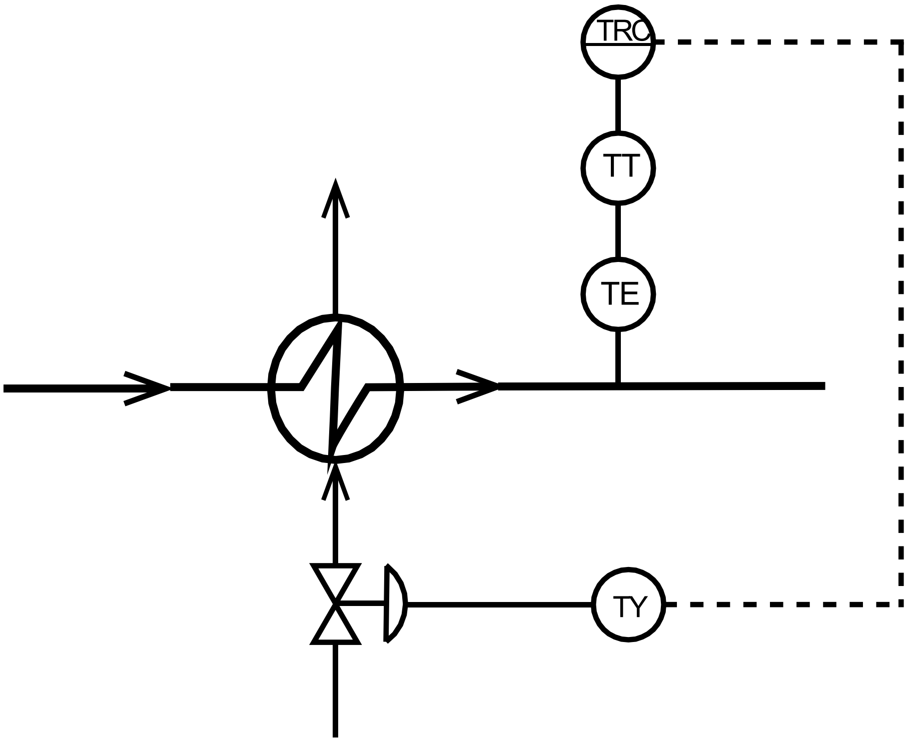


FIGURE 27: TEMPERATURE CONTROL LOOP ON HEAT EXHCENGER (ETHYLENE PREHEATER)

This is a temperature control loop; which controls exit temperature of the process stream by manipulating heating medium's inlet flow rate. Process and sensor transfer functions are derived below for this loop.

8.5.1.1 Sensor Transfer Function

Applying Energy Balance:

$$hA(x\text{-}y) - 0 = mC\frac{dy}{dt}$$

$$x - y = \frac{mC}{hA}\frac{dy}{dt}$$

$$\tau = \frac{mC}{hA}$$

x = Fluid Temperature, y = Sensor Temperature

After introducing deviation variables, and taking Laplace transform on both sides we get,

$$X(s) - Y(s) = \tau(sY(s) - Y(0)) \qquad Y(0) = 0$$

After solving we get:

$$\frac{Y(s)}{X(s)} = \frac{1}{\tau s + 1}$$

For typical industrial temperature sensors, τ = 0.1 s

8.5.1.2 Process Transfer Function

Applying energy balance:

$$\dot{m}C(T_i - T) + q = mC\frac{dT}{dt}$$

$$(T_i - T) + \frac{q}{m\,C} = \frac{mC}{m\cdot C}\frac{dT}{dt}$$

T_i = inlet temp. (is constant)

T = outlet temp.

Q = heat provided by the heating medium

Inserting deviation variables, we get:

$$-T' + \frac{Q}{m\,C} = \tau\frac{dT'}{dt}$$

Taking Laplace transform, we get:

$$-T'(s) + \frac{Q(s)}{m.C} = \tau(sT'(s) - T'(0)) \qquad T'(0) = 0$$

After solving we get:

$$\frac{T'(s)}{Q(s)} = \frac{1/_{m\cdot C}}{\tau s + 1}$$

From the process data we get $1/_{m\cdot C} = 0.00005\ K.s/kJ$

Similarly, $\tau = \frac{m}{m\cdot} = \frac{V}{V\cdot} = 0.008\ s$

8.5.1.3 Simulink Model

A Simulink model is developed for this control loop, which includes PID controller, Sensor transfer function, Process transfer function, Step change, which introduces abrupt change into the system, Comparator, which measures error, by comparing set point and measures value, and scope, which displays the response of the controller. Values calculated previously are fed into the transfer functions.

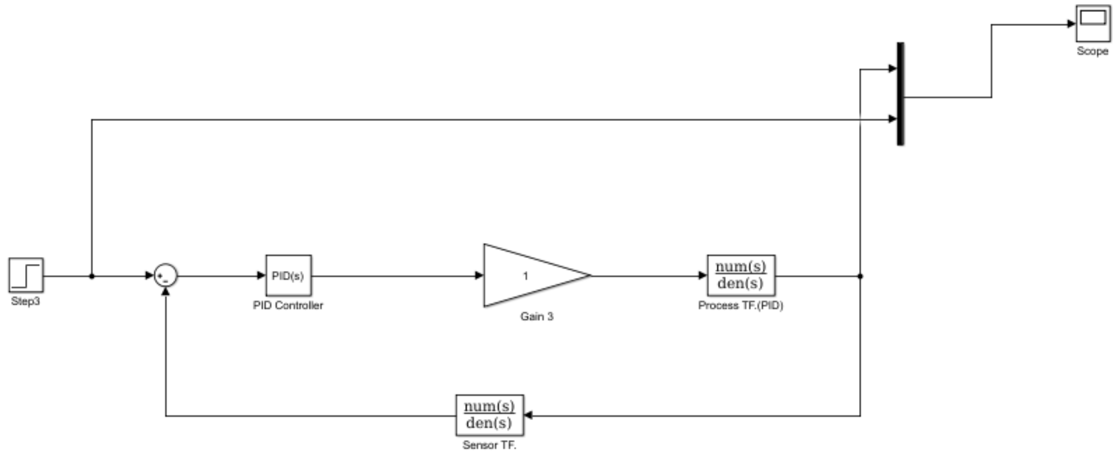


FIGURE 28: SIMULINK MODEL OF TEMPERATURE CONTROL LOOP

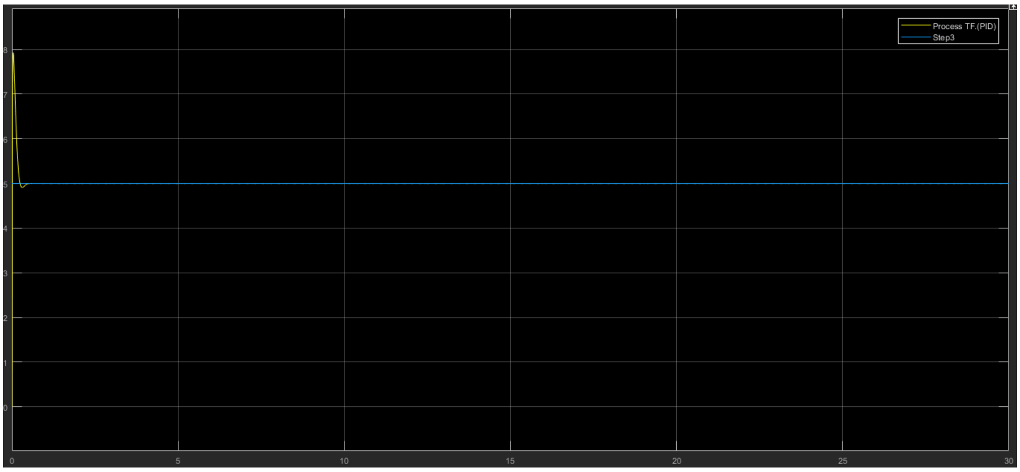


FIGURE 29: RESPONCE OF TEMPERATURE CONTROL LOOP TO STEP CHANGE

The PID controller was autotuned, and the following values are obtained:

P = 3.018 x 10^4, I = 5.103 x 10^5, D = 70.54

8.5.2 Flow Control Loop

Consider the following flow control loop:

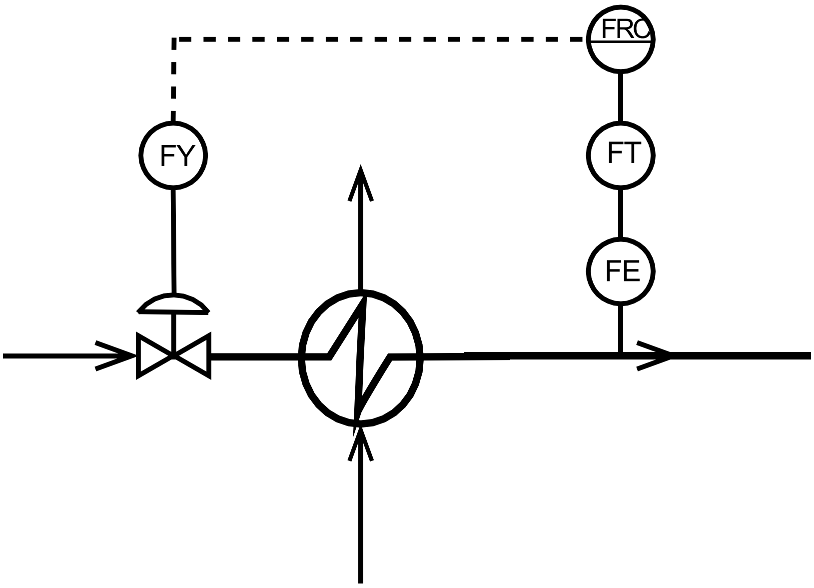


FIGURE 30: FLOW CONTROL LOOP ON HEAT EXCHANGER (ETHYLENE PREHEATER)

In this control loop, heat exchanger's outlet flow is sensed via a flow sensor, it is transmitted to flow recording controller, which accordingly sends signal to lift or force the actuator.

8.5.2.1 Sensor Transfer Function

Turbine type flow sensor is used.

Applying mass balance:

$$\rho x - \rho y = \rho \frac{dV}{dt}$$

$$dV = \beta dT - \kappa dP$$

dT = 0 as temperature change of the fluid remains the same. After substitution we get:

$$x - y = -\kappa \frac{dP}{dt}$$

Where x is inlet flow rate, y is outlet flow rate. P is the pressure with which the fluid impinges on the turbine's vanes. Also, $y = \frac{P}{R}$, where R is the resistance faced by

After introducing deviation variables and taking Laplace transform, we get:

$$X(s) - \frac{P'(s)}{R} = -\kappa(P'(s) - P(0))$$

After simplifying, we get:

$$\frac{P'(s)}{X(s)} = \frac{R}{\tau s + 1}$$

Here τ = -κR, and R has the units of pressure.

Taking τ = 0.1s, and R= 0.01 kPa.

8.5.2.2 Process Transfer Function

Applying mass balance on the heat exchanger:

$$\rho q - \rho q_o = \rho \frac{dV}{dt}$$

Where q is inlet flow rate and q_o is outlet flow rate.

Also, $q_o = \frac{V}{\tau}$

$$q - \frac{V}{\tau} = \frac{dV}{dt}$$

Taking Laplace transform, and simplifying, we get:

$$\frac{V(s)}{Q(s)} = \frac{\tau}{\tau s + 1}$$

As $\frac{V(s)}{\tau} = Q_o(s)$, so the final equation becomes:

$$\frac{Q_o(s)}{Q(s)} = \frac{1}{\tau s + 1}$$

Here, $\tau = \frac{m}{m^{\cdot}} = \frac{V}{V^{\cdot}}$ = 0.008s

8.5.2.3 Simulink Model

A Simulink model was developed, similar to that of temperature control loop. All the components of the model were identical to that of the temperature control loop model. Difference lies in the variable’s values which are changed accordingly. The Simulink model is given below:

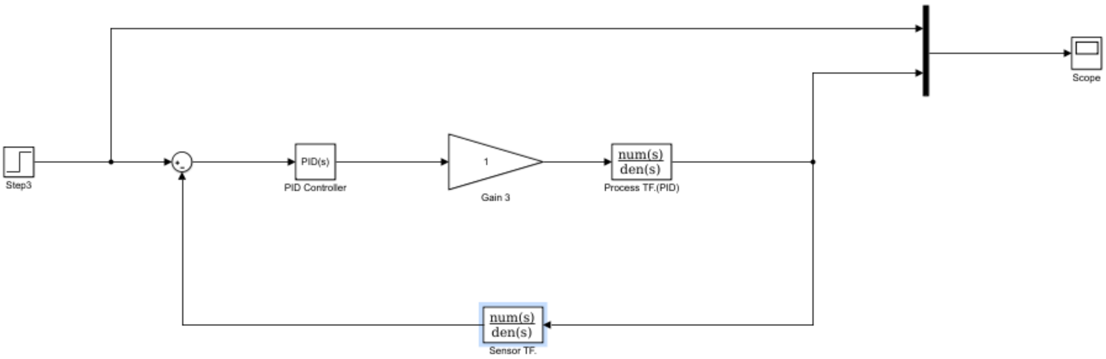


FIGURE 31: SIMULINK MODEL OF FLOW CONTROL LOOP

Here, value of gain is 1, as two similar quantities are compared in the process transfer function. It is also supported by the final form of process transfer function, as its numerator is 1.

In the case of sensor transfer function, gain, the numerator value, isn't 1, and has a value (R), because different physical quantities are compared.

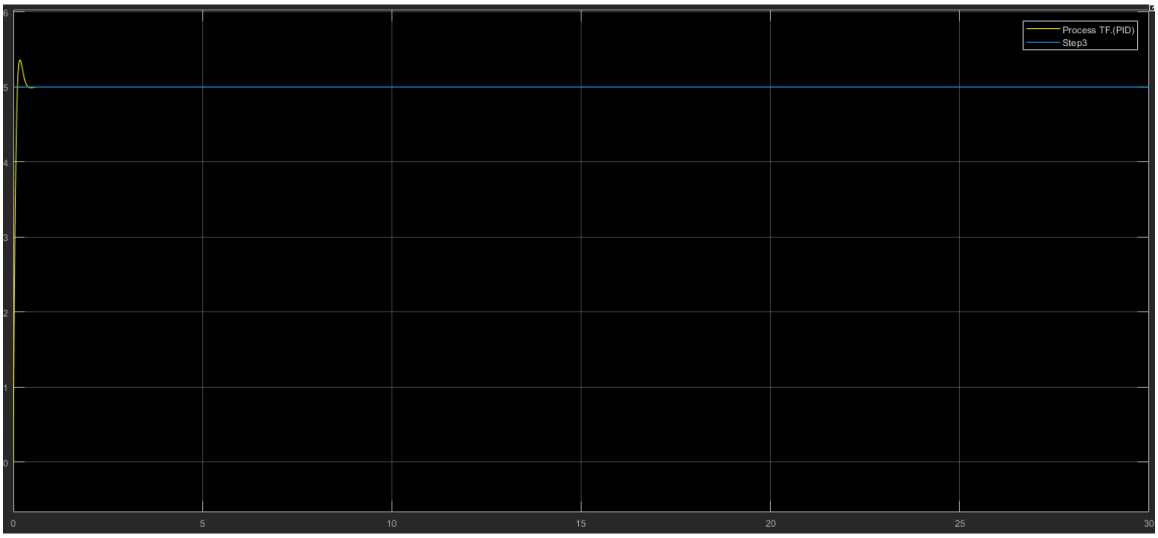


FIGURE 32: RESPONCE OF CONTROLLER TO A STEP CHANGE

The results show that the loop instantly responds to the step change introduced. And within few units of time, achieves the new set point. The blue line is step change introduced, and yellow line is the response of the controller. The PID controller was autotuned, and the values of P, I and D are 150.9, 2552 and 0.3527 respectively.

8.5.3 Pressure Control Loop

Consider the following pressure control loop:

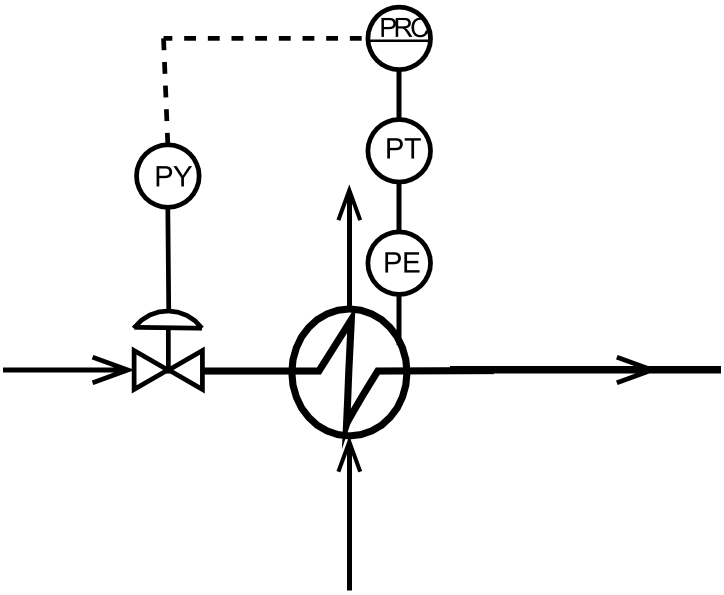


FIGURE 33: PRESSURE CONTROL LOOP ON HEAT EXCHANGER (ETHYLENE PREHEATER)

Pressure of the fluid is sensed at the shell side, it is transmitted to the controller, which sends a signal accordingly to adjust the actuator. The pressure inside the shell is entirely due to the fluid present in it. If the pressure varies from the desired value, the valve is adjusted to adjust the flow of the fluid into the exchanger, consequently adjusting the pressure. Pressure safety valves are installed, in case the pressure exceeds a specific value.

8.5.3.1 Sensor Transfer Function

Capacitive cell type sensor is used.

Applying force balance:

$$P_1A^{\cdot} - P_2A^{\cdot} = A\frac{dP_2}{dt}$$

Where P_1 is the pressure on capacitive cell and P_2 is the pressure the cell transmits. Simplifying, we get:

$$P_1 - P_2 = \tau\frac{dP_2}{dt}$$

Where $\tau = \frac{A}{A\cdot}$, applying Laplace transform, and simplifying, the final form becomes:

$$\frac{P_2'(s)}{P_1'(s)} = \frac{1}{\tau s + 1}$$

Here τ = 0.1s

8.5.3.2 Process Transfer Function

Applying mass balance on the heat exchanger:

$$\rho q - \rho q_o = \rho \frac{dV}{dt}$$

Where q is inlet flow rate and q_o is outlet flow rate.

$$dV = \beta dT - \kappa dP$$

dT = 0 as temperature change of the fluid remains the same. After substitution we get:

$$q - q_o = -\kappa \frac{dP}{dt}$$

Here $q_o = \frac{P}{R}$

$$q - \frac{P}{R} = -\kappa \frac{dP}{dt}$$

Introducing deviation variables, taking Laplace transform and simplifying the equation we get:

$$\frac{P'(s)}{Q(s)} = \frac{R}{\tau s + 1}$$

Where $\tau = -\kappa R = 0.4\ s, R = 4000\ Pa.s,\ \kappa = 1\ x\ 10^{-5}\ Pa^{-1}$

8.5.3.3 Simulink Model

Pressure control loop was simulated on Simulink. Identical components to that of the previous control loops were employed. Here value of gain wasn't 1 as two different quantities were compared i.e. pressure and flow rate. Here value of gain was the value of R.

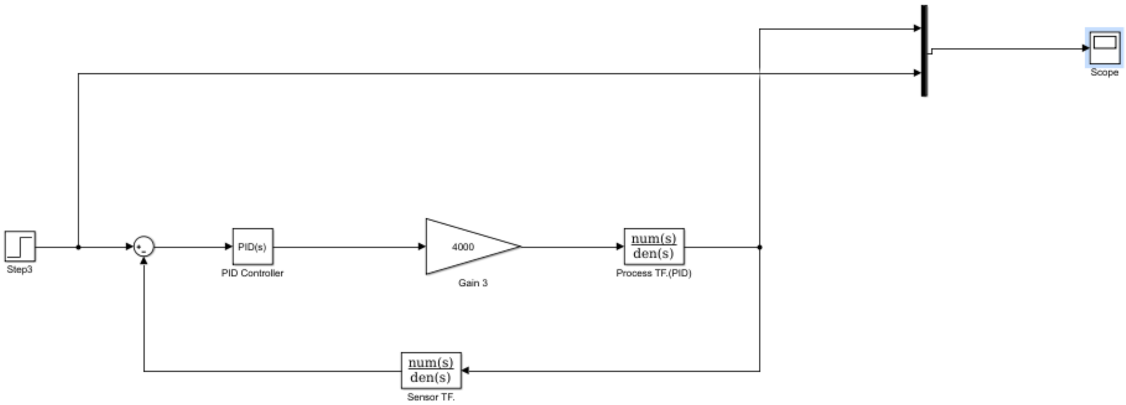


FIGURE 34: SIMULINK MODEL FOR PRESSURE CONTROL LOOP

With a very high value of gain i.e. 4000, lower values of the parameters of PID controller were expected while autotuning. The results are shown below and are as anticipated.

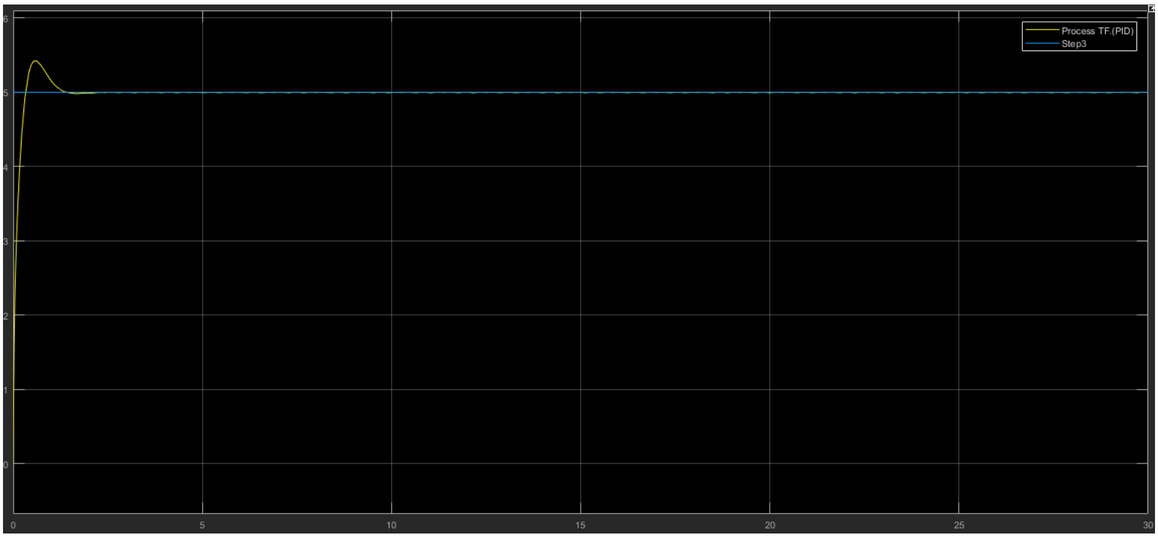


FIGURE 35: CONTROLLER RESPONCE TO A STEP CHANGE

The controller rapidly achieves the new set point, in less than five units of time. One reason for the rapid response is the higher value of gain. A negligible offset is also observed. The values of P, I and D are obtained using autotuning. The values are 0.0005144, 0.001712 and 2.821 x 10^{-5} for P, I and D respectively.

8.5.4 Level Control Loop

Consider the following level control loop:

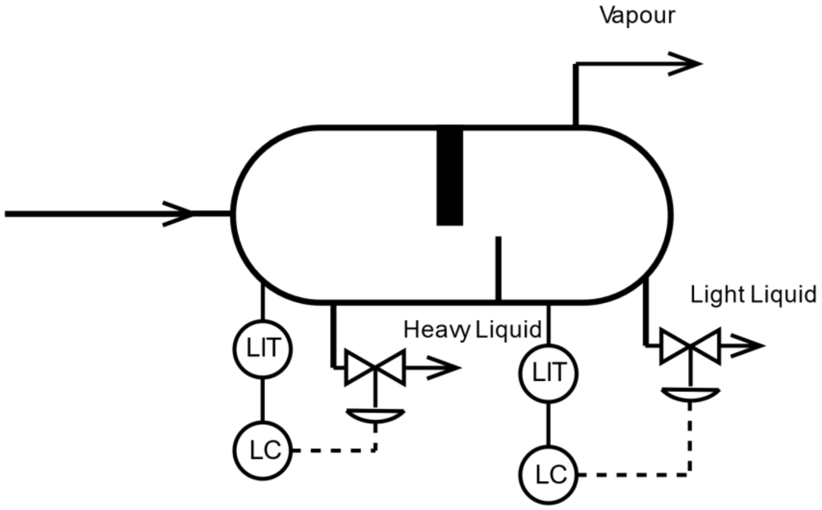


FIGURE 36: LEVEL CONTROL LOOP ON THREE-PHASE SEPARATOR

Level control loop simulation will be carried out for light liquid level control. Here, Liquid level is sensed and transmitted to the controller, which acts accordingly to maintain a certain level by varying the percentage opening of the valve.

8.5.4.1 Sensor Transfer Function

Capacitive type sensor used

Applying mass balance:

$$\rho q - \rho q_o = \rho A \frac{dh}{dt}$$

Where q is inlet flow rate, q_o is outlet flow rate, H is the height sensed by the sensor and A is the area in of liquid in contact with air. Also $q_o = \frac{h}{R}$.

$$q - \frac{h}{R} = A \frac{dh}{dt}$$

Introducing deviation variables, taking Laplace transform and simplifying the equation we get:

$$\frac{H(s)}{Q(s)} = \frac{R}{\tau s + 1}$$

Here $\tau = RA = 0.1s \ and \ R = 1 \ s/m^2$

8.5.4.2 Process Transfer Function

Applying material balance on three-phase separator:

$$\rho q - \rho q_o = \rho A \frac{dH}{dt}$$

Where q is inlet flow rate, q_o is outlet flow rate, H is the height or level of the light liquid and A is the area in of liquid in contact with air. Also $q_o = \frac{H}{R}$. Here A = diameter of vessel * half of the length of the vessel.

$$q - \frac{H}{R} = A\frac{dH}{dt}$$

Introducing deviation variables, taking Laplace transform and simplifying the equation we get:

$$\frac{H(s)}{Q(s)} = \frac{R}{\tau s + 1}$$

Here $\tau = RA = 0.62s \; and \; R = 2\; s/m^2$ and A = d*0.5l = 0.31 m^2

8.5.4.3 Simulink Model

Level control loop for three-phase separator was simulated on Simulink. Similar components were taken from Simulink library. The values for controller parameters were varied according to process conditions.

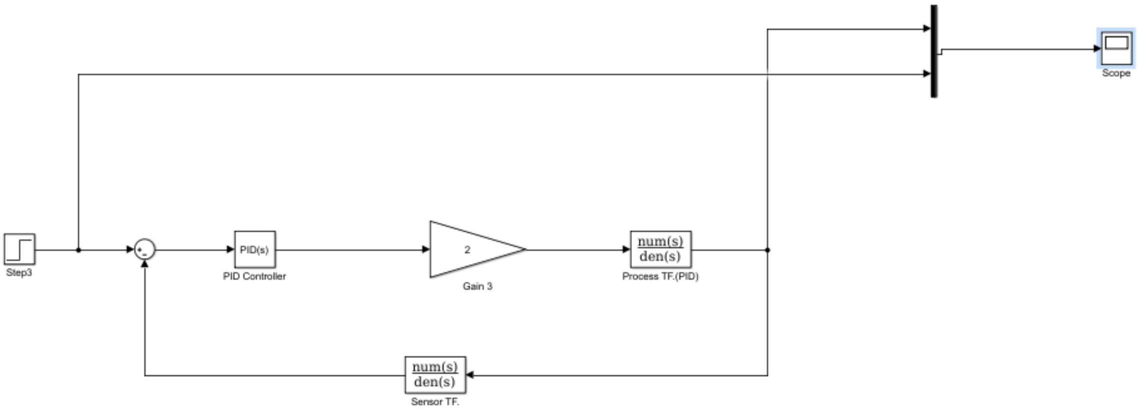


FIGURE 37: SIMULINK MODEL FOR LEVEL CONTROL OF THREE-PHASE SEPARATOR

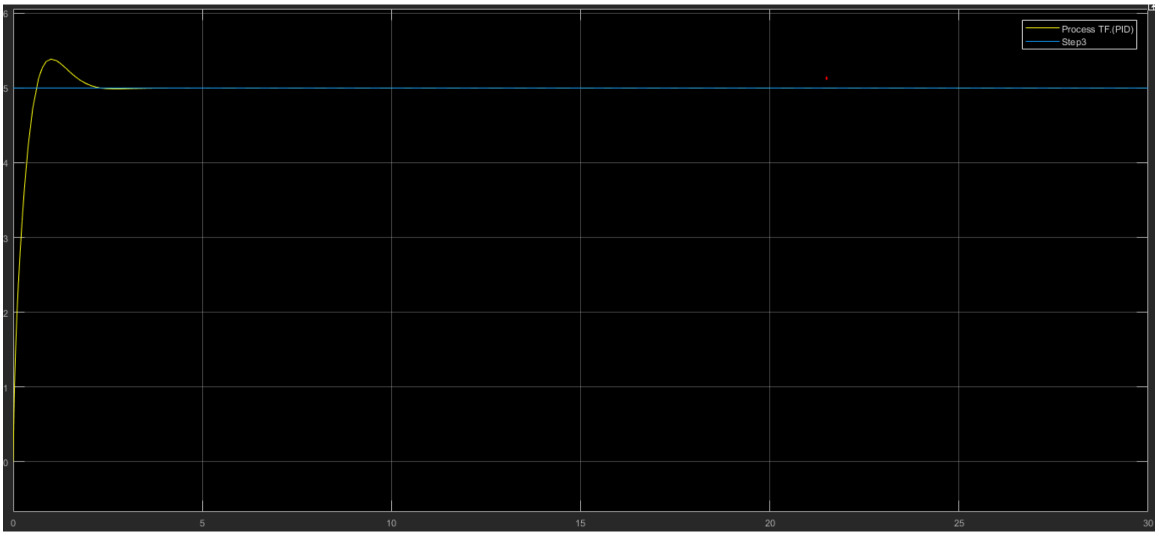


FIGURE 38: CONTROLLER RESPONCE TO STEP CHANGE

Figure 38 shows the response of level controller when subjected to step change of 5 units. The controller achieves the new set point in less than 5 units of time. This can be attributed to lower response times of sensor and process transfer functions. Gain for the process transfer function is, however, quite low. After autotuning the model, the values for P, I and D are 0.8923, 2.165 and 0.04806 respectively.

8.6 Controllers Comparison

Four types of controllers can be employed in control loops.

8.6.1 Proportional Control

Of them all, proportional controller is the simplest. It generates signal proportional to the magnitude of error. The sensitivity of this proportional signal is dictated by proportional gain which is fed by the user by any of the tuning methods available.

Mathematically:

$$p = K_c \varepsilon + p_s$$

p = output signal from controller

K_c = proportional gain

ε = error

p_s = signal of controller at steady state

Error is calculated by subtracting measured variable from set point. Transfer function of proportional controller is given as:

$$\frac{P(s)}{\varepsilon(s)} = K_c$$

One must think if the error increases indefinitely, will the response still be proportional to the error? Ideally, yes but practically it reaches a saturation value. The response is bounded between the signal of 4 mA to 20 mA, 4mA being the lower limit and 20 mA being the upper limit.

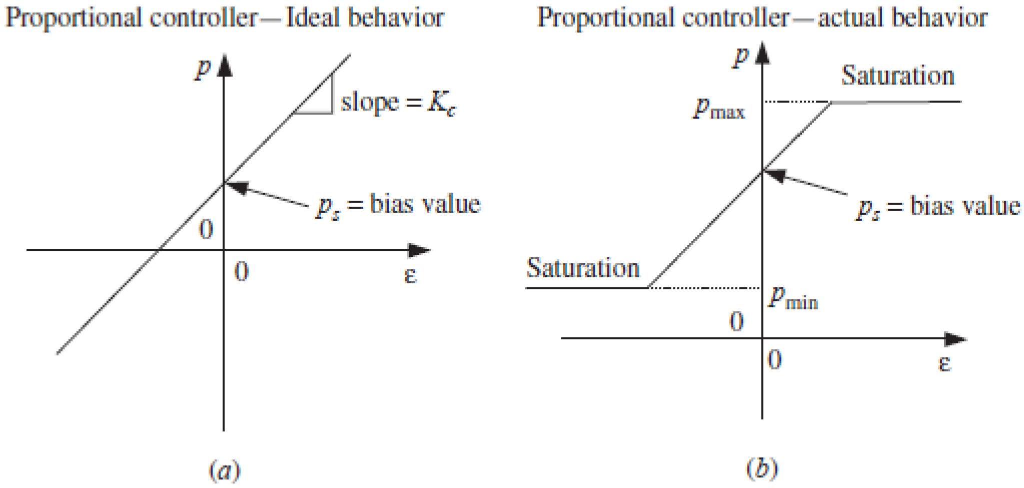


FIGURE 39: COMPARISON OF IDEAL AND REAL BEHAVIOUR OF PROPORTIONAL CONTROLLER

8.6.2 Proportional Integral Control

In proportional integral controller, an additional component is added to the proportional controller which acts to minimize or totally eliminate offset error. Offset error is the steady state error which remains even when the proportional controller is at steady state. To eliminate this, time integral of error is taken and added to the proportional component.

Mathematically:

$$p = K_c\varepsilon + \frac{K_c}{\tau_I}\int_0^t \varepsilon dt + p_s$$

p = output signal from controller

K_c = proportional gain

ε = error

p_s = signal of controller at steady state

τ_I = Integral time, (min)

The response of PI controller to a unit step change is examined, to put things into perspective. The equation for response as a function of time is stated previously. For a unit step change, error is set to 1 and the integral is solved. The final equation turns out to be:

$$p(t) = K_c + \frac{K_c}{\tau_I}t + p_s$$

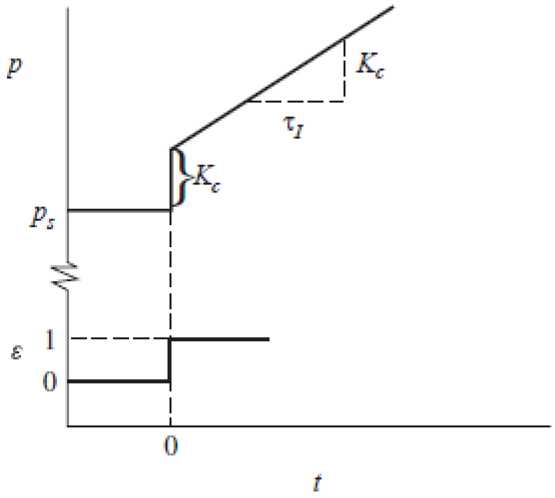


FIGURE 40: PROPORTIONAL INTEGRAL CONTROLLER'S RESPONCE TO UNIT STEP CHANGE

Here an abrupt change of K_c is observed followed by a linear change with a slope of $\frac{K_c}{\tau_I}$. This is how it helps to reduce or eliminate offset error. Transfer function for PI controller is given below:

$$\frac{P(s)}{\varepsilon(s)} = K_c(1 + \frac{1}{\tau_I s})$$

8.6.3 Proportional Derivative Control

Derivative control is another type of control which acts on the derivative of control. It is added to proportional control or proportional derivative control. It is of utmost importance when the change in error is rapid.

Mathematically:

$$p = K_c\varepsilon + K_c\tau_D\frac{d\varepsilon}{dt} + p_s$$

p = output signal from controller

K_c = proportional gain

ε = error

p_s = signal of controller at steady state

τ_D = Derivative time, (min)

To make things clear, the response of PD controller to a linear change in error is observed. Assuming a linear change in error with slope A, the equation of response becomes:

$$p(t) = AK_ct + AK_c\tau_D + p_s$$

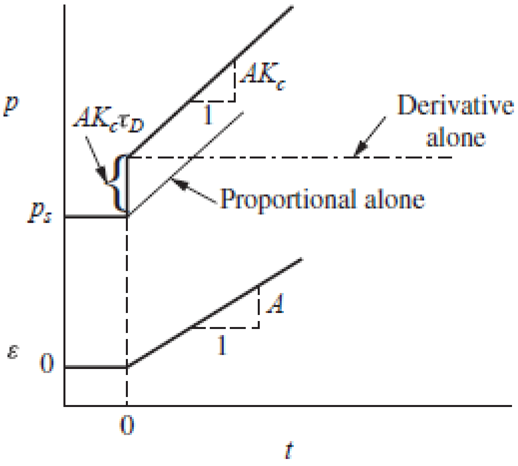


FIGURE 41: PROPORTIONAL DERIVATIVE RESPONCE TO A LINEAR CHANGE IN ERROR

Here an abrupt change of $AK_c\tau_D$ is observed followed by a linear change with a slope of AK_c. In this way, rapid change in error is eliminated or reduced. This is also called disturbance rejection, where a system maintains its set point, despite the external disturbances which cause the system to deviate from the set point.

Transfer function for PD controller is given below:

$$\frac{P(s)}{\varepsilon(s)} = K_c(1 + \tau_D s)$$

8.6.4 Proportional Integral Derivative Control

This type of a controller is a combination of each type of control. It is most complex of all. This controller acts proportionally to the error it senses, tries to eliminate offset error and deals with rapidly changing error as well.

Mathematically:

$$p = K_c\varepsilon + K_c\tau_D\frac{d\varepsilon}{dt} + \frac{K_c}{\tau_I}\int_0^t \varepsilon dt + p_s$$

p = output signal from controller

K_c = proportional gain

ε = error

p_s = signal of controller at steady state

τ_D = Derivative time, (min)

τ_I = Integral time, (min)

Transfer function for PID controller is given below:

$$\frac{P(s)}{\varepsilon(s)} = K_c(1 + \tau_D s + \frac{1}{\tau_I s})$$

The graph below shows the different responses to the same change by different controllers. If no control system is installed, then the error continues to increase until another steady state value is achieved. Proportional control arrests this change but cannot eliminate it. The PI controller acts to eliminate the offset, although with the benefit of elimination of offset, the disadvantage of oscillatory behavior is observed. Derivative control acts to eliminate the oscillations associated with integral control.

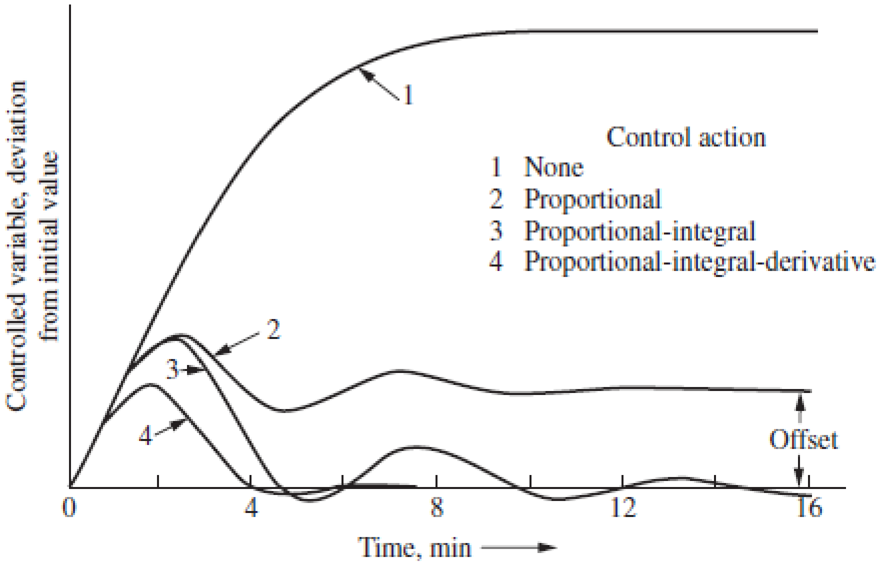


FIGURE 42: COMPARISON OF DIFFERENT CONTROLLERS' RESPONSE

8.6.5 Simulation of Different Controllers

Different controllers were simulated for the same loop, and for the same change, on Simulink. The temperature control loop was simulated with different controllers and the response was displayed on a single graph in order to compare response of each controller. A similar curve is expected for the simulation results as shown in figure 42.

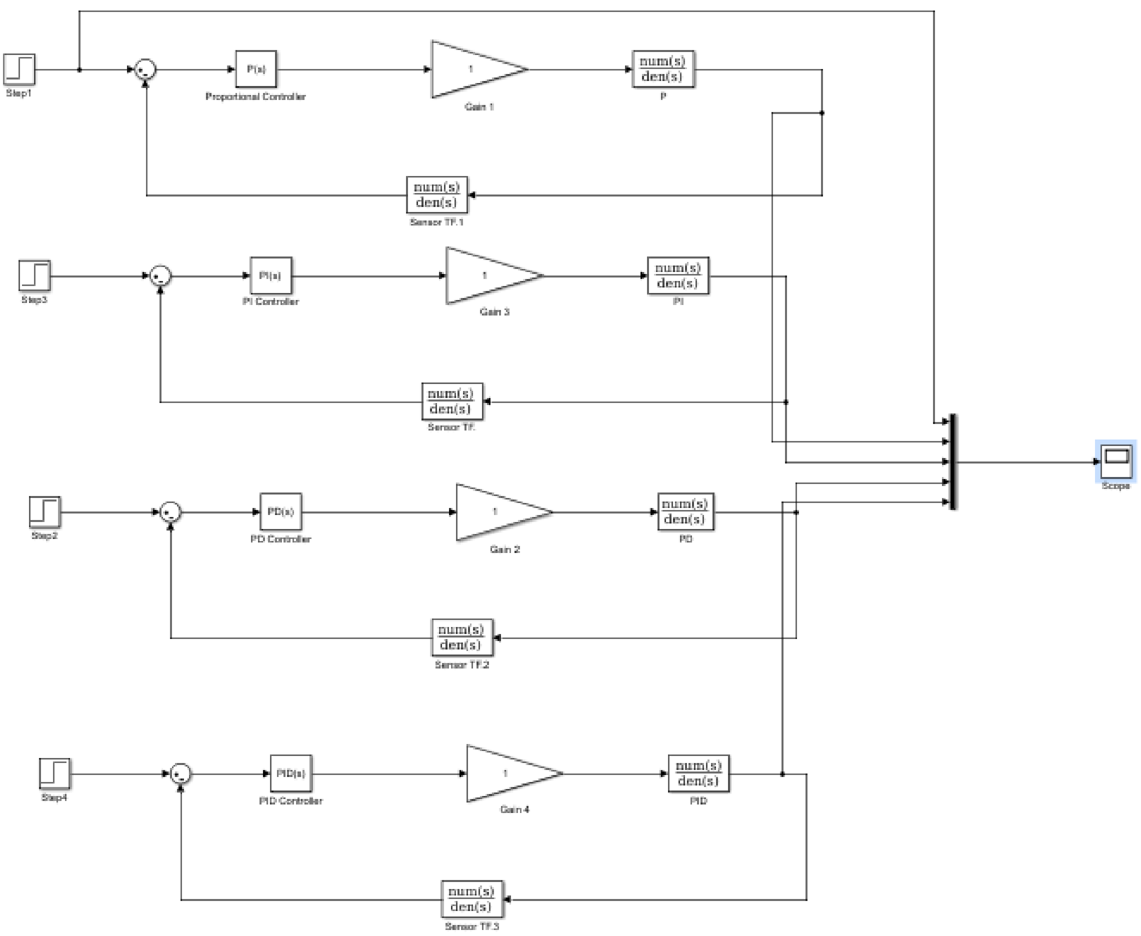


FIGURE 43: TEMPREATURE CONTROL LOOP SIMULINK MODEL WITH DIFFERENT CONTROLLERS

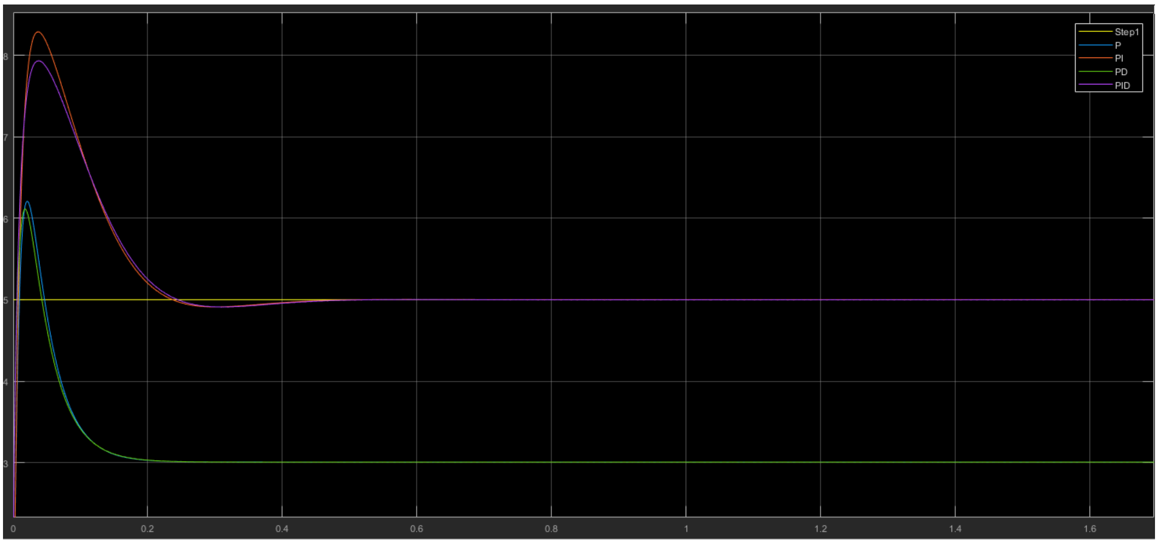


FIGURE 44: DIFFERENT CONTROLLERS' RESPONCE TO A STEP CHANGE

CHAPTER 9

COST ANALYSIS [28]

9.1 Total Investment

9.1.1 HCl Column

Pressure = 20 bar

Diameter = 2 m

Height = 15.9 m

Plate type = Sieve Plate

No of Plates = 26.5

Vessel cost = 46,000 x 2 x 1.2

= $110,400

9.1.1.1 Plates

Plate cost = $600 per plate

Total plate cost = 600 x 27 x 1.7

=$27,540

9.1.1.2 Reboiler

Type = Kettle

Material = Stainless Steel

Area = 240 ft^2

Cost = 40,000 x 1.25 x 1.3

= $65,000

9.1.1.3 Condenser

Type = Fixed tube sheet

Material = Stainless Steel

Area = 190 ft^2

Cost = 30,000 x 0.8 x 1.25

= $30,000

Total Cost = $232,940

9.1.2 VCM Column

Pressure = 20 bar

Diameter = 2 m

Height = 14.6 m

Plate type = Sieve Plates

No of Plates = 24

Vessel cost = 44,000 x 1 x 1.2

= $52,800

9.1.2.1 Plates

Plate cost = $600 per plate

Total plate cost = 600 x 1 x 1.2

=$52,800

9.1.2.2 Reboiler

Type = Kettle

Material = Carbon Steel

Area = 180 ft^2

Cost = 12,000 x 1.25 x 1.3 = $19,500

9.1.2.3 Condenser

Type = Fixed tube sheet

Material = Carbon Steel

Area = 165 ft^2

Cost = 8,000 x 0.8 x 1.25

=$8,000

Total Cost = $94,700

9.1.3 Water Column

Pressure = 20 bar

Diameter = 2 m

Height = 13 m

Plate type = Sieve Plates

No of plates = 21

Vessel cost = 40,000 x 1 x 1.2

= $48,000

9.1.3.1 Plates

Plate cost = $500 per plate

Total plate cost = 500 x 1 x 21

=$10,500

9.1.3.2 Reboiler

Type = Kettle

Material = Carbon Steel

Area = 220 ft^2

Cost = 20,000 x 1.25 x 1.3

= $32,500

9.1.3.3 Condenser

Type = Fixed tube sheet

Material = Carbon Steel

Area = 200 ft^2

Cost = 18,000 x 0.8 x 1.25

=$18,000

Total Cost = $109,700

9.1.4 Three Phase Separator

Pressure = 5 bar

Diameter = 1 m

Length = 5.8 m

Vessel cost = $5000 x 1 x 1

= $5000

9.1.5 Reactors

All the reactors are in essence Shell & Tube type Heat Exchangers, so costing will be done based on area according to shell and tube HE.

9.1.5.1 Direct Chlorination Reactor

Area = 2432 m^2

Material = Stainless Steel

N_t = 5000

a'' = 0.2618 ft^2 /linear ft

L = 20 ft

Area = 5000 x 0.26180 x 20

= 26180 ft^2 = 2432 m^2

Cost = 500,000 x 1.3

= $650,000

9.1.5.2 Oxy-chlorination Reactor

Area = 2106 m^2

Material = Stainless Steel

N_t = 4331

a´´ = 0.2618 ft^2 /linear ft

L = 20 ft

Area = 4331 x 0.26180 x 20

= 22677 ft^2

Cost = 420,000 x 1.3

= $546,000

9.1.5.3 Butadiene Removal Unit

Area = 6202 ft^2

Material = Carbon Steel

N_t = 12,750

a´´ = 0.2618 ft^2 /linear ft

L = 20 ft

Area = 12,750 x 0.26180 x 20

= 66759 ft^2

Cost = 610,000 x 1.3

= $610,000

9.1.6 Furnace

1.647 x 10^4 kW

$C_e = CS^n$

N = 0.77

S = 1.647 x 10^4

C = \$540

Ce = 540 x $(1.647 \times 10^4)^{0.77}$

=\$953,340

9.1.7 Compressors

9.1.7.1 C_2H_4 (Chlorination)

S = 299

C = 1920

n = 0.8

$C_e = 1920\ (299)^{0.8}$

C_e =\$184000

9.1.7.2 Cl_2 (Chlorination)

S = 299

C = 1920

n = 0.8

$C_e = 1920\ (289)^{0.8}$

C_e = \$179000

9.1.7.3 C_2H_4 (Oxychlorination)

S = 712.5

C = 1920

n = 0.8

$C_e = 1920\ (712.5)^{0.8}$

C_e = \$368,000

9.1.7.4 O_2 (Oxychlorination)

S = 372.8

C = 1920

n = 0.8

$C_e = 1920\ (372.8)^{0.8}$

$C_e = \$219000$

9.1.7.5 Post Direct Chlorination

S = 481

C =1920

n = 0.8

$C_e = 1920\ (481)^{0.8}$

$C_e = \$269000$

9.1.8 Pump

Cost = $20,000

9.1.9 Heat Exchangers

9.1.9.1 Chlorine (DC)

Type = Fixed tube sheet

Material = Carbon Steel

Area = 42.5 ft^2

Cost = 2,000 x 0.8 x 1

= $1600

9.1.9.2 Ethylene (DC)

Type = Fixed tube sheet

Material = Carbon Steel

Area = 218.4 ft^2

Cost = 10,200 x 0.8 x 1

= $8160

9.1.9.3 Oxygen gas (OC)

Type = Fixed tube sheet

Material = Carbon Steel

Area = 41.55 ft^2

Cost = 1,900 x 0.8 x 1

= $1520

9.1.9.4 HCl (OC)

Type = Fixed tube sheet

Material = Stainless Steel

Area = 243.35 ft^2

Cost = 3,000 x 0.8 x 1

= $24000

9.1.9.5 Ethylene (OC)

Type = Fixed tube sheet

Material = Carbon Steel

Area = 305 ft^2

Cost = 10800 x 0.8 x 1

= $8640

9.1.9.6 Pre-cracking Fluid

Type = Fixed tube sheet

Material = Carbon Steel

Area = 1001 ft^2

Cost = 30,000 x 0.8 x 1

= $24,000

9.1.9.7 Post Cracking

Type = Fixed tube sheet

Material = Stainless Steel

Area = 600 ft^2

Cost = 60,000 x 0.8 x 1

= $48,000

9.1.9.8 Pre-Butane Removal Unit

Type = Fixed tube sheet

Material = Carbon Steel

Area = 1200 ft^2

Cost = 30,000 x 0.8 x 1

= $24,000

9.1.9.9 Hydrogen Heater

Type = Fixed tube sheet

Material = Carbon Steel

Area = 10 ft^2

Cost = 1,000 x 0.8 x 1

= $800

9.1.9.10 Post VCM Column

Type = Fixed tube sheet

Material = Carbon Steel

Area = 1200ft^2

Cost = 30,000 x 0.8 x 1

= $24000

9.1.9.11 Pre-Three Phase Separator

Type = Fixed tube sheet

Material = Carbon Steel

Area = 805ft^2

Cost = 29,000 x 0.8 x 1

= $23,200

9.1.9.12 Bottoms of EDC

Type = Kettle

Material = Carbon Steel

Area = 936 ft^2

Cost = 28,000 x 0.8 x 1

= $40,040

9.1.10 Total

Heat Exchangers	$227,960
Compressors	$1,219,000
Pumps	$20,000
Distillation Column	$436,640
Three-phase Separator	$5000
Reactors	$1,257,000
Furnace	$953,340
Grand Total (PCE)	**$4,118,940**

PPC = PCE $(1+f_1+f_2+f_3+f_4)$

= $4,118,940(2.55)

=$10,503,297

Fixed Capital = 10,503,297(1.45)

=$15,229,780

Working Capital = 20% of fixed capital

= $3,045,956

Total Investment = 15229780 + 3045956

= $18,275,736

350 working days

9.2 Variable Cost

9.2.1 Raw Materials

9.2.2 Amount

Ethylene	192664 Mt/year
Chlorine	252277 Mt/year
Oxygen	53760 Mt/year

9.2.2.1 Ethylene

Rate = 700$/Mt

Cost per year = 700 x 192664

= $134,864,856

9.2.2.2 Chlorine

Rate = 200$/Mt

Cost per year = 200 x 252277

=$50,455,440

9.2.2.3 Oxygen

Rate = 80$/Mt

Cost per year = 80 x 53760

=$4,300,800

Total Raw Material Cost = $144,211,200

9.2.3 Utilities

9.2.3.1 Electric

-1454 MJ/hr = -12213 GJ/year

Cost = 15 $/GJ

Net Value = -$183195 per year

9.2.3.2 Natural Gas

88883 MJ/hr = 746617 GJ/year

Cost = 7$/GJ

Total cost = $5226319 per year

9.2.3.3 Cooling Water

32000 kg/hr = 269640 Mt/year

Cost = 1cent/Mt

Total Cost = $2696 per year

9.2.3.4 Refrigerant

928654 MJ/hr = 780066 GJ/year

Cost = 15$/GJ

Total Cost = $11,700,990 per year

Utilities Annual Cost = $16746810

9.2.4 Sub Total A

Raw materials	$144,211,200
Utilities	$16,746,810
Miscellaneous Materials	$152297
	$161,110,307

9.2.5 Sub Total B

Maintenance	$1,522,978	*60% of fixed cost*
Operating labour	$40,000	
Lab Cost	$8,000	
Supervision	$8,000	
Plant Overheads	$20,000	
Capital Charges	$1,522,978	
Insurance	$152,297	
Local Taxes	$304,594	
Royalties	$152,297	
	$3,731,144	

Direct Production = A + B = $164,841,251

9.2.6 Sub Total C

Sub Total C= 30% of Direct Production Cost

= $49,452.435

Annual Production Cost = $214,293,886

Vinyl Chloride = 808 kg mole/hr = 50500 kg/hr = 424,200 Mt/year

9.2.7 Production Cost

$$Production\ Cost = \frac{Annual\ Production\ Cost}{Annual\ Production\ Rate}$$

Production Cost = 0.51 $ / kg

9.3 Revenue

Vinyl Chloride = 808 kg mole/hr = 50500 kg/hr = 424,200 Mt/year

Rate = 0.66$/kg = 660 $/Mt

Revenue = $254.5 M

9.4 Profit

Profit = 254.5 – 214.3

= $40.22M

9.5 Rate of Return

$$ROR = \frac{Cumulitaive\ net\ flow\ cash\ at\ end\ of\ project}{Life\ of\ project\ x\ orignal\ investment}$$

ROR = 0.22 per year

9.6 Payback Period

Payback Time = $\frac{1}{Rate\ of\ Return}$

Payback Time = 4.54 years

CHAPTER 10

HAZOP ANALYSIS[28]

The hazard and operability study (HAZOP) is a tool that’s used to find out all the potential ways which might lead to a mishap. There is wide use of the HAZOP as a tool in chemical industry to study any possibility of accident to occur. HAZOP is basically critical thinking approach in which all the parameters that have impact on process are considered.

To detect or predict all possible failures relevant to each unit, for the core reason of prevention of hazards and any accident is the main objective of the HAZOP. In HAZOP analysis each unit of the process is broken down to study it in detail. This kind of technique or approach requires in depth knowledge of every unit. HAZOP study is not a single-handed job and requires complete team in which all members possess detailed understanding and know-how of industrial processes. These members might include safety engineers, chemical engineers, process engineers, electrical engineers, and mechanical engineers. It is very detailed study that cannot be performed in short time but requires in depth study with lots of commitment and dedication from each and every member of the team. For the discussion of all record and parameters that may lead the process of the track, all the members are needed to meet multiple times in a week. Full HAZOP study requires several PFDs and P&IDs which are not easy to understand and require lot of collective effort to be sorted out, and this needs to be done for each unit separately. It is a laborious process and takes more than a month to complete. Although this is very tough technique to perform but it is considered as the best possible method or study for having hands-on approach for any sort of problem that might occur in a process. So, performing a HAZOP analysis of a chemical plant is the most important step in making it safe.

The HAZOP study is performed using the following steps:

1) Prepare the point by point flow sheet and separate it into various units.

2) Select a unit for study, for example, a reactor, flash drum, mixer, and so on.

3) Describe the reason for the choosing unit.

4) Chose a process parameter.

5) Apply the guide words to the process parameter to propose potential deviations from the given guide words introduced in Table underneath.

6) Determine the potential causes and note any systems to prevent.

7) Evaluate the outcomes of the deviation.

8) Recommend possible steps.

9) Note all data.

10.1 Direct Chlorination Reactor

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
Flow				
None	No Flow	1) Compressor failure 2) Line blockage 3) Closed valve	1) No EDC Produced	1) Shutdown System that notifies when there is no flow. 2) Alarm System that notifies when there is no flow.
Line 1: Ethylene				

High	Excess Flow of the reactant	1) Excessive speed of the compressor 2) Control faults 3) Fully open valve	1) Reactor might overfill 2) More ethylene to recovery unit	1) Flow sensor should be installed
Low	Low amount of one reactant	1) Shortage in storage tank 2) Compressor fault	1) Lower production rate 2)Variety of by-products formed	1) Flow sensor should be installed
Line 2: Chlorine				
High	Excess Flow of the reactant	1) Excessive speed of the compressor 2) Control faults 3) Fully open valve	1) Reactor might overfill 2) Many by-products formed	1) Flow sensor should be installed
Low	Low amount of one reactant	1) Shortage in storage tank 2) Compressor fault	1) Lower production rate 2) More Ethylene to recovery unit	1) Flow sensor should be installed

Temperature				
High	Higher temperature	1) Cooling Jacket malfunction 2) Higher temperature of the reactants	1) Temperature increase in reactor 2) Decrease in reaction rate	1) Install high temperature shut down system or automatic temperature regulator

			3) Increase in heat generation rate	2) Regular check of the cooling system
Low	Lower temperature	1) Cooling Jacket malfunction 2) Reactants entering at lower temperature	1) Temperature decreases in Reactor 2) Increased reaction rate	1) Install temperature indicating alarms 2) Periodic inspection and maintenance

Pressure				
High	Higher pressure	1) Product line blockage 2) Compressor malfunction	1) Higher than the required pressure in reactor 2) Too high pressure might lead to reactor rapture	1) Install high pressure alarm 2) Install automatic sensors and control devices
Reverse	Back pressure	1) Blockage in pipeline outlet 2) Compressor malfunction	1) Products flows to the reactor 2) Reactor stops	1) Install low pressure alarm 2) Install automatic sensors and control devices

Electricity				
Low	Less power delivered to compressors	1) Voltage drop from grid 2) line damage	1) Lesser flow rate of reactants 2) lower production rate	1) Should have backup generator for such situations
High	High power delivered to compressors	1) Voltage drop from grid 2) line damage	1) Higher flow rate of reactants 2) Compressor might be damaged	1) Circuit breakers should be installed

10.2 Oxychlorination Reactor

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
Flow				
None	No Flow	1) Compressor failure 2) Line blockage 3) Closed valve	1) No EDC Produced	1) Install Shutdown System that notifies when there is no flow. 2) Alarm System that notifies when there is no flow.
Line 2: Ethylene				

High	Excess Flow of the reactant	1) Excessive speed of the compressor 2) Control faults 3) Fully open valve	1) Reactor might overfill 2) More ethylene to recovery unit	1) Flow sensor should be installed
Low	Low amount of one reactant	1) Shortage in storage tank 2) Compressor fault	1) Lower production rate 2)Variety of by-products formed	1) Flow sensor should be installed
Line 4: Oxygen				
High	Excess Flow of the reactant	1) Excessive speed of the compressor 2) Control faults 3) Fully open valve	1) Product deterioration	1) Flow sensor should be installed
Low	Low amount of one reactant	1) Shortage in storage tank 2) Compressor fault	1) More byproducts	1) Flow sensor should be installed
Line 5: HCl				
High	Excess Flow of the reactant	1) Excessive speed of the compressor 2) Control faults	1) Byproducts formed	1) Flow sensor should be installed

Low	Low amount of one reactant	1) Shortage in storage tank 2) Compressor fault	1) Excess of the ethylene to recovery unit	1) Flow sensor should be installed

Temperature				
High	Higher temperature	1) Cooling Jacket malfunction 2) Higher temperature of the reactants	1) Temperature increase in reactor 2) Decrease in reaction rate 3) Increase in heat generation rate	1) Install high temperature shut down system or automatic temperature regulator 2) Regular check of the cooling system
Low	Lower temperature	1) Cooling Jacket malfunction 2) Reactants entering at lower temperature	1) Temperature decreases in Reactor 2) Increased reaction rate	1) Install temperature indicating alarms 2) Periodic inspection and maintenance

Pressure				
High	Higher pressure	1) Product line blockage 2) Compressor malfunction	1) Higher than the required pressure in reactor 2) Too high pressure might lead to	1) Install high pressure alarm 2) Install automatic sensors and

			reactor rapture	control devices
Reverse	Back pressure	1) Blockage in pipeline outlet 2) Compressor malfunction	1) Products flows to the reactor 2) Reactor stops	1) Install low pressure alarm 2) Install automatic sensors and control devices

Electricity				
Low	Less power delivered to compressors	1) Voltage drop from grid 2) line damage	1) Lesser flow rate of reactants 2) lower production rate	1) Should have backup generator for such situations
High	High power delivered to compressors	1) Voltage drop from grid 2) Line damage	1) Higher flow rate of reactants 2) Compressor might be damaged	1) Circuit breakers should be installed

10.3 Butadiene Removal Unit

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
		Flow		
None	No Flow	1) Compressor failure 2) Line blockage	1) No pure VCM Produced	1) Install Shutdown System that notifies when there is no flow.
		Temperature		
High	Higher temperature	1) Cooling Jacket malfunction 2) Higher temperature of the reactants	1) Temperature increase in reactor 2) The conversion decreases	1) Install automatic temperature regulator
Low	Lower temperature	1) Cooling Jacket malfunction 2) Reactants entering at lower temperature	1) Temperature decreases in Reactor 2) The conversion decreases	1) Install temperature indicating alarms 2) Periodic inspection and maintenance

Pressure				
High	Higher pressure	1) Product line blockage 2) Compressor malfunction	1) No impact on conversion or selectivity from 1-6 bar	1) Install high pressure alarm 2) Install automatic sensors and control devices
Low	Lower pressure	1) Inlet line leakage 2) Reactor leakage	1) Kinetics might be disturbed	1) Install low pressure alarm 2) Install automatic sensors and control devices

Electricity				
Low	Less power delivered to compressors	1) Voltage drop from grid 2) line damage	1) Lesser flow rate of reactants 2) lower production rate	1) Should have backup generator for such situations
High	High power delivered to compressors	1) Voltage drop from grid 2) Line damage	1) Higher flow rate of reactants 2) Compressor might be damaged	1) Circuit breakers should be installed

10.4 Furnace

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
Flow				
None	No Flow	1) Compressor failure 2) Line blockage	1) No Cracking	1) Install no flow alarm 2) Check compressor and lines

Temperature				
High	Higher temperature	1) More fuel entered in the furnace 2) Higher temperature of the reactants entering	1) Temperature increase in furnace 2) Reaction rate increases 3) Selectivity is disturbed	1) Install temperature alarms 2) Install system to maintain the temperature constant
Low	Lower temperature	1) Lesser fuel to furnace 2) Heat losses	1) Temperature decreases in furnace 2) Decreased EDC cracking	1) Install temperature alarms 2) Install system to maintain the temperature constant

Pressure				
High	Higher pressure	1) Product line blockage 2) Higher temperature leading to high pressure	1) Change in the pressure changes the conversion of the reactor	1) Install high pressure alarm 2) Install automatic sensors and control devices
Reverse	Back pressure	1) Blockage in pipeline outlet 2) Compressor malfunction	1) Furnace might blast 2) Process stops	1) Install NRVs 2) Install automatic sensors and control devices

10.5 Distillation Column - 1

(For the separation of the unreacted ethylene from the EDC)

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
Flow				
None	No Flow	1) Line blockage 2) 3-phase separator not working	1) No Separation	1) Install no flow alarm 2) Check flow meters regularly

Temperature				
High	Higher temperature	1) More heating supplied 2) Feed entering at higher temperature	1) Higher than the desired temperature 2) Improper separation of Ethylene & EDC	1) Install temperature alarms 2) Install system to maintain the temperature constant
Low	Lower temperature	1) Not enough heating supplied 2) Heat losses due to improper packing	1) Column temperature is lower than the desired temperature 2) Improper separation of Ethylene & EDC	1) Install temperature alarms 2) Install system to maintain the temperature constant

Pressure				
High	Higher pressure	1) Product line blockage 2) Higher temperature leading to high pressure	1) Improper Separation 2) Column might leak or blast	1) Install high pressure alarm 2) Install PSVs
Low	Lower Pressure	1) Leakage in the lines 2) Leakage in Column	1) Pressure in the distillation column drops 2) Improper separation	1) Install low pressure indicator 2) Check for leakages

Reverse	Back pressure	1) Blockage in pipeline outlet	1) Column might blast 2) Process stops	1) Install automatic sensors and control devices 2) Shutdown the process check for problem

10.6 Distillation Column - 2

(For the separation of the HCl from the rest of mixture)

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
Flow				
None	No Flow	1) Line blockage 2) Heat exchanger outlet blocked	1) No Separation	1) Install no flow alarm 2) Check flow meters regularly
Temperature				
High	Higher temperature	1) More heating supplied 2) Feed entering at higher temperature	1) Acidic impurities in the final product 2) Improper separation of HCl	1) Install temperature alarms 2) Install system to maintain the temperature constant
Low	Lower temperature	1) Not enough heating supplied 2) Heat losses due to improper packing	1) Acidic impurities in the final product 2) Improper separation of	1) Install temperature alarms 2) Install system to maintain the

			HCl from the rest mixture	temperature constant
Pressure				
High	Higher pressure	1) Product line blockage 2) Higher temperature leading to high pressure	1) Improper Separation HCl 2) Column might leak or blast	1) Install high pressure alarm 2) Install PSVs
Low	Lower Pressure	1) Leakage in the lines 2) Leakage in Column	1) Pressure in the distillation column drops 2) Improper separation HCl	1) Install low pressure indicator 2) Check for leakages
Reverse	Back pressure	1) Blockage in pipeline outlet	1) Column might blast 2) Process stops	1) Install automatic sensors and control devices 2) Shutdown the process check for problem

10.7 Distillation Column – 3

(For the separation of the unreacted EDC from VCM monomer)

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
Flow				
None	No Flow	1) Line blockage 2) Heat exchanger outlet blocked	1) No Separation	1) Install no flow alarm 2) Check flow meters regularly

Temperature				
High	Higher temperature	1) More heating supplied 2) Feed entering at higher temperature	1) Impurities in the final product 2) Loss of EDC	1) Install temperature alarms 2) Install system to maintain the temperature constant
Low	Lower temperature	1) Not enough heating supplied 2) Heat losses due to improper packing	1) Impurities in the final product 2) Loss of EDC	1) Install temperature alarms 2) Install system to maintain the temperature constant

Pressure				
High	Higher pressure	1) Product line blockage 2) Higher temperature leading to high pressure	1) Improper Separation EDC 2) Column might leak or blast 3) Product quality deteriorates	1) Install high pressure alarm 2) Install PSVs
Low	Lower Pressure	1) Leakage in the lines 2) Leakage in Column	1) Pressure in the distillation column drops 2) Improper separation of EDC 3) Impurities in the product	1) Install low pressure indicator 2) Check for leakages
Reverse	Back pressure	1) Blockage in pipeline outlet	1) Column might explode 2) Process stops	1) Install automatic sensors and control devices 2) Shutdown the process check for problem

10.8 Three-Phase Separator

Guide word	Deviation (Process Parameter)	Possible causes	Consequences	Action Required
		Flow		
None	No Flow	1) Line blockage or rupture	1) No Separation	1) Install no flow alarm 2) Check flow meters regularly
		Temperature		
High	Higher temperature	1) Over heating in the heat exchanger	1) Impurities in distillation column feed 2) Poor separation	1) Install temperature alarms
		Pressure		
High	Higher pressure	1) Outline blockage of 3-phase separator	1) Improper Separation 2) Vessel might leak or blast	1) Install high pressure alarm 2) Install PSVs
Low	Lower Pressure	1) Leakage in the lines	1) Improper separation 2) lower pressure to the distillation column	1) Install low pressure indicator 2) Check for leakages

CONCLUSION

Results

1. Reduction of multistep treatment of butadiene to single step

Previously multiple steps were employed to remove butadiene i.e. initially, treatment with an acid, specifically HCl, which was followed by caustic treatment to remove any unconverted HCl. This stream was allowed to settle, so that the neutralization byproducts are separated from the desired products. Even then, some acid would remain, which was termed as residual acid. This process also increased the moisture content of the final product.

The proposed process treats butadiene with hydrogen, in a single step. 99.5 % of the total butadiene present is removed using this process. This process bypasses the multistep procedure and achieves the same results in a single step.

2. Removal of residual acidity

The unreacted acid caused problems to the final product, as it inhibits the polymerization of VCM later on. This residual acidity is taken care of, by the proposed process, as no acid is required to treat butadiene, therefore, residual acidity is removed.

3. Maintaining the moisture content value

One way to deal with the acidity was to increase the moisture content. This increase in moisture content would result in dilution of the acid and consequently rendering negligible acidity. The proposed process keeps in view this constraint and removes acidity by an entirely different process i.e. treatment with hydrogen. The proposed process reduces the moisture content even further, as the neutralization reaction step is removed., which adds extra moisture to the final product.

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